CA

PROCESSES AND PROPERTIES INDEX

Catalytic replacement of halogen by hydroxyl in the aromatic series. I. Catalytic activity of silica gels and their deactivation. L. Kh. Freidlin, A. A. Balandin, A. I. Lebedeva, and G. A. Fridman (Inst. of Org. Chem., Acad. Sci. U.S.S.R.). *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1945, 53-60(in English, 60-1); cf. *C.A.* 39, 4792^{1}.—The activity of SiO_2 gels in the vapor-phase hydrolysis of PhCl was investigated. PhCl and water were introduced from two automatically regulated Balandin burets into an evaporator, and from there into a reaction tube placed in an elec. oven (variation in temp. ±1°). The temp. was measured by a thermocouple placed inside the catalyst. The temp. and the space velocity are the most important factors affecting the direction and the rate of the reaction. Wt. ratio H_2O/PhCl, if it is not lower than 0.7-1, is less important. It was found that SiO_2 gels are deactivated at temps. above 550-600° (Okatov's SiO_2 gel), and some of them are deactivated even at as low a temp. as 480° (German SiO_2 gel). The yield of phenol in the presence of Okatov's gel is around 7% at 480°, 10.9% at 500°, and reaches 22.9% of the theoretical at 542°, with space velocity 300. The regeneration of SiO_2 gels (which have been heated to 550°) by the treatment of air does not reëstablish their original activity. When Okatov's gel was used at 480°, its activity remained at the same level for many hrs. (yield of phenol 7-8%) and did not change after the treatment with air. The impregnation of SiO_2 gel with 3-8% PCl_5, H_3PO_4, cobaltous phosphate or NH_4 phosphomolybdate completely deactivates the former. The impregnation of SiO_2 gel with H_3PO_4 deactivates it for the vapor-phase hydrolysis of PhCl, but makes it 24 times as active than unpoisoned SiO_2 gel in the reaction of dehydration of alc. G. L.

Inst. Organic Chem., AN SSSR.

METALLURGICAL LITERATURE

C H

2

The kinetics of catalytic hydrogenation. A. A. Balandin (Inst. Org. Chem., Acad. Sci. U.S.S.R.). *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1943, 339-60 (English summary); cf. *C.A.* 39, 1867.—A theory is developed on the assumption of two kinds of active centers: *K*, capable of activating the adsorbed H, and *K'*, activating only the hydrogenatable org. substance. Both *K* and *K'* adsorb both H and the initial, intermediate, or final products; the establishment of the adsorption equil. is faster than the subsequent reaction. Activated H gives two HM where M = an atom of the metal of the catalyst. Hydrogenation proceeds over an intermediate half-hydrogenated product. Quant. treatment of these assumptions leads to reaction-rate equations for the cases of hydrogenation, dehydrogenation, and deuterium exchange, in terms of concns. of the initial, final, and extraneous products and of H pressure, and of the rate consts. of the elementary steps of adsorption, activation, and chem. reaction. In the case of benzene on Ni, the *K* centers would be located along the lattice edges with the inter-atom distances of 3.52 A., the *K'* centers are constituted by the sextet in a plane with the distance 2.49 A. With the aid of simplifying assumptions, involving in particular equality of adsorption rates on *K'* of the initial and final product, a simple expression is obtained for the rate of dehydrogenation showing independence of pressure and confirmed by the example methylcyclohexane-toluene, between 300° and 300°. Another simplified expression is obtained for the hydrogenation under high pressure; the rate remains const. during the progress of the reaction as long as there remains a sufficient amt. of hydrogenatable substance. This is confirmed for toluene at 75° and 120 atm. and at 190° and 33 atm. At low temp., 70°, the rate is independent of both H pressure and toluene concn., in the pressure range 9-140 atm. In this case the *K* centers are predominantly occupied by toluene, the *K'* centers by H. Practically, this leads to the conclusion that it is useless to increase the pressure beyond satn. At higher temp., near 200°, the limiting rate expression is of the first order with respect to H, as confirmed for toluene at 200°, 20-135 atm. The theory also explains the observed inversion of the temp. coeff. of the rate; it is shown that the difference of the apparent activation energies at low and high temp., resp., $E_0 - E_1 = L_0 - L_1$, the heats of adsorption on the *K'* centers for H and the hydrogenatable substance, resp. This leads to the exact condition of the inversion. In the case of toluene, $E_0 - E_1 = 26{,}630$ cal./mole. This can also be deduced from exptl. data on the hydrogenation rate of toluene at medium temp., 120-190°; the fraction of *K'* area covered by H, under 70 atm., at 120°, 130°, 150°, 194°, is calcd. as 83, 67, 47, 7%, resp. In further agreement with the theory, the temp. coeff. of the rate increases with increasing pressure. Poisoning phenomena are amenable to treatment by the theory, provided the structure of the surface is not disrupted. As an example, the first order with respect to H of the hydrogenation of ethyl cinnamate on Ni and the pressure independence of the rate in the presence of CO, are explained quantitatively. Pease's exptl. data on the rate of hydrogenation of ethylene on Cu can be calcd.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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CA

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Catalytic replacement of halogen by hydroxyl in the aromatic series. II. Activators of silica gel. L. Kh. Freidlin, A. A. Balandin, O. A. Fridman, and A. I. Lebedeva (Inst. Organic Chem., Acad. Sci. U.S.S.R.). *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1945, 375-83 (English summary); cf. preceding abstr.—In the gas-phase exchange reaction between chlorobenzene and water vapor, resulting in the formation of phenol and HCl, it has been variously claimed that alk. earth salts may enhance the activity of the silica gel catalyst. Thorough exptl. study of the reaction between 480° and 600° proved this conclusion to be incorrect. The error is ascribed to the use of silica gel catalysts of very low activity. With highly active SiO_2 catalysts, treated with HNO_3 and carefully washed and dried, in quartz or Pyrex reaction tubes 18-30 mm. long, vol. of catalyst 30 ml., temp. const. within ±1°, most inorg. salts were actually found to lower the catalytic activity of SiO_2 gel with regard to the yield of phenol. It is essential to det. the yield of both phenol and HCl, as a substantial yield of HCl coupled with a poor yield of phenol indicates preponderance of side reactions; consideration of the yield of HCl alone has in the past led to erroneous conclusions. A series of runs were made with SiO_2 gel impregnated with various salts, using a total amt. of about 13-17 g. C_6H_5Cl in each run and varying amts. of H_2O, from H_2O/C_6H_5Cl = 0.6 to 8.5. Between runs, the catalyst was regenerated by heating in a stream of air at 600° for 5 hrs. With $CrCl_3$ (5%) in the catalyst, the activity is lowered in the whole temp. range 480° 650°; at 650°, the yield in phenol is 8-10%, as compared with the 20-22% without salt. Ammonium molybdate (3%) leaves the activity of the SiO_2 gel catalyst practically unchanged. At 450°, HgCl (5%) lowers the activity considerably; the effect disappears at 600° and above, due no doubt to volatilization of the HgCl at higher temp. In the presence of LiCl (3%), no phenol was formed even after 3 hrs.; the yield in HCl was 5-6% of the theory; the catalyst remained white, indicating total inactivity. Lowering of catalytic activity (from 10-12% to 8% yield in phenol) was also observed with $MnCl_2$ (10%); after regeneration at 600°, the catalyst appears to be entirely inactive with regard to formation of phenol, although it remains somewhat active with respect to HCl. A highly active SiO_2 gel catalyst (phenol yield at 600° up to 44.6% of the theory) became considerably less active when impregnated with $BaCl_2$, $CaCl_2$, or $MgCl_2$ (10%); at 600° within about 3 hrs., with 10% $BaCl_2$, $CaCl_2$, or $MgCl_2$, yields of phenol were, resp., 21%, 8.6%, 14.4%, as compared with 44.6% without salt. The only case of pos. activation by addn. of salt is $CuCl_2$; with 3% $CuCl_2$, the yield of phenol attained 75% of the theory; Tishchenko's ternary catalyst "DT" contg. 3% $CuCl_2$ and 10% $MgCl_2$ gave a yield of 77.5%. The increased activity is entirely due to the presence of $CuCl_2$; the addn. of $MgCl_2$ resulted in a slight lowering of the specificity of the catalyst. Catalysts rendered inactive by inorg. salts can be fully restored by impregnation with $CuCl_2$.

N. Thon

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Inst. Org. Chem. AN SSSR

PROCESSES AND PROPERTIES INDEX

BC

Distribution of active centres on a mixed catalyst. I. Catalysis of isopropyl alcohol on Al_2O_3–ZnO. A. A. Balandin and V. K. Vasserberg (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1948, 434—443).—The kinetics of the decomp. reaction of PrOH in a unimol. layer were investigated on a mixed catalyst composed of 90% Al_2O_3 and 10% ZnO at varying densities of surface cover. With respect to the alcohol the reaction is of the first order independently of the density of cover. Areas of low activity were found in the region of low density. The heat of activation is 8000 g.-cal. per mol. for average densities and 1800 g.-cal. per mol. for low densities, the no. of active centres being 17 × 10^{18} per g. of catalyst. The areas of highest activity are found at the interfaces of the solid phases of the catalyst. The existence of areas of high adsorption and areas of high catalytic activity was established.

H. C.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

2

Heat of activation of unimolecular catalytic reactions and the variation in volume in a flow system. A. Kh. Bork and A. A. Balandin. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1945, 404-8.—Based on B. and B.'s previous studies of the case of catalytic unimol. reactions in a system of flow at const. pressure of ~1 atm., and in agreement with their kinetic equation, it is shown that the change in vol. does not affect the value of the heat of activation or the values of the velocity coeffs., which vary with temp. in agreement with Arrhenius' equation.
H. A.

M

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

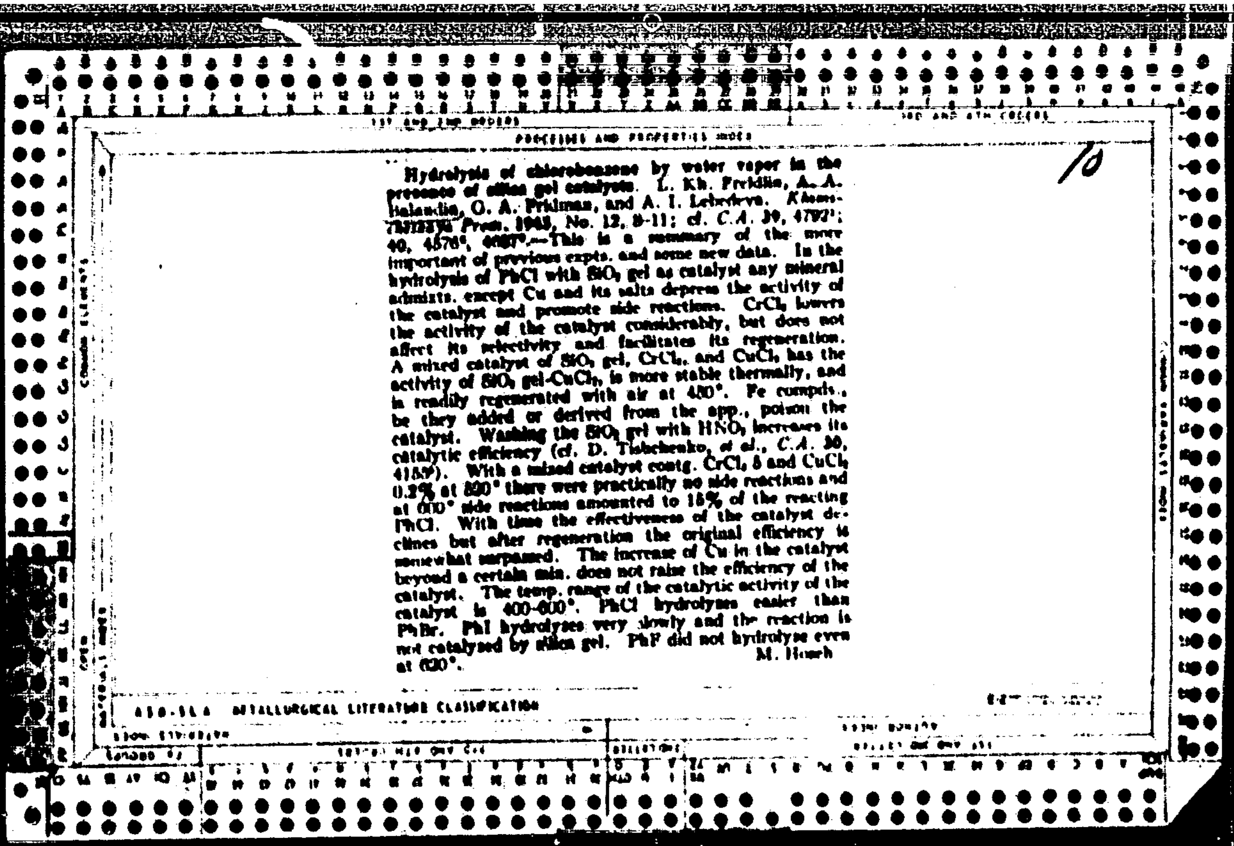
PROCESSES AND PROPERTIES INDEX

Cu

10

Mechanism of vapor-phase catalytic substitution by hydroxyl of halogen attached to aryl group L. Kh. Freidlin, A. A. Balandin, G. A. Fridman, and A. F. Lebedeva. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1945, No. 2, 154 (in English, 162). A theory of the vapor-phase hydrolysis of aryl halides, catalyzed in the liquid phase by Cu and in the vapor phase by SiO₂ gel, is advanced. G. Lebedeff

A-S-L-A METALLURGICAL LITERATURE CLASSIFICATION



1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

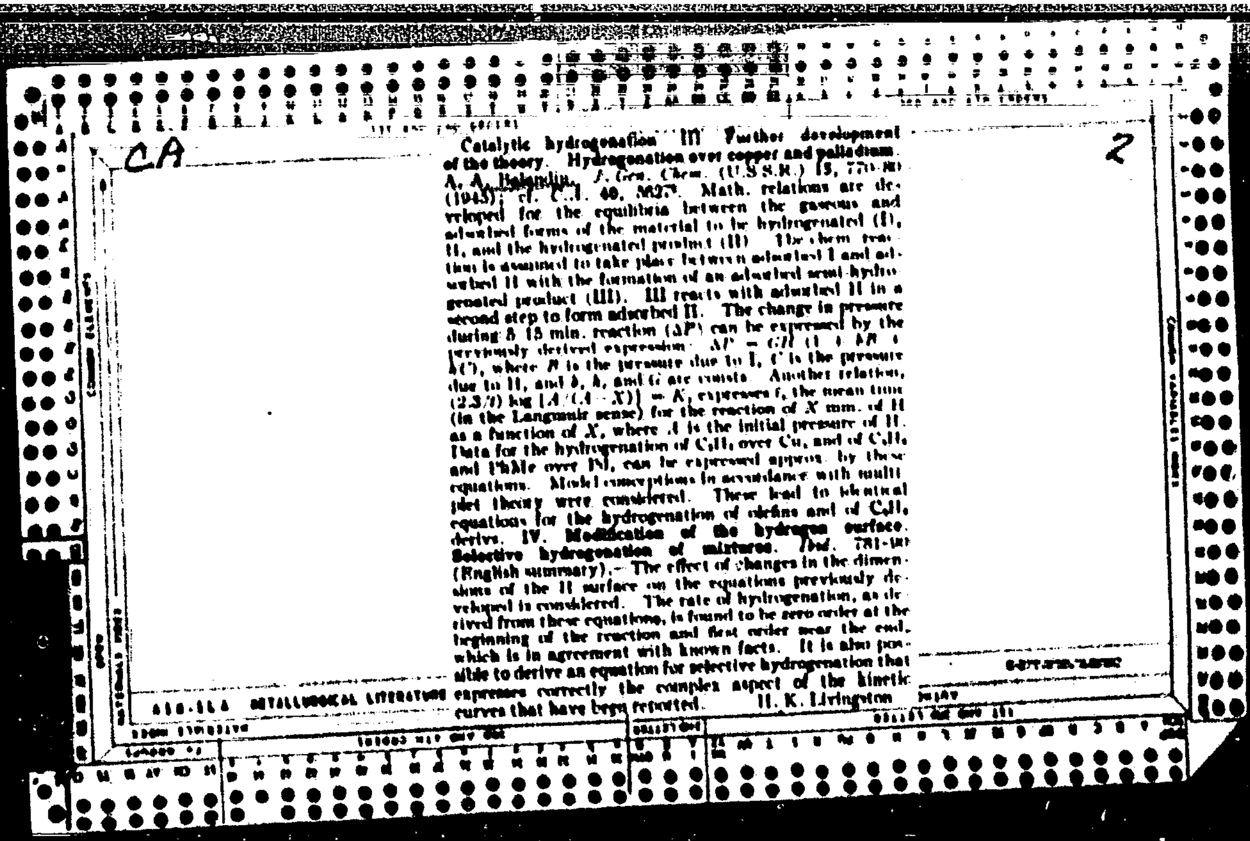
10

Hydrolysis of chlorobenzene by water vapor in the presence of silica gel catalysts. L. Kh. Freidlin, A. A. Balandin, O. A. Prikman, and A. I. Lebedeva. *Khim. Prom.* 1945, No. 12, 8-11; cf. *C.A.* 39, 4792¹; 40, 4576⁶, 6087⁶.—This is a summary of the more important of previous expts. and some new data. In the hydrolysis of PhCl with SiO_2 gel as catalyst any mineral admixts. except Cu and its salts depress the activity of the catalyst and promote side reactions. $CrCl_3$ lowers the activity of the catalyst considerably, but does not affect its selectivity and facilitates its regeneration. A mixed catalyst of SiO_2 gel, $CrCl_3$, and $CuCl_2$ has the activity of SiO_2 gel-$CuCl_2$, is more stable thermally, and is readily regenerated with air at 480°. Fe compds., be they added or derived from the app., poison the catalyst. Washing the SiO_2 gel with HNO_3 increases its catalytic efficiency (cf. D. Tishchenko, *et al.*, *C.A.* 30, 4159⁹). With a mixed catalyst contg. $CrCl_3$ 5 and $CuCl_2$ 0.2% at 520° there were practically no side reactions and at 600° side reactions amounted to 15% of the reacting PhCl. With time the effectiveness of the catalyst declines but after regeneration the original efficiency is somewhat surpassed. The increase of Cu in the catalyst beyond a certain min. does not raise the efficiency of the catalyst. The temp. range of the catalytic activity of the catalyst is 400-600°. PhCl hydrolyzes easier than PhBr. PhI hydrolyzes very slowly and the reaction is not catalyzed by silica gel. PhF did not hydrolyze even at 620°.

M. Hosch

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

"On the Catalytic Hydrogenation. I. Kinetic Equation for Hydrogenation and Dehydrogenation over Nickel Catalysts," Zhur. Obshch. Khim., 15, No. 7-8, 1945. Lab. Kinetic Contact Organic Reactions, Inst. Organic Chemistry, Acad. Sci. SSSR, - 1944-.



CA

2

Catalytic hydrogenation III Further development of the theory. Hydrogenation over copper and palladium. A. A. Balandin. *J. Gen. Chem.* (U.S.S.R.) 15, 770-80 (1945); cf. C.A. 40, 5627. Math. relations are developed for the equilibria between the gaseous and adsorbed forms of the material to be hydrogenated (I), H, and the hydrogenated product (II). The chem. reaction is assumed to take place between adsorbed I and adsorbed H with the formation of an adsorbed semi-hydrogenated product (III). III reacts with adsorbed H in a second step to form adsorbed II. The change in pressure during 5-15 min. reaction (ΔP) can be expressed by the previously derived expression: $\Delta P = CB/(1 + bB + kC)$, where B is the pressure due to I, C is the pressure due to H, and b, k, and G are consts. Another relation, $(2.3/t) \log [A/(A - X)] = K$, expresses t, the mean time (in the Langmuir sense) for the reaction of X mm. of H as a function of X, where A is the initial pressure of H. Data for the hydrogenation of C_6H_6 over Cu, and of C_6H_6 and PhMe over Pd, can be expressed approx. by these equations. Model conceptions in accordance with multiplet theory were considered. These lead to identical equations for the hydrogenation of olefins and of C_6H_6 derivs. **IV. Modification of the hydrogen surface. Selective hydrogenation of mixtures.** *Ibid.* 781-90 (English summary).—The effect of changes in the dimensions of the H surface on the equations previously developed is considered. The rate of hydrogenation, as derived from these equations, is found to be zero order at the beginning of the reaction and first order near the end, which is in agreement with known facts. It is also possible to derive an equation for selective hydrogenation that expresses correctly the complex aspect of the kinetic curves that have been reported. H. K. Livingston

ASM-SLA METALLURGICAL LITERATURE

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

CA

2

Catalytic hydrogenation. I. Kinetic equation of hydrogenation and dehydrogenation over nickel catalyst. A. A. Balandin (Acad. Sci. U.S.S.R.). J. Gen. Chem. (U.S.S.R.) 18, 808-18(1948).—Math.-theoretical. A new theory of catalytic activity is proposed, according to which hydrogenation requires different areas of Ni catalyst for activation of the hydrogenating substance and for activation of H. The adsorption on the active points of either type occurs according to the Langmuir isotherm. The kinetic equations deduced from these considerations explain the quant. relations observed in hydrogenation of toluene over a Ni catalyst on an Al_2O_3 carrier. II. Catalytic hydrogenation over nickel and platinum. Hydrogenation by deuterium. Ibid. 819-27.- The theory proposed in part I is applied to explanation of variation of temp. effect with pressure, and the change of reaction order in catalyst poisoning by CO; the order of reaction in the liquid phase differs from that in the gaseous phase. Hydrogenation by D is discussed. The application of the new concept depends purely on the chem. process involved and on adsorption; diffusion effects have no importance.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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CR

10

Production of α-methylstyrene by catalytic dehydrogenation of isopropylbenzene. A. A. Balandin and G. M. Marukyan (Inst. Org. Chem., Acad. Sci. U.S.S.R.). *Compt. rend. acad. sci. U.R.S.S.* 48, 498-9(1945).—The catalytic dehydrogenation of iso-PrPh (I), b. 149-53°, d_4^{20} 0.8606, n_D^{20} 1.4907, in the presence of CO_2 (1 C_9H_{12}:3 CO_2) by a procedure previously described for PhEt (temp. 625°, velocity of flow 480-600 ml. of liquid I per l. of catalyst per hr.) (cf. Balandin, *et al.*, *C.A.* 36, 417), gives 40-71% of α-methylstyrene (II), b. 160-3°, d_4^{20} [illegible], n_D^{20} 1.5380. Analysis (Br addn. method) of a 200-g. sample of II thus prepd. proved it to contain 96% of II. In the absence of CO_2 the yields of II are somewhat lower.

B. L. May

Cor. Mbr., AN SSSR

Inst. Org. Chem., AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BC

Rôle of the principle of conservation of the valency angle in the multiplet theory of catalysis. A. A. Balandin and J. T. Eidus (*Compt. rend. Acad. Sci. U.R.S.S.*, 1948, [illegible], 655—658).—It is shown that the principle of conservation of the valency angle is a highly important factor during the adsorption of a reacting mol. on a catalyst to form an intermediate multiplet complex, in every way similar to a stable mol. except for instability in the direction of the reaction co-ordinate. Thus, internuclear distances of the catalyst must be related to the dimensions of the adsorbed mol. in order that there may be min. stress in the multiplet complex. Optimum internuclear distances may be calc. by applying the principle of conservation of the valency angle. The different activities of the (110) and (111) planes of Ni in catalysing the hydrogenation of olefines confirm the result of a calculation of the optimum internuclear distance based on the above theory. H. R. C.

Inst. Organic Chem., AN SSSR
Cw. Mbk, AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

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Inst. Organic Chem., AN SSSR 10

Conversion of aryl halides and elimination of aromatically bound halogen by water vapor. L. Kh. Freidlin, A. A. Balandin, A. I. Lebedeva, and O. A. Fridman. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1940**, 439-46.—A new direction of the reaction of ArX with steam was found; this results in elimination of the halogen (replacement by H) and is catalyzed by $CuCl_2$ deposited on oxides of Ti or Sn. Only 2-3% PhOH is formed, while the gas effluent contains HCl, CO, CO_2; Cl, O, and H are absent. It is believed that the initial reaction is an oxidation: $PhCl + 6H_2O \rightarrow HCl + 6CO + 8H_2$; CO is then oxidized by H_2O to CO_2, while H reacts with PhCl and gives HCl and C_6H_6. Cl is eliminated more readily than Br, while dichlorobenzenes give a stepwise reaction yielding C_6H_6 and PhCl. Passage of 16.6 g. PhCl and 13.8-18 g. H_2O over TiO_2 contg. 5% $CuCl_2$ at 500° with a space velocity of 134-281 gave 1.6-2.7% PhOH and 46.1-54.9% HCl; a similar catalyst based on SnO_2 gave 0.7-1.0% PhOH and 18-32% HCl. Either TiO_2, SnO_2, or Cu alone are poorly active. The yields of benzene range about 85% at 500°, with noticeable drop at lower temps., using the combination catalysts (no detailed yields of C_6H_6 are given). The catalyst slowly loses its activity and must be regenerated by air blowing at 500° and satn. with $CuCl_2$. The "elimination" reaction begins at about 400° on the combined catalysts. A TiO_2-$CuCl_2$ catalyst used at 500-50° with PhBr and 1-$C_{10}H_7Cl$ gave similar results: very little ROH forms, while PhBr reacts some 20% less than PhCl under comparable conditions; 1-$C_{10}H_7Cl$ gives about 40% smaller yields than are obtained from PhCl. Passage of a 1:1 mixt. (by wt.) of comm. $Cl_2C_6H_4$ and H_2O over TiO_2-$CuCl_2$ at 500° with a space velocity 307-367 gave 52% HCl, and the products contained PhCl and C_6H_6 in a 6:1 ratio. Passage at 500° of 23.8 g. PhCl and 3.5 l. H in 115 min. (space velocity 242) over the TiO_2-$CuCl_2$ catalyst gave 60% HCl; similar passage of PhCl mixed with 1.3 parts H_2O gave only 28% HCl; this confirmed the theory of the process given above, showing that H liberated by catalysts is capable of complicating the usual aryl halide catalytic hydrolysis. Obviously, catalysts suitable for this "elimination" reaction are undesirable for the conversion of aryl halides into phenols.

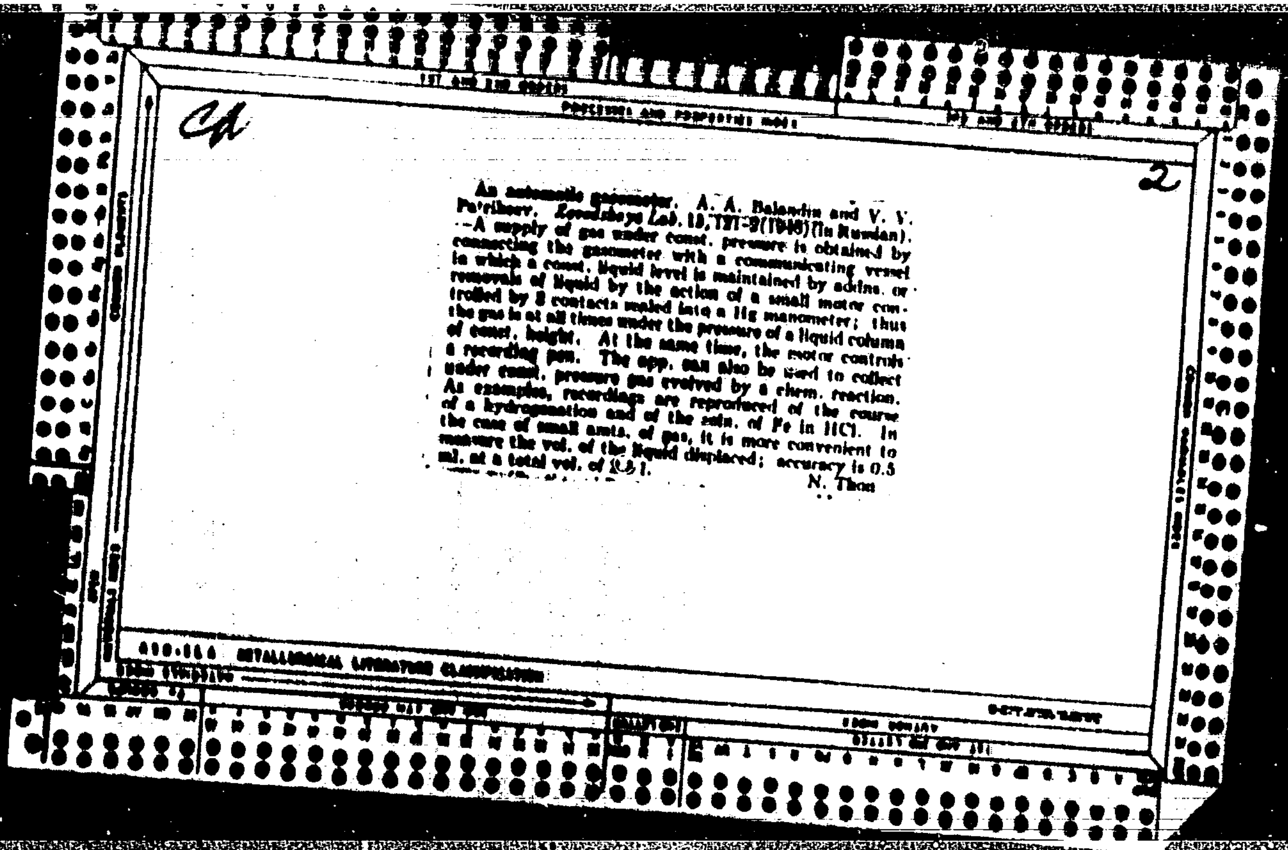
G. M. Kosolapoff

ASD-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A. A.

Kinetics of the dehydrogenation of butylene on a chromium catalyst. A. A. Balandin, O. K. Bogdanova, and A. P. Shcheglova (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1946, 497-513; cf. *C.A.* 40, 6701^4.—(1) All expts. were made with the same type of Cr catalyst ("No. 41") tested for const. activity by the rate of dehydrogenation of butylene (I) to butadiene (II) at const. space velocity and temp., and regenerated in an air stream between runs. Convenient conditions for kinetic study are 540-70° and high space velocity, 11,600 l./l. catalyst/hr.; in this temp. range, under p = 0.25 atm. (final pressure), equil. lies at not less than 30% dehydrogenation to II. Higher temp. favors side reactions. The amt. of II formed is independent of the length of the run (6, 9, and 12 min.). At a time of contact τ = 0.3 sec., the apparent activation energy of I → H_2 + II is 26.26-27.04 kcal./mole at 551-600° and 34.31-34.74 at 535-550°. Examples of balance for 4 min., τ 0.1 sec., vol. of catalyst 2 ml., p 180 mm. Hg: at 540°, I passed 1.51 l., gas collected 1.56 l. (in vol. %: II, by maleic anhydride, 5.5, absorbed in H_2SO_4 90.3, absorbed in Br 0.4, H_2 3.2, satd. hydrocarbons 0.1), yield of II 5.8 mole %; at 570°, 1.02, 1.80 (5.9, 95.1, 0.6, 3.9, 0.4) 5.7; at 598°, 1.02, 2.0 (7.8, 92.0, 0.6, 6.3, 1.1) 8.1. For τ = 0.3 sec., 12 sec., vol. of catalyst 5 ml., p 180 mm Hg: at 551°, 3.63, 3.84 (6.8, 91.4, 0.4, 7.5, 0.0) 7.1; at 593°, 3.62, 4.16 (14.5, 82.7, 0.4, 15.4, 1.2) 10.6; at 600° (15 min.) 5.0, 5.58 (16.73, 81.1, 0.4, 17.2, 1.2) 19.1. (2) Variation of p from 180 to 350 mm. decreased the yield only from 5.5 to 4.8 mole % (at 547°, τ 0.1 sec., 5 min.). This confirms, on the whole, complete coverage of the catalyst surface, the deviation being ascribed to some extent of decompn. of II. (3) In mixts. of I + II, over the same catalyst, both the dehydrogenation I → II and decompn. of II occur. The decompn. increases with the temp. and with the initial content of II in the mixt.; at 547 and 600°, the rate of decompn. of II exceeds that of its formation when the content of II is 29.7%. Examples of balance: vol. of catalyst 2 ml. + 8 ml. crushed quartz, τ 0.1 sec., p 180 mm. Hg, 2 l. mixt. passed in 5 min.: at 547°, I in initial mixt. 100, 87.8, 70.3, and 50.6 mole %, II obtained 100, 275, 574,

OVER →



CA

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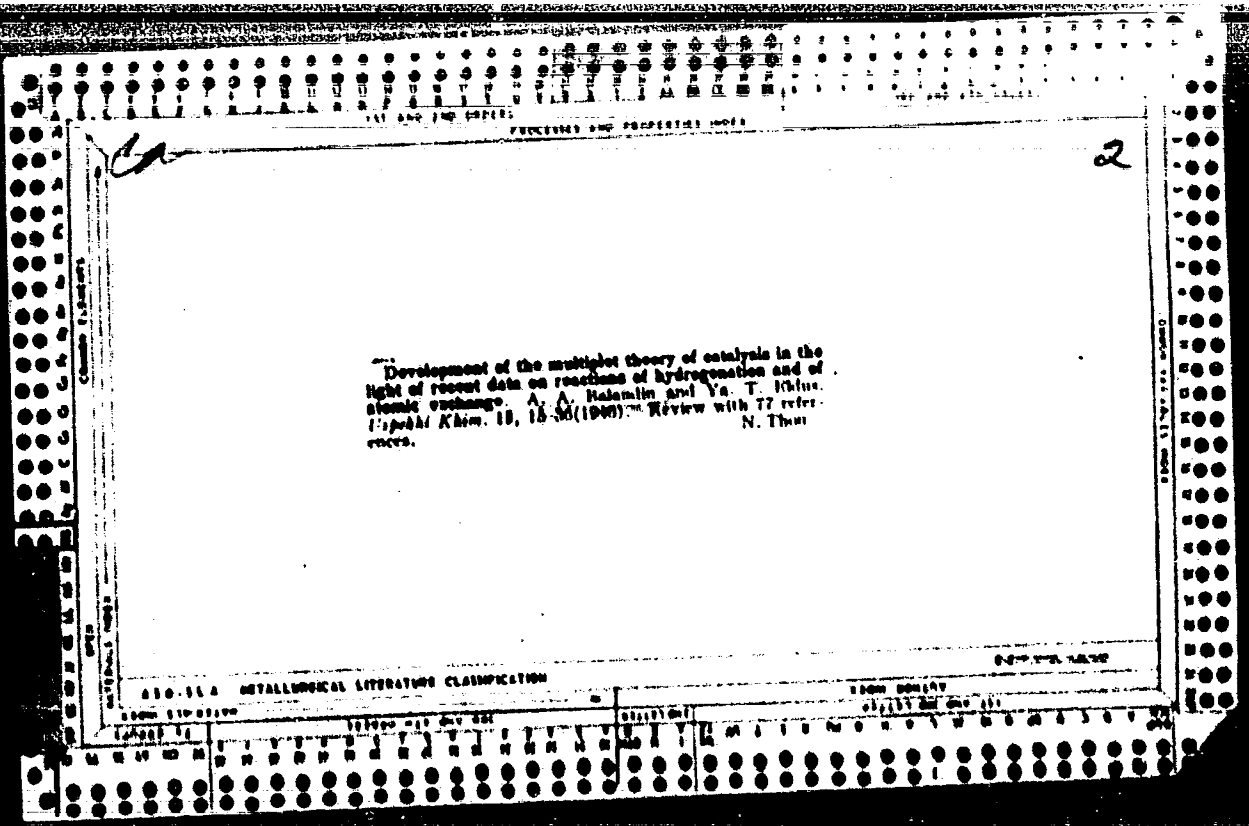
An automatic gasometer. A. A. Balandin and V. V. Patrikeev. *Zavodskaya Lab.* 12, 721-3(1946)(In Russian). —A supply of gas under const. pressure is obtained by connecting the gasometer with a communicating vessel in which a const. liquid level is maintained by adding or removals of liquid by the action of a small motor controlled by 2 contacts sealed into a Hg manometer; thus the gas is at all times under the pressure of a liquid column of const. height. At the same time, the motor controls a recording pen. The app. can also be used to collect under const. pressure gas evolved by a chem. reaction. As examples, recordings are reproduced of the course of a hydrogenation and of the soln. of Fe in HCl. In the case of small amts. of gas, it is more convenient to measure the vol. of the liquid displaced; accuracy is 0.5 ml. at a total vol. of 0.5 l.

N. Thon



Ca

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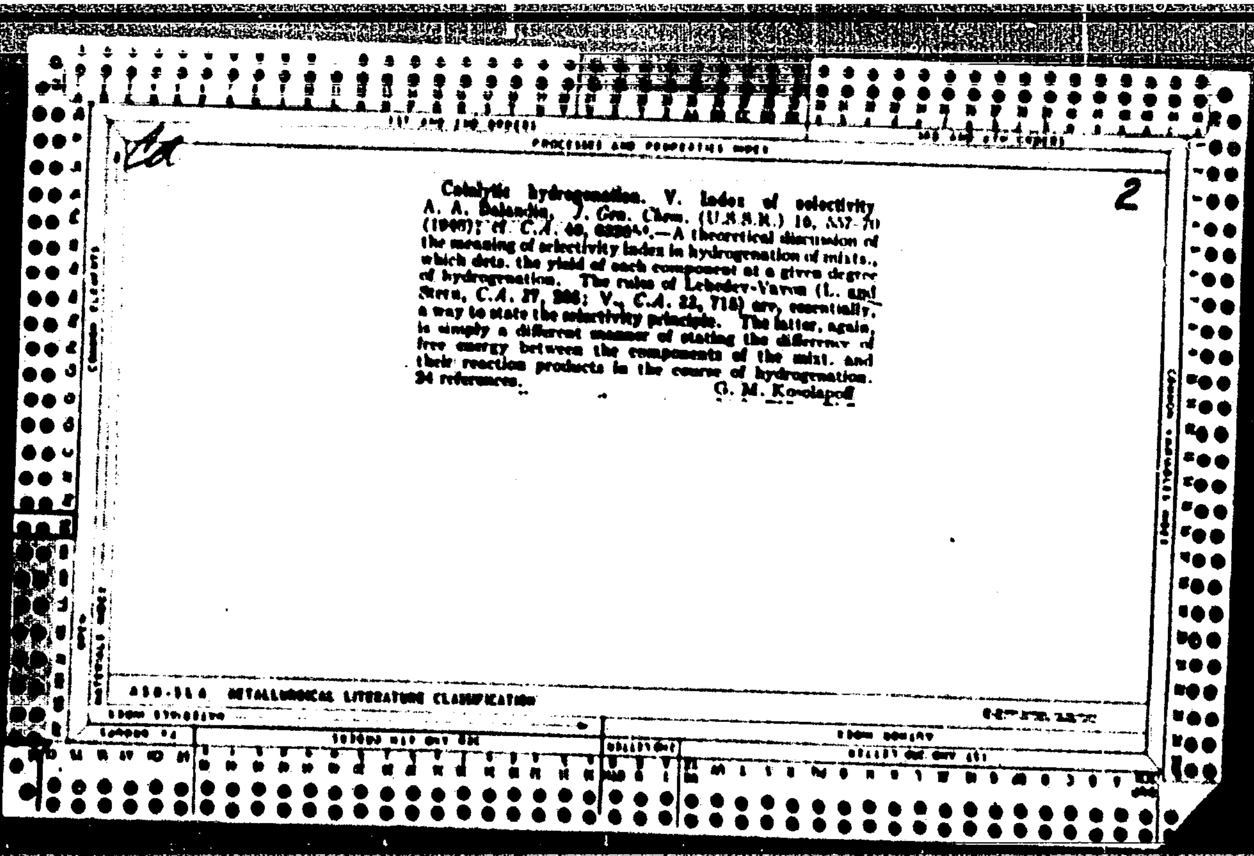
Development of the multiplet theory of catalysis in the light of recent data on reactions of hydrogenation and of atomic exchange. A. A. Balandin and Ya. T. Eidus. *Uspekhi Khim.* 18, 15-30(1949).—Review with 77 references. N. Thon

ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION



PROCESSES AND PROPERTIES INDEX

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Catalytic hydrogenation. V. Index of selectivity. A. A. Balandin. J. Gen. Chem. (U.S.S.R.) 10, 557-70 (1940); cf. C.A. 40, [illegible].—A theoretical discussion of the meaning of selectivity index in hydrogenation of mixts., which detn. the yield of each component at a given degree of hydrogenation. The rules of Lebedev-Yavum (L. and Stern, C.A. 27, 288; V., C.A. 22, 718) are, essentially, a way to state the selectivity principle. The latter, again, is simply a different manner of stating the difference of free energy between the components of the mixt. and their reaction products in the course of hydrogenation. 24 references.

G. M. Kosolapoff

ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A. A.

"On the Theory of the Selection of Catalysts " by A. A Balandin (p. 804)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1946, Volume 16, No.

PROCESSES AND PROPERTIES INDEX

Ca

10

Production of styrene through catalytic dehydrogenation of ethylbenzene. II. A. A. Balandin and O. M. Marukyan. *J. Applied Chem.* (U.S.S.R.) 19, 623-31(1946)(in Russian); cf. *C.A.* 36, 417^7.—(1) On a Cu-Cr catalyst, in EtPh dild. with CO_2 (1:2 mols.) at 600°, the amt., *s*, of $PhCH:CH_2$ produced (in % of the condensate) remained practically independent (46.9–49.8) of the rate of feeding, *f*, between 330 and 900 ml./hr./l. catalyst; at 575°, *s* falls rapidly with increasing *f*, e.g., when *f* = 67 and 300, *s* = 68.5 and 30.5, resp. (2) At 650°, without diln., *s* is lower than in EtPh dild. with CO_2 and falls, but slowly, with increasing *f*: for *f* = 730, 1200, 1640, 2025, 3100, *s* = 35.4, 34.9, 31.8, 30.7, 22.4, resp.; hence, the productivity, *P* = *sf'*, (expressing *f'* in kg./hr./l.) can be higher at a higher *f*, e.g., diln. 1:2, *f* = 450, *P* = 0.214; no diln., *f* = 3100, *P* = 0.317 kg./hr./l. (3) Variation of the length of the column of catalyst from 20 cm. (holding 34 ml. catalyst) to 11 cm. (25 ml.) had no effect on *s* at 600–625° and *f* 300–500. (4) Example of a balance of a 5-hr. run: total EtPh passed 43 g., at 600°, *f* 470, diln. EtPh:CO_2 = 1:2 mols.; product 41.8 g. condensate, 15.5 l. gas; *s* = 49.7%, yield 46.2% based on EtPh passed; in the condensate, PhMe 0.26 g., PhEt 19.0 g., the rest polymerized styrene; hence, the yield with respect to PhEt converted, 81%; gas, CO_2 5.4, unsatd. 0.6, O_2 0.6, CO 40.6, H_2 39.8, the rest CH_4, C_2H_6, N_2. (5) A fresh catalyst gave *s* 51.3, after 30 hrs. *s* 41, after a 1st regeneration *s* 48.8, falling to 34 after 21 hrs.; on 2nd regeneration after 71 hrs., *s* = 50.4. (6) Regeneration of a catalyst fallen from *s* 51.3 to 39 (at 650°) in an air stream at 500° for 2 hrs. restored its full original activity; the same effect was attained with an air-steam mixt. (1:1) at 300 l./hr./l. for 2 hrs.; steam alone restored the activity only to *s* 45; it is recommended to regenerate every 20–23 hrs. (7) Under a pressure reduced to 300 mm. Hg, *s* was 41 as against 30 under 1 atm. and 48 in 1:2 mol. diln. with CO_2 (at 600°); consequently, diln. with CO_2 is more effective than reduced pressure. (8) Activation of the freshly prepd. catalyst, at 500°, in H, resulted in *s* 45.4 as against *s* 37.7 in CO_2; no activation in H is necessary after regeneration. (9) Spectroscopic traces of Ba inactivate the Cu-Cr catalyst. (10) Addn. of H_3PO_4 raises the activity but this effect cannot be restored on regeneration. (11) *To det. $PhCH:CH_2$* in the condensate, 0.1–0.2 g. is dissolved in 10 ml. $CHCl_3$, then 10–20 ml. of 0.1 *N* Br in AcOH added until a light-yellow tint is obtained; after 15 min. standing in the dark, 10 ml. of 10% KI is added and the excess iodine titrated with $Na_2S_2O_3$; accuracy 0.75%.

N. Thon

A S M - S L A METALLURGICAL LITERATURE CLASSIFICATION

Pyrolysis of ethylbenzene and of styrene. S. A. Balandin, O. M. Marukyan, and A. A. Tolstopyatova (Inst. Org. Chem. Acad. Sci. U.S.S.R. and Moscow State Univ.). *J. Applied Chem.* (U.S.S.R.) 19, 1079-92(1946)(in Russian).—In noncatalyzed pyrolysis of PhEt, the av. yield of condensate is const., about 80%. The content S of PhCH:CH$_2$ in the condensate rises with the temp. up to a max., then falls; example, time of contact τ = 20-24 sec., at 550, 575, 625, 650, 675°, S = 0.7, 11.3, 29.3, 32.0 (max.), 26.3%. The same variation is found on diln. with CO$_2$ (1:2 mol.), at τ = 8-9 (corresponding to 20-24 with respect to undild. PhEt), S = 0.51, 6.2, 30.5, 38.5 (max.), 31.4%. Yields are consequently lower throughout than in Cu-Cr-catalyzed conversion, but in all cases there is a max. at 650°. The homogeneous nature of the noncatalyzed reaction was demonstrated by comparative expts. in virgin quartz, porcelain, steel, and iron tubes, and with silica gel and carbon packings; neither the latter nor the nature of the wall have an effect on the yield, except that in steel and iron carbon black dendrites are deposited abundantly after a few hrs.; this does not occur on Cu or on enamel-primed Fe. The S-increasing effect of diln. with CO$_2$ is also found with N$_2$ and H$_2$, i.e., the action of the inert diluent is not specific. At the const. temp. 650°, lengthening of τ results in a steep increase of S up to a max. (≈ 39% with 1:2 CO$_2$) at τ 8 sec., followed by a very slow decline with further increasing τ; the max. has nothing to do with reaching an equil., since S can attain much higher values with catalysts; it merely indicates that, beyond the max., the rate of decompn. of PhCH:CH$_2$ has a higher temp. coeff. than its formation. A typical condensate contains PhCH:CH$_2$ 32, C$_6$H$_6$ 6.4, toluene 7.5, PhEt 54.3. The absence of significant amts. of PhC$_6$H$_4$Et and of PhCH$_2$CH$_2$C$_6$H$_4$Me and the presence of toluene in the condensate conflict with Pease and Morton's (*C.A.* 27, 4062) assumption of the formation of CH$_4$ and C$_2$H$_6$ in the gas from these compds.; rather, CH$_4$ and C$_6$H$_6$ are formed by way of hydrogenolysis of PhEt and PhCH:CH$_2$; inasmuch as diln. with H$_2$ is indifferent, this hydrogenolysis may be due to H and, if so, would be a chain reaction. This could not be directly proved—but neither was it disproved—by applying Hinshelwood's CH$_3$CH:CH$_2$ criterion which did not inhibit formation of PhCH:CH$_2$. The degree η of pyrolytic decompn. of PhCH:CH$_2$ (dild. with 1:2 CO$_2$) increases from 550 to 650°, the faster the lower τ. At τ 30 sec., η rises from 3% to 11% between 550 and 650°; at 650°, τ 140-180 sec., η = 27%; without diln., this η is reached at 610°, with τ 90. Hence, diln. slows decompn. of PhCH:CH$_2$. Also, under all conditions, the decompn. of PhCH:CH$_2$ is slower than its formation from PhEt. Addn. of PhNH$_2$, known to inhibit polymerization, lowers η, e.g., at 650°, τ 71, from 26.9 to 20.8% with 5.2 wt. % PhNH$_2$, and to 24.7% with 3.2%; at smaller τ, the effect is significant only with the higher (5.2%) contents of PhNH$_2$. Likewise, addn. of 5% PhOH lowered η from 11 to 6.3 at τ 28 and from 26.9 to 16.1 at τ 71; smaller amts. of PhOH (1%) are effective only at the longer τ. On this basis, addn. of PhOH has a beneficial effect on S on the pyrolysis of PhEt: at 650°, τ 71, S rose from 33 to 40% on addn. of 1.65% PhOH owing to a slowing down of the decompn. which would normally be significant at such long τ. Polymerization of PhCH:CH$_2$ is catalyzed by C; thus, a condensate contg. 77.6% PhCH:CH$_2$, passed over activated C at 300 ml./l./hr. at 450° was converted into a more viscous liquid contg. only 31.2% PhCH:CH$_2$. The effect is much weaker at 650°. N. Thon

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Ca

10

Dehydrogenation of ethylbenzene in its mixtures with xylene. A. A. Balandin and G. M. Marukyan (Inst. Org. Chem., Acad. Sci. U.S.S.R.). *J. Applied Chem.* (U.S.S.R.) 19, 1277-80(1946)(in Russian); cf. preceding abstr.—Instead of attempting to sep. PhEt from the close-boiling $C_6H_4Me_2$ in xylenic fractions by distn., it is more convenient to utilize the former by dehydrogenating it directly to PhCH:CH_2 without previous sepn.; not only does $C_6H_4Me_2$ not inhibit the reaction but it even promotes it without itself undergoing decompn. Even though at 625°, diln. with CO_2 1:3, Cu-Cr catalysts, vol. rate 400-800 ml./l./hr., the styrene content in the condensate does decrease, with the $C_6H_4Me_2$ content in the initial mixt. increasing at the expense of PhEt, the fall is distinctly *slower* than the decrease of the latter; thus, with initial PhEt 60, 34, and 10%, the PhCH:CH_2 obtained (reduced to standard catalyst activity) was 37.5, 34.5, and 21% of the condensate, and hence the *relative* dehydrogenation 84, 101, and 110%, resp., i.e., actually rising with increasing diln. by $C_6H_4Me_2$ (figures exceeding 100% being of course due to exptl. errors, particularly at low PhEt) which is tantamount to a promoting effect of $C_6H_4Me_2$. In PhEt-$C_6H_4Me_2$ mixts., the catalysts are exhausted faster than in pure PhEt but can be fully regenerated with the same ease in an air stream at 600-650°. As in exptl. PhEt-$C_6H_4Me_2$ mixts., high yields of PhCH:CH_2 were obtained with industrial xylenic fractions with 20-30% PhEt: at 635 and 680°, 13.7 and 28.6% styrene in the condensate, resp. Diln. with CO_2 is beneficial. Extn. by fractionation of the styrene formed being difficult on account of the closeness of the b.ps., polymerization with the aid of Bz_2O_2, followed by distn. of the liquid components, is recommended; the monomer, needed for the manuf. of synthetic rubber, can be recovered by depolymerization. N. T.

ASB-SLA METALLURGICAL LITERA

CA

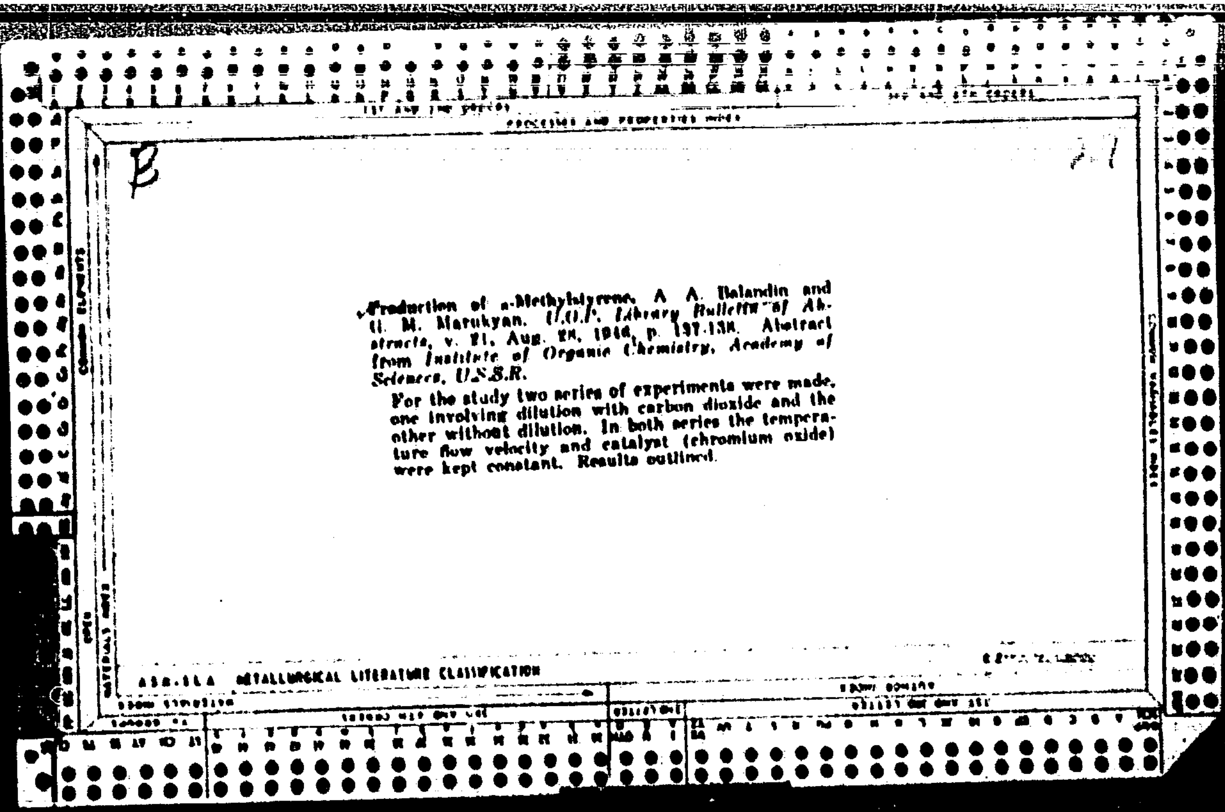
PROCESSES AND PROPERTIES INDEX

2

The mechanism of the vapor-phase catalytic substitution of hydroxyl for aryl halogen. L. Kh. Freidlin, A. A. Balandin, A. I. Lebedeva, and G. A. Fridman (Acad. Sci. of U.S.S.R., Moscow). *Acta Physicochim. U.R.S.S.* 11, 55-78(1939).—The present work on the vapor-phase reaction of aryl halides with H_2O in the temp. range of 400°-600° is compared with past work, particularly in the case of chlorobenzene (I). The unique role of SiO_2 gel (II) as a catalyst for the replacement of aryl halogen by OH is pointed out, as well as the fact that only Cu and its salts promote the action of II, whereas other salts decrease it. A theory of the process based on the formation of intermediate silicate esters is proposed which explains the previous facts as well as the other observed phenomena assocd. with the vapor-phase hydrolysis of I to phenol.

P. J. Elving

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



PROCESSES AND PROPERTIES INDEX

B

21

Production of α-Methylstyrene. A. A. Balandin and G. M. Marukyan. *U.O.P. Library Bulletin of Abstracts*, v. 21, Aug. 28, 1946, p. 137-138. Abstract from *Institute of Organic Chemistry, Academy of Sciences, U.S.S.R.*

For the study two series of experiments were made, one involving dilution with carbon dioxide and the other without dilution. In both series the temperature flow velocity and catalyst (chromium oxide) were kept constant. Results outlined.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

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2

The distribution of active centers on mixed catalysts. I. Decomposition of isopropyl alcohol on Al_2O_3-ZnO. A. Balandin and V. Vaserberg (Inst. Org. Chem., Moscow). *Acta Physicochim. U.R.S.S.* 21, 678-88(1946) (in English); cf. *C.A.* 30, 3308^9; 29, 6124^4.—Isopropyl alc., 0.5-5 mm. pressure, was completely absorbed by 1.04 g. of 90% Al_2O_3-10% ZnO catalyst (cf. *C.A.* 37, 6231) which had been dried at 300° for 40-50 hrs. to 0.0001 mm. pressure. The reaction was followed at 82°-100° by measuring C_3H_6 pressure. The results were independent of the order of performing the expt. At sparse surface covering, from 0.06 to 0.15 cc. (N.T.P.) per g., the reaction velocity rises linearly; it remains const. to about 0.8 cc. per g., above which the const. falls. The activation energy at sparse covering of the surface is 18,000 cal. per mol., and is 8,900 in the horizontal range. The results differ from those of Dohse (*C.A.* 25, 5327) at low coverage of the surface. The results are interpreted to indicate that the most active catalyst patches are at the interfaces of the two solids. The active centers, estd. at 1.7×10^{19} per g. from the horizontal section of the curve, capable of the strongest adsorption need not be the most active catalytically.

A. Fleischer

Inst. Organic Chem., Moscow-AN SSSR

ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A.

USSR/Chemistry - Catalysts
Chemistry - Silica, Collodial

ep/Oct 46

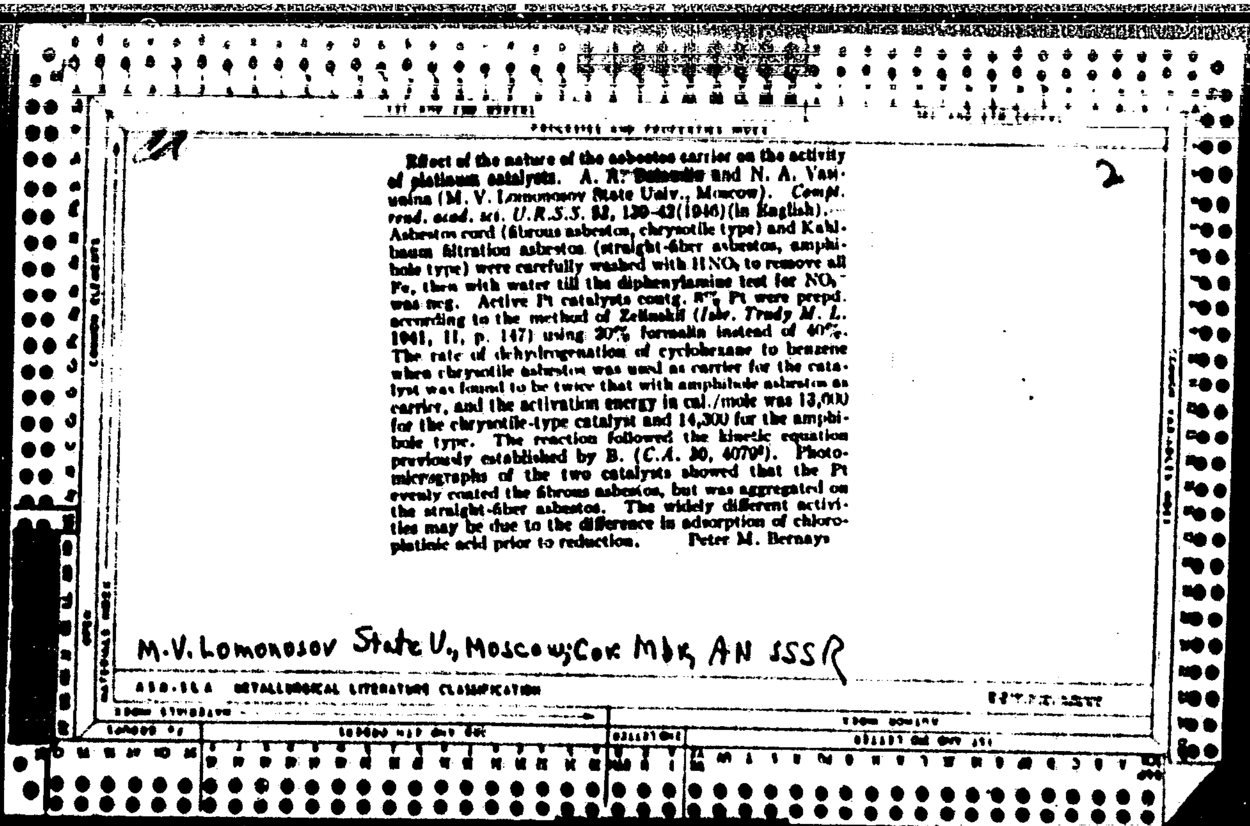
"A Physicochemical Study of Silica-Gel Catalysts," T. Rode, A. Balandin, Inst Org Chem, Acad Sci USSR, MOSCOW, 16 pp

"Acta Physicochimica URSS" Vol XXI, No 5

Gives differential heating curves for silica-gel catalysts. Plots curves of rate of sorption of water, at room temperature, by catalysts after preliminary heat treatment for several days at temperatures 465, 545, 700, 790, and 1030°C. Shape of these curves indicates that the thermal irreversible inactivation of catalyst, which starts 480-550°C, is not due to any inner structural change but probably to elimination of definite amount of chemically bound water. Received, 12 Oct 1945.

PA 54T40

Inst. Organic Chem., AN SSSR



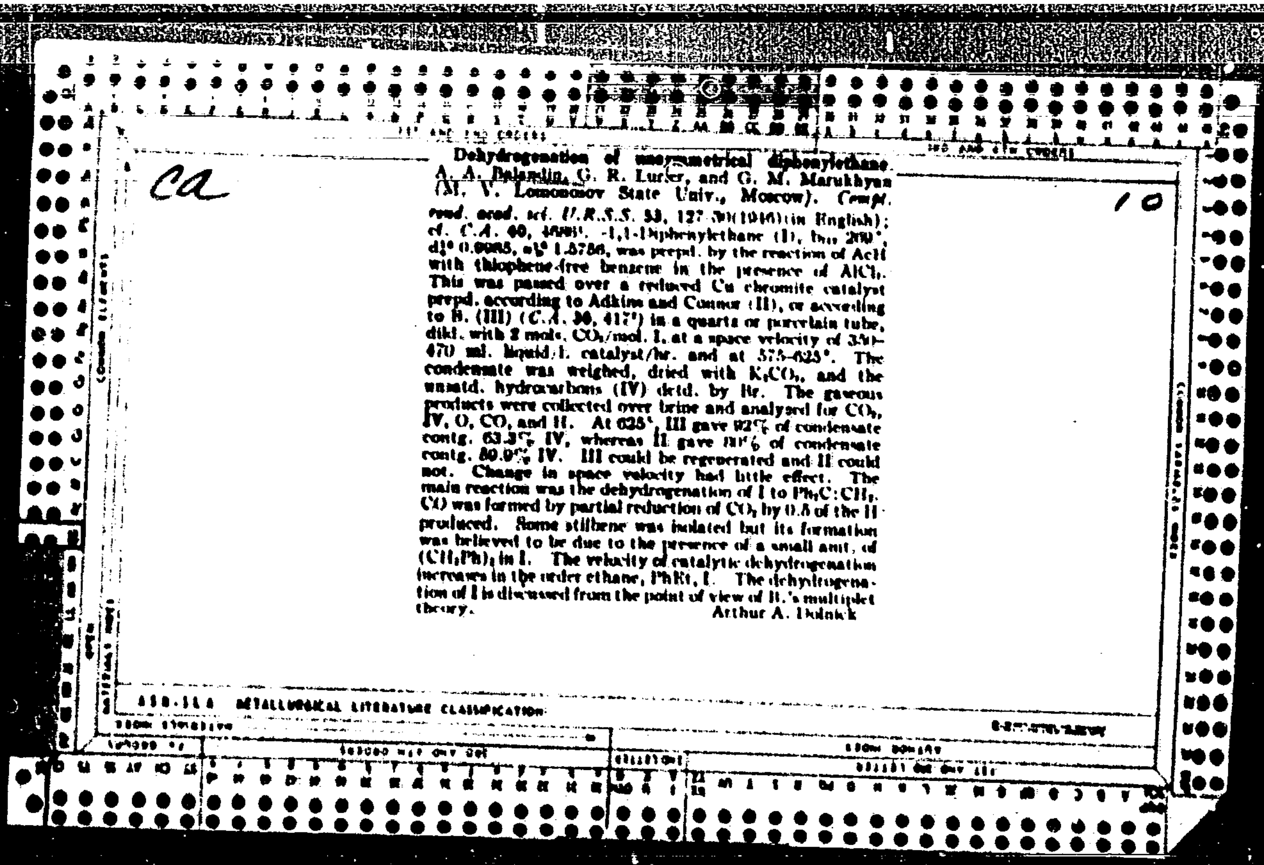
PROCESSES AND PROPERTIES INDEX

2

Effect of the nature of the asbestos carrier on the activity of platinum catalysts. A. A. Balandin and N. A. Vasyunina (M. V. Lomonosov State Univ., Moscow). *Compt. rend. acad. sci. U.R.S.S.* 52, 139-42(1946)(in English).—Asbestos cord (fibrous asbestos, chrysotile type) and Kahlbaum filtration asbestos (straight-fiber asbestos, amphibole type) were carefully washed with HNO_3 to remove all Fe, then with water till the diphenylamine test for NO_3^- was neg. Active Pt catalysts contg. 8% Pt were prepd. according to the method of Zelinskii (*Izbr. Trudy M. L.* 1941, II, p. 147) using 20% formalin instead of 40%. The rate of dehydrogenation of cyclohexane to benzene when chrysotile asbestos was used as carrier for the catalyst was found to be twice that with amphibole asbestos as carrier, and the activation energy in cal./mole was 13,000 for the chrysotile-type catalyst and 14,300 for the amphibole type. The reaction followed the kinetic equation previously established by B. (*C.A.* 30, 4070^8). Photomicrographs of the two catalysts showed that the Pt evenly coated the fibrous asbestos, but was aggregated on the straight-fiber asbestos. The widely different activities may be due to the difference in adsorption of chloroplatinic acid prior to reduction. Peter M. Bernays

M.V. Lomonosov State U., Moscow; Cor Mbr, AN SSSR

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION



Ca

10

Dehydrogenation of unsymmetrical diphenylethane. A. A. Balandin, G. R. Lurie, and G. M. Marukhyan (M. V. Lomonosov State Univ., Moscow). *Compt. rend. acad. sci. U.R.S.S.* 53, 127-30(1946)(in English); cf. *C.A.* 40, 4680^1.—1,1-Diphenylethane (I), b_{760} 280°, d_4^{20} 0.9985, n_D^{20} 1.5756, was prepd. by the reaction of AcH with thiophene-free benzene in the presence of $AlCl_3$. This was passed over a reduced Cu chromite catalyst prepd. according to Adkins and Connor (II), or according to B. (III) (*C.A.* 30, 417^7) in a quartz or porcelain tube, dild. with 2 mols. CO_2/mol. I, at a space velocity of 350-470 ml. liquid I/l. catalyst/hr. and at 575-625°. The condensate was weighed, dried with K_2CO_3, and the unsatd. hydrocarbons (IV) detd. by Br. The gaseous products were collected over brine and analyzed for CO_2, IV, O, CO, and H. At 625°, III gave 92% of condensate contg. 63.3% IV, whereas II gave 91% of condensate contg. 80.9% IV. III could be regenerated and II could not. Change in space velocity had little effect. The main reaction was the dehydrogenation of I to $Ph_2C:CH_2$. CO was formed by partial reduction of CO_2 by 0.5 of the H produced. Some stilbene was isolated but its formation was believed to be due to the presence of a small amt. of $(CH_2Ph)_2$ in I. The velocity of catalytic dehydrogenation increases in the order ethane, PhEt, I. The dehydrogenation of I is discussed from the point of view of B.'s multiplet theory.

Arthur A. Dolnick

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A. A., KHARINA, Z. V., TEYS, R. V.

"Isotopic Exchange in the Hydrogenation of Benzene with Deuterium over Platinum and Chromic Oxide Catalysts," Z. V. Kharina, R. V. Teys
"Compt Rend Acad Sci Urss" Vol 53, 1946, pp715-18

During the hydrogenation of benzene over a Pt-on-asbestos catalyst and over Cr_2O_3, it was observed that exchange with D occurred. Under the conditions of the experiment, i.e., at 100^0 with the Pt catalyst and with a H-benzene mole ratio of 4, complete hydrogenation was achieved, but with the Cr_2O_3 catalyst at 160^0 and with the other conditions the same, the degree of hydrogenation was about 8-12%, whereas the degree of isotopic exchange amounted to as much as 74%.

SO: W-336, 31 Mar. 48.

"The Mechanism of the Vapour Phase Catalytic Substitution of Hydroxyl for Aryl Halogen,"

Dok AN55, No. 1, 1946. Acad. of Sci., Inst. of Organic Chem. Moscow. -c1945-.

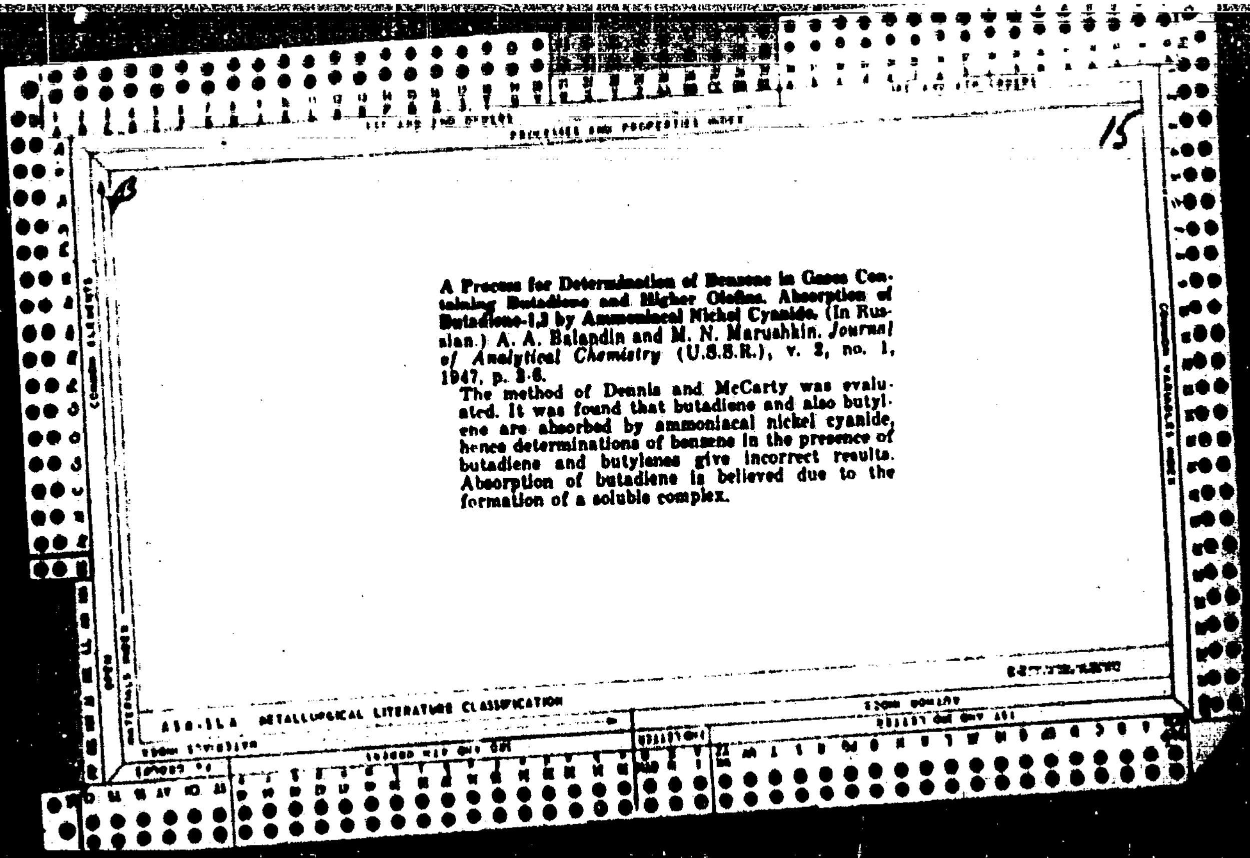
CA

PROCESSES AND PROPERTIES INDEX

10

Catalytic exchange of halogen for hydroxyl in the aromatic series. III. Activating effect of copper. L. Kh. Freidlin, A. A. Balandin, A. I. Lebedeva, and G. A. Fridman. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1947, 515-22 (in Russian); cf. *C.A.* 40, 4577^1; 39, 4702^4; 40, 5027^9.—The catalytic activity of silica gel in the gas-phase conversion of PhCl into PhOH by H_2O vapor is strongly increased by Cu. The catalyst is prepd. by impregnation of silica gel with 0.2% $CuCl_2$ and admixt. of metallic Cu (6%) to compensate for loss of Cu through volatilization, which is noticeable above 400° and marked above 450-500°. With metallic Cu added, the activity of the catalyst is fully preserved up to 550° but falls off somewhat on heating above that temp.; pure silica gel suffers thermal deactivation in about the same temp. range (500-550°). In tubes of 15-20 mm. diam., vol. of catalyst 50 ml., with 15.6 g. PhCl and about 10-15 g. H_2O passed in each run, at 450°, 500°, 550°, and 600°, 40-50 min., the yields of PhOH were approx. twice those obtained with the same catalyst without Cu. Complete regeneration is achieved by heating in an air stream 6 hrs. at 500°. Yields of PhOH attained were over 30% of the PhCl passed. Catalysts poisoned by H_3PO_4, $MgCl_2$, or $CrCl_3$ can be almost completely restored by impregnation with $CuCl_2$ but Cu is without effect on thermally deactivated catalysts. Thus, treatment with Cu salts can be used to distinguish between reversible and irreversible deactivation. Activation with $CuSO_4$ is equally effective, $CuCl_2$ being formed in the course of the reaction. Cu alone does not catalyze the exchange. N. Thon

ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION



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B

A Process for Determination of Benzene in Gases Containing Butadiene and Higher Olefins. Absorption of Butadiene-1,3 by Ammoniacal Nickel Cyanide. (In Russian.) A. A. Balandin and M. N. Marushkin. *Journal of Analytical Chemistry* (U.S.S.R.), v. 2, no. 1, 1947, p. 3-6.

The method of Dennis and McCarty was evaluated. It was found that butadiene and also butylene are absorbed by ammoniacal nickel cyanide, hence determinations of benzene in the presence of butadiene and butylenes give incorrect results. Absorption of butadiene is believed due to the formation of a soluble complex.

BALANDIN, A. A.

Kinetics of the catalytic formation and decomposition of styrene. A. A. Balandin and A. A. Tolstopyatova (Acad. Sci. U.S.S.R. and Moscow State Univ.). *J. Gen. Chem.* (U.S.S.R.) 17, 2182-92(1947)(in Russian); cf. *C.A.* 41, 5117i.—In order to det. quantitatively the yields of PhCH:CH$_2$ from PhEt as a function of temp., space velocity, and time of contact, 30-min. runs were made under rigorously controlled conditions with catalysts of medium activity, regenerated at frequent intervals for just the time necessary (15-25 min.) to keep the activity unchanged; this was checked by standard runs, before and after each expt., with 273 ml. liquid PhEt/l. catalyst/hr., PhEt:CO$_2$ = 1:2 mols., at the given temp. With frequent short regenerations, one portion of the catalyst kept a const. activity during 78-80 runs. The contents *x* of PhCH:CH$_2$ in the condensate were corrected in each case for the slight difference between the actual activity of the catalyst in the main run and that shown in the 2 control runs, and refer consequently to the same activity. In a special 7-hr. expt. at 650°, it was ascertained that the condensate contains only PhCH:CH$_2$ and unreacted PhEt. At 550° and 575°, with 20 ml., 7 cm. of catalyst, diln. PhEt:CO$_2$ = 1:2 mols., increase of the space velocity resulted in rapid decrease of *x*; e.g., at 550°, 100 and 500 ml./l./hr., *x* = 70 and 30% resp.; at 575°, 60 and 31.5%, resp.; the 2 curves (550 and 575°) intersect at about 150 ml./l./hr., *x* = 48.5%. At 650°, *x* first increases with increasing space velocity, passes through a very flat max. (*x* about 40%, at about 380 ml./l./hr., then slowly decreases, to 33% at 2203 ml./l./hr. Correspondingly, plots of *x* against the time of contact $\tau = 60\pi r^2 l/v$, where r = radius of the tube, l = length of catalyst, $v = [(22410\,cd/tM) + a]\,(T/273)$ (where c = ml. of liquid PhEt, of sp. gr. d, passed in t min., M = mol. wt., a = velocity of the dilg. gas (CO$_2$) in ml./min., T = abs. temp.), at 550° and 575°, show uniform increase with increasing τ, faster at lower τ; at 650° *x* first rises steeply with increasing τ, to about 40% at τ = 3.5 sec., then decreases slowly. The obvious interpretation that the fall of *x*, at 650°, at very low space velocities, is due to decompn. of the PhCH:CH$_2$ formed, was confirmed directly by passing it over the same catalyst, dild. with CO$_2$ (1:2 moles), at 100 and at 273 ml. liquid/l./hr.; at the former space velocity, at 650°, up to 30% of the PhCH:CH$_2$ passed is decompd. The degree of decompn. increases with the temp. and with τ. That the max. of *x*, observed at 650°, is actually a result of decompn. of PhCH:CH$_2$ is shown by extrapolating the curve of *x* against τ, beyond the max.; this extrapolation would give, at τ = 7.1 sec., *x* = 72% as against the actual 45%; the deficit, 27%, equals very closely the degree of decompn. found directly at that temp. and τ. The velocity of catalytic decompn. of PhCH:CH$_2$ is considerably higher than that of its pyrolytic decompn.; thus, at 625°, pyrolysis left 95.3% PhCH:CH$_2$ unchanged, whereas in catalytic decompn., at the same temp., and a shorter τ, 18.2 sec., only 68.2% re-

See other side!

BALANDIN, A. A. PA40T8

USSR/Chemistry - History Sep/Oct 1947
Chemistry - Biographies

"Soviet Chemistry on Eve of Thirtieth Anniversary of October Revolution," A. A. Balandin, B. M. Berkengeym, A. N. Nesmeyanov, Moscow, 20 pp

"Uspekhi Khimii" Vol XVI, No 5

General historical article briefly recounts more important works of Soviet scientists, such as Lomonosov, Gess, Bakh, Vernadskiy, Fersman, etc. Pictures of the more important of these scientists.

LC 40T8

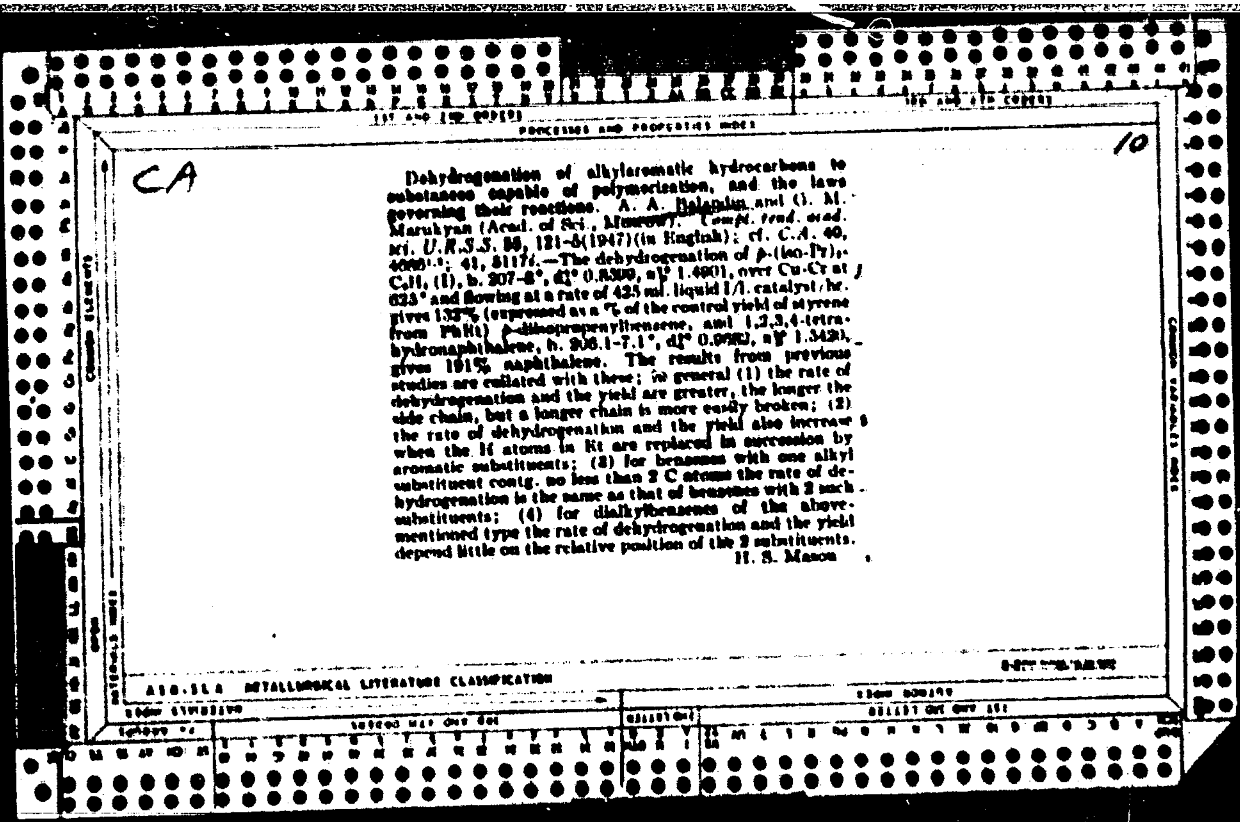
1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

M

Kinetics of Hydrogenation and of Related Reactions. I. The Mechanism of Hydrogenation, Dehydrogenation, and Deuterium Exchange. II. Kinetics of Hydrogenation with Nickel, Platinum, and Copper. III. Selective Hydrogenation. A. Balandin (*Acta Physicochim. U.R.S.S.*, 1947, 22, (1), 81–100; 101–120; (2), 238–256). (In English). (I.—) A new theory of hydrogenation is advanced. (II.—) The kinetics of hydrogenation on nickel, platinum, and copper are treated from the point of view of the new theory of hydrogenation. The theory agrees with the facts, many of which could not be accounted for by previous theories. (III.—) The new theory is applied to the catalytic hydrogenation of mixtures. —N. H.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



PROCESSES AND PROPERTIES INDEX

CA

10

Dehydrogenation of alkylaromatic hydrocarbons to substances capable of polymerization, and the laws governing their reactions. A. A. Balandin and O. M. Marukyan (Acad. of Sci., Moscow). *Compt. rend. acad. sci. U.R.S.S.* 56, 121-4(1947)(in English); cf. *C.A.* 40, 4060; 41, 5117*i*.—The dehydrogenation of *p*-(iso-Pr)$_2$C$_6$H$_4$ (I), b. 207-8°, d_4^{20} 0.8509, n_D^{20} 1.4901, over Cu-Cr at 623° and flowing at a rate of 425 ml. liquid/l. catalyst/hr. gives 133% (expressed as a % of the control yield of styrene from PhEt) *p*-diisopropenylbenzene, and 1,2,3,4-tetrahydronaphthalene, b. 206.1-7.1°, d_4^{20} 0.9682, n_D^{20} 1.5420, gives 191% naphthalene. The results from previous studies are collated with these; in general (1) the rate of dehydrogenation and the yield are greater, the longer the side chain, but a longer chain is more easily broken; (2) the rate of dehydrogenation and the yield also increase when the H atoms in Et are replaced in succession by aromatic substituents; (3) for benzenes with one alkyl substituent contg. no less than 2 C atoms the rate of dehydrogenation is the same as that of benzenes with 2 such substituents; (4) for dialkylbenzenes of the above-mentioned type the rate of dehydrogenation and the yield depend little on the relative position of the 2 substituents.

H. S. Mason

METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

CA

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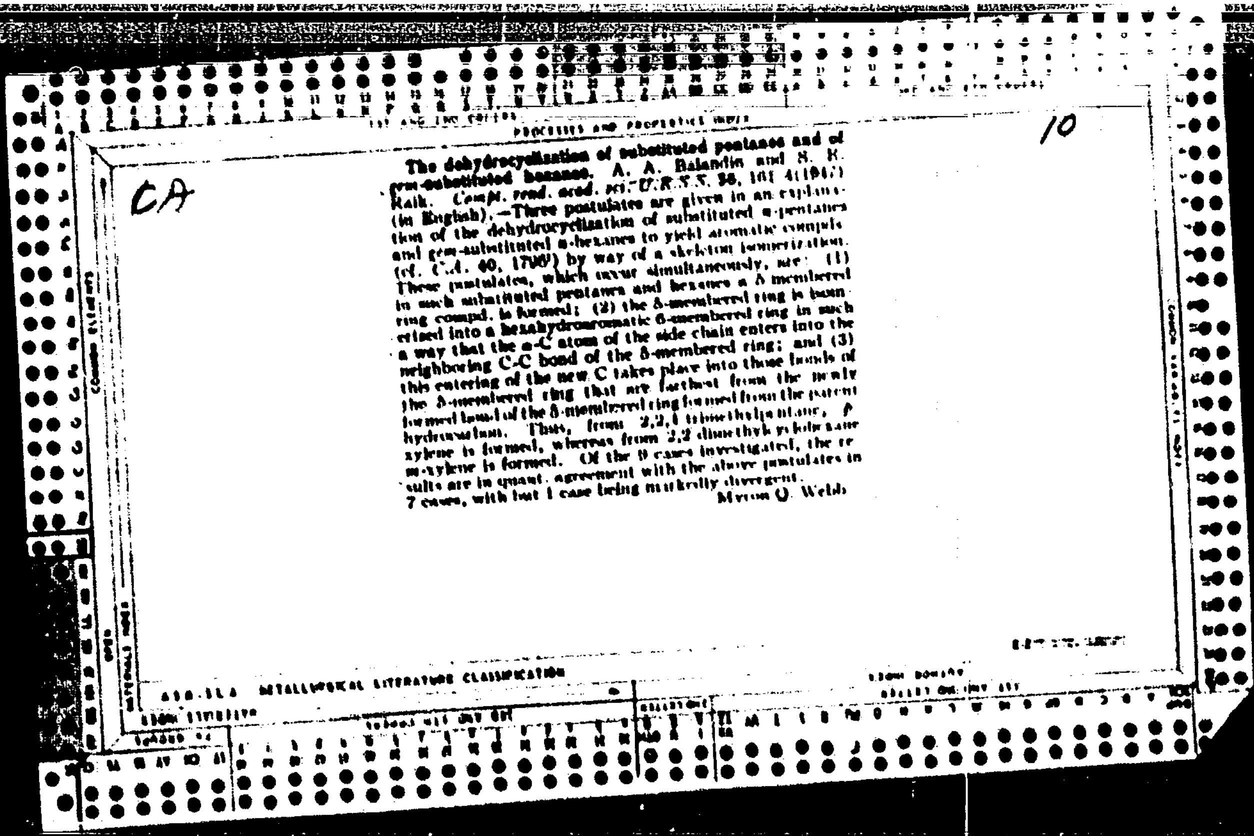
Comparative velocity of the catalytic dehydrogenation of monoalkylbenzenes and dialkylbenzenes. A. A. Balandin and O. M. Marukyan (Inst. of Org. Chem., Acad. of Sci., U.S.S.R.). *Compt. rend. acad. sci. U.R.S.S.* 55, 215-18 (1947)(in English); cf. preceding abstr.—EtPh (I) and *p*-$Et_2C_6H_4$ (II) were alternately passed over a Cu-chromia catalyst, using the same app., catalyst, reactants, and method of analysis as previously. The length of catalyst layer was 11 cm.; diam. of tube, 15 mm.; temp., 625°; space velocity, 300 ml. (liquid)/l./hr. for I and equiv. for II. The hydrocarbon vapors were dild. (1:2 mols.) with CO_2. Over a freshly regenerated catalyst the rate of dehydrogenation was higher for I (52.1%) than for II (41.0%), but the difference became negligible as the catalyst was fatigued (38.8% and 39.0%). The analytical results (percent of unsaturates in condensate) were calcd. for the formation of 1 double bond in the monoalkylbenzenes and 2 double bonds in the dialkylbenzenes. H_2O_2 decompn. of the nonvolatile prepd. from the dehydrogenation product of II gave only HCO_2H and *p*-$(HO_2C)_2C_6H_4$; no *p*-$EtC_6H_4CO_2H$ (the article reads *p*-ethylbenzene) was found. Similar results were obtained on dehydrogenation of iso-PrPh and *p*-$(iso\text{-}Pr)_2C_6H_4$, the initial rates being 56.6% and 50.7%, decreasing to fatigued rates of approx. 50% for both. An attempt was made to interpret exptl. data by a consideration of the crystal structure of the catalyst. Starting with the shape and size of I and II, the presence of a face-centered lattice of Cu with faces (111), and the fact that for the parallel dehydrogenation of 2 Et groups 2 doublets are needed, a model for dehydrogenation was constructed in agreement with the multiplet theory.

R. W. Fleming

METALLURGICAL LITERATURE CLASSIFICATION



PROCESSES AND PROPERTIES INDEX

CA

10

The dehydrocyclization of substituted pentanes and of gem-substituted hexanes. A. A. Balandin and S. K. Kaik. *Compt. rend. acad. sci. U.R.S.S.* 56, 161-4(1947) (in English).—Three postulates are given in an explanation of the dehydrocyclization of substituted n-pentanes and gem-substituted n-hexanes to yield aromatic compds. (cf. C.A. 40, 1760) by way of a skeleton isomerization. These postulates, which occur simultaneously, are: (1) in such substituted pentanes and hexanes a 5-membered ring compd. is formed; (2) the 5-membered ring is isomerized into a hexahydroaromatic 6-membered ring in such a way that the α-C atom of the side chain enters into the 5-membered ring; and (3) this entering of the new C takes place into those bonds of the 5-membered ring that are farthest from the newly formed bond of the 5-membered ring formed from the parent hydrocarbon. Thus, from 2,2,4-trimethylpentane, p-xylene is formed, whereas from 2,2-dimethylhexane m-xylene is formed. Of the 9 cases investigated, the results are in quant. agreement with the above postulates in 7 cases, with but 1 case being markedly divergent.

Myron O. Webb

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA 2

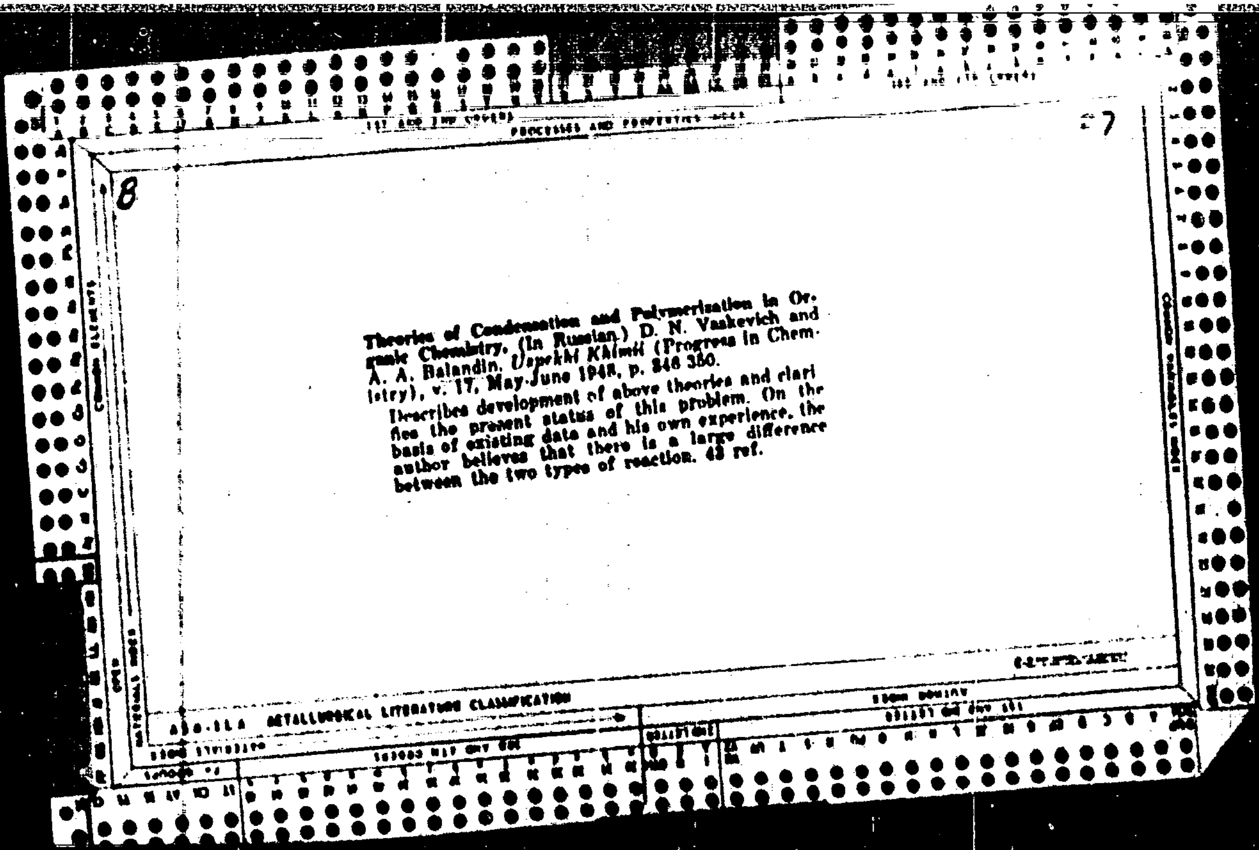
The catalytic properties of the pentoxides of columbium and tantalum. A. A. Balandin and N. P. Egorova (State Univ., Moscow). *Doklady Akad. Nauk S.S.S.R.* 56, 255-8(1947); *Chem. Zentr.* (Russian Zone Ed.) 1948, I, 1169; cf. *C.A.* 43, 1634*i*.—The 12 catalytic prepns. studied included: Cb_2O_5 + Ta_2O_5 in varying proportions alone, on asbestos, on Al_2O_3, also with the addn. of Cb or Ta metal; pure Cb and Ta metals; and V_2O_5 alone and on asbestos. These prepns. were tested as catalysts for reactions at 300-600°, which included oxidation (of naphthalene), dehydration (isopropyl alc., cyclohexanol), and esterification (isoamyl alc. + HOAc). The oxides were more effective catalysts than the prepns. contg. metallic Cb and Ta. The catalytic activity of Ta_2O_5 was about 1.3 times that of Cb_2O_5. Comparison with V_2O_5 showed that the latter was especially effective as a catalyst for dehydrogenation whereas Cb_2O_5 and Ta_2O_5 catalyzed dehydration reactions predominantly. This observation is in good agreement with the multiplet theory (cf. *C.A.* 43, 2852*h*), since the point of attack for the catalysts (C-C = 1.54 A., C-O = 1.43 A., and O-H = 1.01 A.) approximates the ionic radius (V = 1.36, Cb = 1.47, and Ta = 1.49 A.). Dehydrogenation is closely related to oxidation and dehydration is closely related to esterification. Accordingly, Cb_2O_5 and Ta_2O_5 are weak oxidizing but good esterifying catalysts. M. O. Moore

C/A

1C

Catalytic dehydrogenation of 1,3,5-triethylbenzene
A. A. Balandin and O. K. Marukyan (Izvest. Akad
Nauk S.S.S.R., Otdel. Khim. Nauk 1948, 451-8. cf
C.A. 41, 7384i.—In pursuance of the previous findin
Kamal, C.A. 41, 5863g) that PhEt and p-$C_6H_4Et_2$ are
dehydrogenated at the same rate, and that, in the de
hydrogenation of the latter, the only product is p-C_6H_4
$(CH:CH_2)_2$, never the intermediate p-Et$C_6H_4CH:CH_2$,
comparative dehydrogenations, with catalysts of equa
activity, were carried out, at 625°, with 1,3,5-$C_6H_3Et_3$
m-$C_6H_4Et_2$, and PhEt, at feed rates of 200-400 ml./l./hr
The space velocity affects the yield of unsatd. compds
only very little. In, resp., 60, 20, and 30 min., feed
rates, resp., 400, 300, and 200, the contents of unsatd
compds. in the condensates (calcd., resp., for 3, 2, and 1
double bond) were practically equal, 20.5, 25.5, and
20.2%. Consequently, the alkyl chains in mono-, di-
and trisubstituted benzenes are dehydrogenated at the
same rate, and one is justified in concluding that, in the
di- and trisubstituted derivs., all substituents are dehydro
genated simultaneously. On the basis of these results
one can construct, true to scale, the multiplet model o
the aggregate between 1,3,5-$C_6H_3Et_3$ and the catalys
surface. The active center includes 7 atoms, and the
mol. lies flat on the surface, with 1 catalyst atom occupy
ing the center of the ring, and 3 pairs of catalyst atom
disposed each on the 2 sides of each Et group. With
more catalyst atoms inserted in the gaps, so as to complete
the pattern of an octahedral crystal face, the complete
model includes 10 atoms, in a regular triangle of 4 atoms
along each side, i.e. a sextet plus one more row of 4 atoms

N. Thon



PROCESSES AND PROPERTIES INDEX

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7

Theories of Condensation and Polymerization in Organic Chemistry. (In Russian.) D. N. Vaskevich and A. A. Balandin. *Uspekhi Khimii* (Progress in Chemistry), v. 17, May-June 1948, p. 348-360.

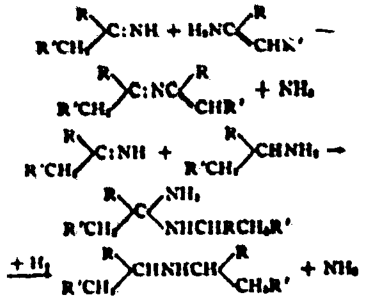
Describes development of above theories and clarifies the present status of this problem. On the basis of existing data and his own experience, the author believes that there is a large difference between the two types of reaction. 43 ref.

ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

10

Catalytic dehydrogenation of amines and its kinetics. I. Dehydrogenation of 1-diethylamino-4-aminopentane. A. A. Balandin and N. A. Vasyunina. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 398-406(1948).—This reaction was investigated as a representative of a conversion of the $>C-N<$ bond into $>C=N-$ as a result of splitting off one H_2 mol. The main reaction, $Et_2NCH_2CH_2CH_2CHMeNH_2 \rightarrow H_2 + Et_2NCH_2CH_2CH_2CMe{:}NH$, gives a ketimine; possible side reactions, resulting in the appearance of NH_3, are ($R = Me$, $R' = Et_2NCH_2CH_2$):



$Et_2NCH_2CH_2CH_2CMeNH_2 \rightarrow Et_2NCH_2CH_2CH_2{:}CHMe + NH_3$. Depending on the conditions, the main reaction predominates to various degrees, max. dehydrogenation (90%) being attained on a Pt catalyst at 323° and space velocity of 830 ml./l./hr.; 70% dehydrogenation, with NH_3 practically absent, is attained on a Pd catalyst at 320°, 850 ml./l./hr. Besides NH_3, some Et_2NH (about 8%) may also be formed by the side reaction $Et_2NCH_2CH_2CH_2CHMeNH_2 \rightarrow Et_2NH + CH_2{:}CHCH_2CHMeNH_2$. (1) On a Pt catalyst (on chrysolite asbestos) 6 g. (14 ml.), feed rate 0.2 ml./min. (unless otherwise stated), at 254, 280, 282, 303, 323, 317° (0.5 ml./min.), the yields of H_2 were 28.8, 27.5, 41.6, 48.5, 90.5, 30.1 mol. % of the amine passed, yields of NH_3 16.0, 14.2, 12.6, 13.1, 18.8, 6.4 mol. %. First runs with a given catalyst batch usually gave higher activities and larger amts. of NH_3. From the rates of evolution of H_2, the activation energy is 11.5 kcal./mol. (2) With Pd catalysts, the yields were somewhat lower than with Pt, the activation energy 10.5 kcal./mol. After dehydrogenation of $Et_2NCH_2CH_2CH_2CHMeNH_2$ (evolution of 15 ml./min. H_2 at 300° and 0.2 ml./min.), the cyclohexane-dehydrogenating activity of this catalyst (6 g.) dropped from 30 to 10 ml./min. H_2 (at 300° and 0.2 ml./min.), although its amine-dehydrogenating activity remained unchanged. (3) On a Cu catalyst, prepd. by impregnating 9 g. purified chrysolite asbestos with 34 g. fused $Cu(NO_3)_2.6H_2O$, igniting until complete elimination of N oxides, and reduction with H_2 at 250-300°, 35-40 hrs., the best H_2 yield obtained was only 33 mol. % of the amine passed (at 325°, 0.2 ml./min.). The activity of the catalyst falls and cannot be restored. Plots of the log of the H_2 yield against $1/T$ are not linear, i.e. the Arrhenius equation is inapplicable and no activation energy can be calcd. (4) Depending on the temp., the catalyzates were yellow (at 250-280°) or brick-red (280-320°). E.g., the catalyzate obtained on Pd was fractionated into b_{10} 37-57° (2.3 vol. %), 57-80° (4.7),

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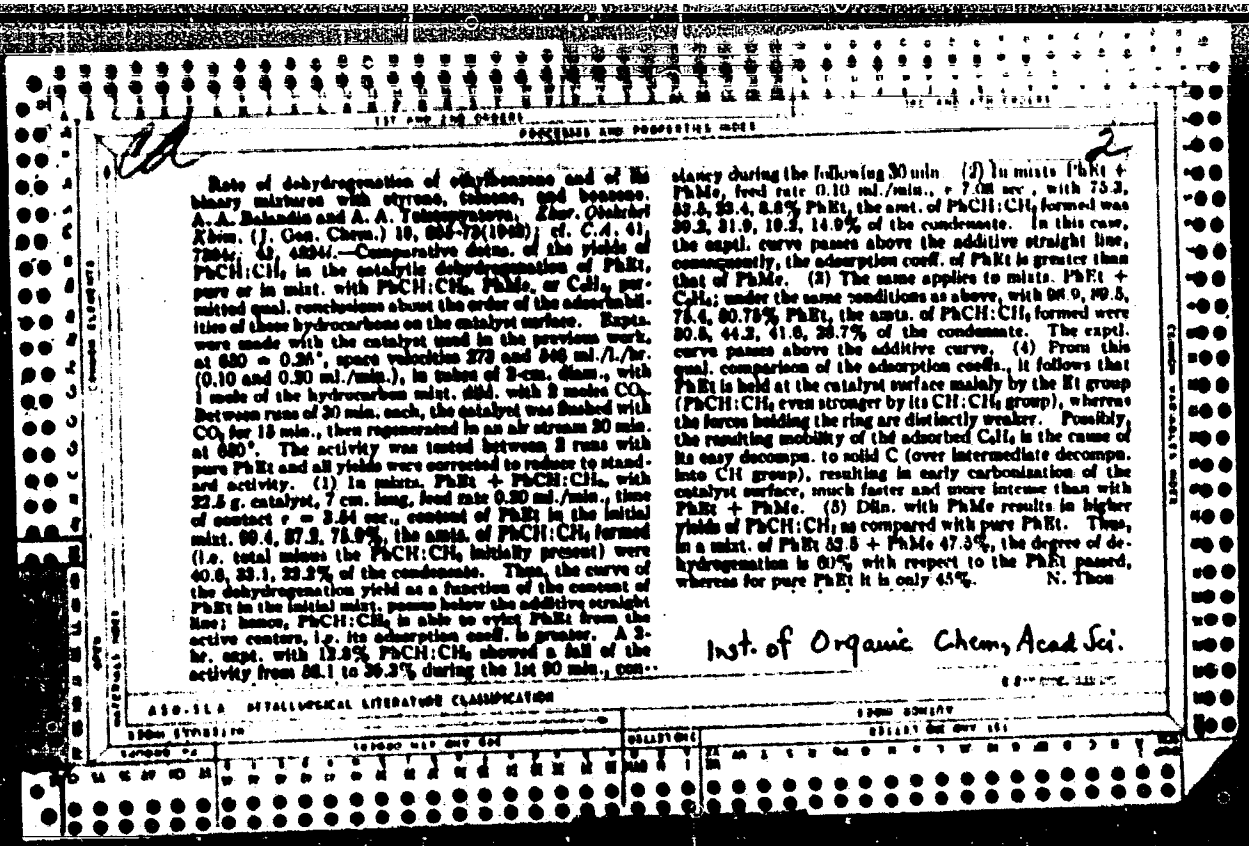
80-100° (9.3), 100-175° (12.2), 175-195° (63.5), residue and losses (7.0). The small amt. of products b. above 195° proves that side reactions of the condensation type occur only to a very limited extent, owing undoubtedly to the short time of contact (4 sec.). The fraction b. 37-57° contains Et_2NH. The main fraction, b_{760} 175-95° (b_{15} 75-90°), contains the main product, the ketimine, as evidenced by the formation of the ketone on hydrolysis with 1:3 HCl at room temp., $Et_2NCH_2CH_2CH_2CMe:NH \xrightarrow{H_2O} Et_2NCH_2CH_2CH_2CMe:O + NH_3$. Further, the same fraction, treated with HNO_2, gives an orange-red oil sol. in ether. Finally, the ketimine was identified by its Raman spectrum, specifically by the intense line 1656 $cm.^{-1}$ characteristic of the >C:N— bond. N. Thon

Tertiary amines of cyclized pentaerythritol. J. Cazier and O. Steyaert. *Bull. soc. chim. belges* 57, 224-31 (1948)(in French); cf. following abstr.—3,3-Bis(bromomethyl)oxacyclobutane (I) (61 g.), 60 g. $NHMe_2$, and 30 g. H_2O heated 5 hrs. at 100° in a sealed tube yielded 77% *3,3-bis(dimethylaminomethyl)oxacyclobutane* (II), b_{16} 90°; in alc. the yield was 70%; *II.2HBr* m. 231° (from EtOH); II *picrate*, m. 183° (from H_2O); *II.2HClO₄*, m. 191° (from EtOH); *II.HClO₄*, m. 208° (from EtOH); *II.MeI*, m. 172° (from abs. EtOH), was prepd. in 80% yield from II and MeI. One mol. II and 9 mols. 66% aq. HBr gave 78% *bis(dimethylaminomethyl)(hydroxymethyl)(bromomethyl)methane.HBr* m. 174°. I (30 g.) and 45 g. $NHEt_2$ heated 15 hrs. at 60° yielded *3,3-bis(diethylaminomethyl)oxacyclobutane* (III), b_{16} 130°; III *picrate* m. 195-6° (from EtOH); *III.HClO₄.H₂O* m. 158-9° (from aq. EtOH). Tribromopentaerythritol (0.2 mol.) and 1.5 mols. $NHMe_2$ 15 hrs. at 140° yielded 46% *tris(dimethylaminomethyl)(hydroxymethyl)methane* (IV), b_{16} 130.5°. *IV.3MeBr* (*C.A.* 43, 1876c) was also prepd.

J. H. E. Herbst



PROCESSES AND PROPERTIES INDEX

2a

2

Rate of dehydrogenation of ethylbenzene and of its binary mixtures with styrene, toluene, and benzene. A. A. Balandin and A. A. Tolstopyatova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 865-72(1948); cf. *C.A.* 41, 7204e; 42, 4804i.—Comparative detns. of the yields of PhCH:CH$_2$ in the catalytic dehydrogenation of PhEt, pure or in mixt. with PhCH:CH$_2$, PhMe, or C$_6$H$_6$, permitted qual. conclusions about the order of the adsorbabilities of these hydrocarbons on the catalyst surface. Expts. were made with the catalyst used in the previous work, at 580 ± 0.25°, space velocities 273 and 546 ml./l./hr. (0.10 and 0.20 ml./min.), in tubes of 2-cm. diam., with 1 mole of the hydrocarbon mixt. dild. with 3 moles CO$_2$. Between runs of 30 min. each, the catalyst was flushed with CO$_2$ for 15 min., then regenerated in an air stream 30 min. at 580°. The activity was tested between 2 runs with pure PhEt and all yields were corrected to reduce to standard activity. (1) In mixts. PhEt + PhCH:CH$_2$, with 22.5 g. catalyst, 7 cm. long, feed rate 0.20 ml./min., time of contact τ = 3.84 sec., content of PhEt in the initial mixt. 90.4, 87.2, 75.9%, the amts. of PhCH:CH$_2$ formed (i.e. total minus the PhCH:CH$_2$ initially present) were 40.6, 33.1, 23.2% of the condensate. Thus, the curve of the dehydrogenation yield as a function of the content of PhEt in the initial mixt. passes below the additive straight line; hence, PhCH:CH$_2$ is able to evict PhEt from the active centers, i.e. its adsorption coeff. is greater. A 3-hr. expt. with 12.8% PhCH:CH$_2$ showed a fall of the activity from 88.1 to 36.2% during the 1st 90 min., constancy during the following 30 min. (2) In mixts. PhEt + PhMe, feed rate 0.10 ml./min., τ 7.68 sec., with 75.3, 52.5, 33.4, 8.8% PhEt, the amt. of PhCH:CH$_2$ formed was 30.2, 31.9, 19.2, 14.9% of the condensate. In this case, the exptl. curve passes above the additive straight line, consequently, the adsorption coeff. of PhEt is greater than that of PhMe. (3) The same applies to mixts. PhEt + C$_6$H$_6$; under the same conditions as above, with 98.9, 89.5, 76.4, 50.75% PhEt, the amts. of PhCH:CH$_2$ formed were 50.6, 44.3, 41.6, 26.7% of the condensate. The exptl. curve passes above the additive curve. (4) From this qual. comparison of the adsorption coeffs., it follows that PhEt is held at the catalyst surface mainly by the Et group (PhCH:CH$_2$ even stronger by its CH:CH$_2$ group), whereas the forces holding the ring are distinctly weaker. Possibly, the resulting mobility of the adsorbed C$_6$H$_6$ is the cause of its easy decompn. to solid C (over intermediate decompn. into CH group), resulting in early carbonization of the catalyst surface, much faster and more intense than with PhEt + PhMe. (5) Diln. with PhMe results in higher yields of PhCH:CH$_2$ as compared with pure PhEt. Thus, in a mixt. of PhEt 52.5 + PhMe 47.5%, the degree of dehydrogenation is 60% with respect to the PhEt passed, whereas for pure PhEt it is only 45%. N. Thon

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ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION

2

Thermodynamic properties of adsorption complexes in heterogeneous catalysis. A. A. Balandin. *Doklady Akad. Nauk S.S.S.R.* 63, 33-6(1948).—The abs. and the relative adsorption coeffs., a_a and a_r of a substance r (a_r relative to substance l), have the meanings, resp., of an adsorption equil. const. for r and of a displacement const. of r by l from the adsorbed layer: $a_a = [A_rS]/[S][A_r]$ and $a_r = [A_rS][A_l]/[A_lS][A_r]$, where S, A_lS, and A_rS represent, resp., the surface concns. of unoccupied active centers and of adsorption complexes of S with l or r. This permits formulation of the standard thermodynamic functions $\Delta F°$, $\Delta H°$, $\Delta S°$ for adsorption of r and displacement of r by l, by the known expressions in terms of a_a and a_r. In the case of dehydrogenations of cyclohexane hydrocarbons on Pt, Pd, and Ni, $a_1 = a_2$; $a_3 = 0$ (subscripts 1, 2, and 3 referring, resp., to the cycloparaffin, the aromatic hydrocarbons, and H_2), and, consequently, all three $\Delta°$ for adsorption are equal for 1 and 2, and all three $\Delta°$ for displacement = 0. From data of Lozovoi and D'yakova (*C.A.* 33, 5266^1, 8267^1) there are calcd. for the displacement of H_2 by methylcyclohexane on a Ni catalyst surface, at 128 and 172°, $\Delta H° = 27.1$ and 25.6 kcal./mole, $\Delta F° = -2.9$ and -4.8 kcal./mole, $\Delta S° = 75.4$ and 68.4 cal/mole/degree. Consequently, higher temp. should favor displacement of H_2. From data of Bork (*C.A.* 34, 6981^1) on the dehydrogenation of alcs. to aldehydes or ketones on Cu at 240-275°, it follows that the entropy changes accompanying the formation of adsorption complexes between Cu and any alc., or the corresponding aldehyde or ketone, are equal. On the other hand, in the dehydrogenation of butylene to butadiene on Cr_2O_3 at 600° (B., Bogdanova, and Shcheglova, *C.A.* 42, 6318e), a_r (butadiene) = 9.5 and a_r (H_2) = 0.82; hence, for the displacement of C_4H_8 by C_4H_6, $\Delta F° = 3.7$, and for the displacement of H_2 by C_4H_6, $\Delta F° = 0.3$ kcal./mole. N. Thon

Mbr., AN SSSR
Inst. Org. Chem., AN SSSR
and
Moscow State U. im. Lomonosov

ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

CIA

10

Determination of the adsorption coefficients by the reaction-kinetic method in the dehydrogenation of hydroaromatic hydrocarbons A. A. Balandin and O. V. Isagulyants. *Doklady Akad. Nauk S.S.S.R.* 63, 139-42 (1948); cf. following abstr. The relative adsorption coeffs. $k = a_2/a_1$, where a = abs. adsorption coeff., the substrates 1 and 2 corresponding, resp., to the cycloparaffin and to the product of the dehydrogenation (aromatic hydrocarbon or H_2), were calcd. by $k = [(m_0/m) - 1]/[(100/p) - 1]$ (m = rate of evolution of H_2, in ml./10 min., from a mixt. of p% cycloparaffin and the corresponding aromatic hydrocarbon or H_2, m_0 = the same rate with the pure cycloparaffin), from data of m on a Cr_2O_3 catalyst on asbestos (1:1), with the binary mixts. methylcyclohexane (I)–PhMe, at 461°, p = 100, 76.1, 53.2, 40.2, m = 122, 101, 72.5, 52; I–H_2, at 461°, p = 100, 87, 40, m = 94, 81, 62; 1,3-dimethylcyclohexane (II)–m-xylene, at 474°, p = 100, 70.5, 48.5, 27, m = 85, 65, 43.5, 30. The k calcd. from these detns. are very nearly independent of p, thus, for the above 3 systems, resp., k = 0.86, 0.80, and 0.92; for cyclohexane–C_6H_6, k = 0.81, for tetrahydronaphthalene (III)–$C_{10}H_8$, 0.35, for 2-methyl-5,6,7,8-tetrahydronaphthalene (IV)–2-$C_{10}H_7Me$, 0.31; k is practically independent of the temp., e.g., for C_6H_{12}–C_6H_6 between 419 and 466°, in complete analogy with the temp. independence of k in dehydrogenation of dimethylcyclohexane on Ni and Al_2O_3 between 210 and 290°, of EtOH on Cu between 240 and 290°, or of C_6H_{12} on Cr (Bork and B., *C. A.* 30, 6278; Bork, *C. A.* 31, 279). For the pairs cyclohexane–C_6H_6, I–PhMe, II–m-$C_6H_4Me_2$, III–$C_{10}H_8$, and IV–2-$C_{10}H_7Me$, k for H_2 is calcd., resp., to be 0.65, 0.60, 0.52, 0.47, and 0.61; the free energy of desorption of the aromatic hydrocarbon from the active centers by the corresponding cycloparaffin, at 451°, is, resp., 250, 58, 120, 1500, and 1500, the corresponding free energy for the evolution of H_2 by the cycloparaffin, resp., 610, 760, 910, 1100, and 1300. The adsorption coeffs. of the cycloparaffins, relative to that of H_2, are, resp., 1.54, 1.60, 1.90, 2.86, and 2.50, those of the aromatic hydrocarbons, 1.91, 1.61, 1.75, 0.95, and 0.81. In all these cases, the cycloparaffins show a much greater affinity for the catalytically active centers than the products of dehydrogenation. The adsorption coeffs. increase with the no. of Me groups. N. Thon

C/1

10

Kinetics of the catalytic dehydrogenation of cyclic hydrocarbons on chromium oxide. A. A. Balandin and G. V. Isagulyants. [illegible] 63, 261 [illegible] [illegible] of preceding abstr. For the 5 dehydrogenation reactions listed in the foregoing abstr., the apparent activation energies Q were detd., assuming zero order reaction [illegible], from the linear plots of log m (for the notation, see the foregoing abstr.) against 1/T, giving, for the dehydrogenation of cyclohexane, I, II, III, and IV, resp., Q = 25.0, 21.7, 22.2, 20.7, and 20.1 kcal./mole. With the aid of the z values given in the foregoing abstr., the reaction rate consts. D calcd. by the equation of B., Bogdanova, and Shcheglova (C.A. 42, 6210e) are very little different from m, and, consequently, the true activation energies E are very little different from Q. The consts. D depend only on the temp. and not on the partial pressures of the reactants. Thus, in the system II + C_6H_5Me at 452°, D remains practically const. = 101.7 [illegible] at the feed rates [illegible] = const. [illegible] feed rate of the cycloparaffin, in ml. [illegible] complete dehydrogenation per 10 min., [illegible] = the same for the aromatic hydrocarbon) [illegible] and 194, 102 and 108, 151 and 450, and the same value of D = [illegible] is found, at 474°, with A_0 = 610, A_1 = 0. The complete kinetic equation can be written down for each system on the basis of the general equation (B., C. A. 37, 2645?); e.g., for the system with V, it is 2.303 [illegible] = D [illegible] = feed rate of [illegible] It permits prediction of the degree of conversion under stated conditions, e.g., with A_0 = 314, A_1 = 102, A_2 = 0, with the exptl. D = [illegible], one calculates m = 22.7 ml. [illegible] min. and [illegible] = 21.2%, in agreement with the exptl. 21.3%. The values of z obtained previously (cf. foregoing abstr.) and the values of D = [illegible] = cross section of the catalyst tube, l = length of the column [illegible] tained in a flow system satisfy the differential equations [illegible] the above kinetic equation.

Inst. Org. Chem., AN SSSR
Mbr, AN SSSR

2

Reversible and complex-reversible poisoning of a nickel catalyst in dehydrogenation. A. A. Balandin and S. L. Kiperman. *Doklady Akad. Nauk S.S.S.R.* 63, 397-400 (1948).—Rates of dehydrogenation of equimol. mixts. of cyclohexane with C_6H_6 (I), toluene (II), m-$C_6H_4Me_2$ (III), o-$C_6H_4Me_2$ (IV), mesitylene (V), PhEt (VI), C_7H_{16} (VII), C_8H_{18} (VIII), and 2,2,4-trimethylpentane (IX), at 330°, rate of flow 0.2 ml./min., on a Ni-on-Al_2O_3 catalyst (B. and Rubinshtein, *C.A.* 29, 7775) 2.4 cm. high (3 cm. before reduction) in a 2.3 cm. diam. tube, expressed in ml. H_2 evolved in 3 min., corrected for const. activity of the catalyst by intermediate runs with cyclohexane, and plotted against the amt., in %, of cyclohexane in the mixt., give displacement curves composed of rectilinear, convex, and concave portions. Complete linearity in case IX indicates equality of the relative adsorption coeffs. of cyclohexane and the other hydrocarbon (*C.A.* 37, 2048; 43, 1834f); initial rectilinear portions are exhibited by I, II, and III, and possibly also in IV, V, and VI. This and previous results (B. and Rubinshtein, *C.A.* 28, 8049; B. and Yur'ev, *C.A.* 38, 7127), show that cyclohexane, methylcyclohexane, the dimethylhexanes, and their dehydrogenation products, C_6H_6, toluene, and $C_6H_4Me_2$, have the same adsorption coeffs. Poisoning, in this case, is typically reversible, owing to displacement of the reactant mols. by the competing mols., and can be easily eliminated through removal of the poisoning substance. The concave portions in I to V illustrate "complex-reversible" poisoning, due to deposition of condensation products which can be removed by volatilization, e.g., by heating in an air stream. Such poisoning occurred within 6 to 12 min. from the beginning of a run. The rate of formation of condensation products increases in the order I, II, III, IV, V, and, correspondingly, the rectilinear portions of the curves become increasingly shorter in the same order. Concavity is particularly pronounced in VI, owing to polymerization of the styrene formed; this is borne out by the similarity of curve VI to the displacement curve of Ph-Et PhCH:CH_2 on a Cr-Cu catalyst (Kazanskii and Plate, *Zhur. Obshchei Khim.* 7, 328(1937)). In VII and VIII, the S-shape of the curves indicates partial aromatization of C_7H_{16} and C_8H_{18}, with the aromatic products undergoing increasing condensation as the amt. of the paraffins in the mixt. increases. On the other hand, diln. of the aromatic products with C_7H_{16} and C_8H_{18} mols. counteracts condensation; hence, passage of pure C_7H_{16} gives rise to no poisoning. The strict linearity found in case IX is due to the inability of isoöctane to aromatize.

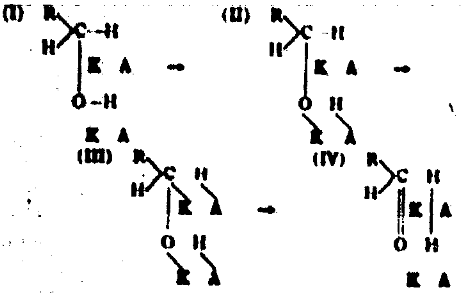
N. Thon

Moscow State U. im. Lomonosov

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

2

The multiplet theory and the transition-state theory. A. A. Balandin. *Doklady Akad. Nauk S.S.S.R.* 63, 33-6(1948).—If A_i is the initial reactant, A_f the product in the gas phase, A_{ia} and A_{fa}, resp., the adsorption complexes between A_i and A_f and the catalyst surface, A^* the intermediate activated complex, the heterogeneous reaction can be written in the form $A_i \rightleftarrows A_{ia} \rightleftarrows A^* \to A_{fa} \rightleftarrows A_f$. The previously established equality of the adsorption equil. consts., a_i and a_f, of the initial reactant and the product, and of a_i and a_f for a series of homologs in the catalytic dehydrogenation of alcs. to aldehydes or ketones (B. and Isagulyants, C.A. 42, 1793e), is substantiated by statistical thermodynamics. (1) With f, f_a, and f_s designating, resp., the partition function of the reactant in the gas phase, of the adsorbed molc., and of the unoccupied active centers at the surface, the adsorption equil. const. $a = f_a/(f f_s).\exp. (\Delta H_a/RT)$, where ΔH_a = heat of adsorption. The ratio f_a/f is evaluated by the usual factorization wherein, in the adsorbed state, the translational factor obviously disappears; there are 2 rotational and 2 vibrational degrees of freedom, whereas the internal degrees of freedom remain unchanged. With the change of the moment of inertia taken into account by $I_a = \rho I$ (ρ = const.), one arrives at $f_a/f = a\theta(\rho/\theta_0)^{1/2}$ (where ε = elasticity coeff., θ = torsional elasticity coeff., a = const. including the temp.). As θ and ε depend only on the catalyst and are detd. only by the CO groups of the molc., f_a/f = const., equal for the initial reactant and the product, and equal for homologs. This means also equality of the entropies, and, on account of the identity of ΔH_a, also $a_i = a_f$, the same for all homologs. (2) By the abs.-rate theory, the rate of dehydrogenation $v = (kT/h)[f^*/(f_s f_a)] \exp. (-\Delta H^*/RT) [A_a][S] = (kT/h)(f^*/f_a) \exp. [-(\Delta H^* - \Delta H_a)/RT][A_aS]$, where f^* = partition function of the activated complex, ΔH^* = heat of activation, $[S]$ = concn. of unoccupied active centers, $[A_aS]$ = concn. of adsorbed molc. The pressure independence of v indicates complete coverage. In the initial stages, $[A_aS]$ = const. (zero-order reaction), $\Delta H^* - \Delta H_a$ is identical for the various homologous alcs., hence v is detd. solely by f^*/f_a. This ratio is evaluated with the aid of a model of the intermediate state, based on the representation of the dehydrogenation reaction by the 4 consecutive steps, where K and A represent, resp.,



active-center atoms of the 1st and 2nd kind, and the rate-detg. step is the transition II → III. If the products of the rotational and vibrational partition functions of the activated and of the adsorbed complex are proportional,

and all the internal degrees of freedom are the same in the
two states, with the only exception that one valence-
vibrational degree of freedom of the adsorbed state goes
over, in the activated state, into translation along the
reaction coördinate, $f^{\ddagger}/f_a = \prod_{s}(h\nu/kT)^{1/s}$, i.e. the same

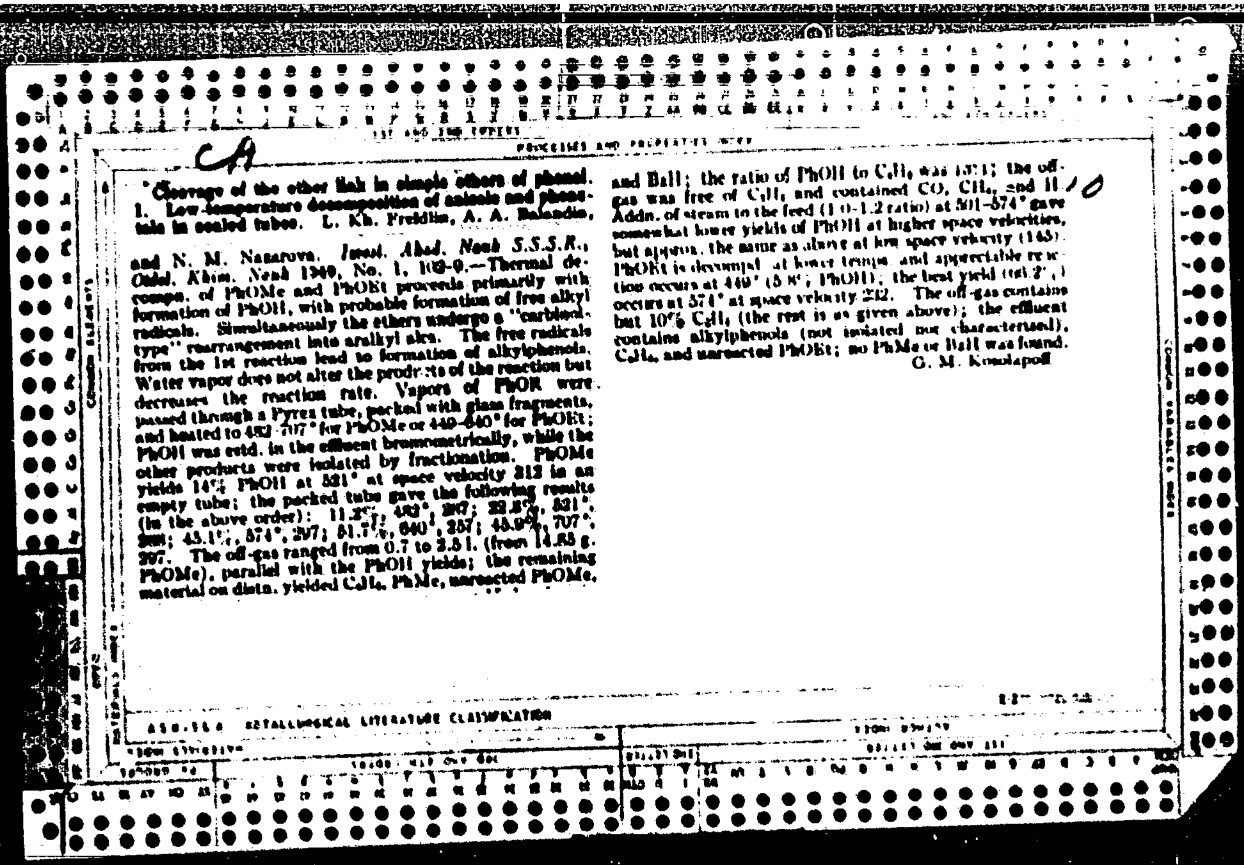
for the various homologs and independent of the temp.
Consequently, the rates of catalytic dehydrogenation
must also be the same for the various homologs, in agree-
ment with exptl. findings. N. Thon

BALANDIN, A. A.

"Studies of the Speed of Dehydrogenation of Ethyl-Benzene in Its Binary Mixture with Styrene, Toluene, and Benzene," Zhur. Obshch. Khim., 16, No 6, 1946

CA

Rupture of the ether bond in phenol ethers. II. Catalytic decomposition of anisole and phenetole. L. Kh. Freidlin, A. A. Balandin, and N. M. Nazarova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1949**, 198-204; cf. C.A. 43, 5784i.—In uncatalyzed low-temp. pyrolysis of PhOMe and PhOEt (in the temp. range of 482-707° and 449-640°, resp.), in glass tubes, the primary step, PhOR → PhOH + R: (where R: is an alkylidene radical, C_2H_4) is followed by R: + PhOH → RC_6H_4OH, and accompanied by a side reaction of the rearrangement type, PhOMe → $PhCH_2OH$, the latter giving, on further decompn., BzH and CO. The max. yields of PhOH, from PhOMe and PhOEt, are 51.7 and 60.2%, at 640° and at 574°, resp. They fall with further rising temp. These yields can be substantially improved only if the reactions are conducted at lower temps. in the presence of catalysts. No PhOH was obtained from PhOMe at 443° on silica gel in the absence of H_2O. With mixts., PhOMe + H_2O (1:1 or 2:1 by wt.), at 574° and 607°, space velocity approx. 300 g./l. catalyst/hr., the yields were 34 and 48%, resp. (relative to the PhOH passed) i.e. of the same order as in glass tubes, and 24%, at 647°; in both cases, H_2O only promotes the pyrolysis, but does not react, as evidenced by the absence of products of hydrolysis (MeOH). In contrast to glass and to silica gel, active silicates catalyze the pyrolysis efficiently. With PhOMe (without H_2O), at a space velocity ~300 g./l. catalyst/hr., in 40-min. runs, at 282, 346, 410, 443, and 482°, the yields of PhOH were 17.0, 51.7, 75.2 (max.), 60.4, and 53.3%. Decompn. begins about 250° lower than in the uncatalyzed reaction, and is max. at 410°, whereas without catalyst there is no reaction yet at 443°. In the presence of a catalyst, no gas is evolved at 443°, and only 400 ml. gas is evolved from 9.64 g. PhOMe at 482° (CH_4, CO, and H_2, no unsatd.). The catalyzate contains PhOH and cresols, but no BzH and no $PhCH_2OH$; consequently, the isomerization reaction which takes place as a side reaction in uncatalyzed pyrolysis is suppressed. H_2O vapor lowers the yields of PhOH, e.g., at 346°, H_2O:PhOMe = 0.9:1 (by wt.), PhOH = 25%, and, at 444°, H_2O:PhOMe = 0.6:1, PhOH = 51%. This neg. effect of H_2O is ascribed to screening of active centers, and indicates absence of a hydrolytic reaction between PhOMe and H_2O. The activity of the catalyst can be fully restored by treatment with air at 550-75°. The yield of PhOH from PhOEt is 50.2%, at 257°, and is max., 81.2%, at 346°. The amt. of gas evolved is less than in uncatalyzed pyrolysis, but it contains more C_2H_4 (81.1%, at 481°). The liquid catalyzate contains PhOH and alkylphenols, no BzH. The yields of PhOH are decreased in the presence of H_2O. N. Thon



1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

CA

"Cleavage of the ether link in simple ethers of phenol. I. Low-temperature decomposition of anisole and phenetole in sealed tubes. L. Kh. Freidlin, A. A. Balandin, and N. M. Nazarova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1949, No. 1, 102-9.—Thermal decompn. of PhOMe and PhOEt proceeds primarily with formation of PhOH, with probable formation of free alkyl radicals. Simultaneously the ethers undergo a "carbinol-type" rearrangement into aralkyl alcs. The free radicals from the 1st reaction lead to formation of alkylphenols. Water vapor does not alter the products of the reaction but decreases the reaction rate. Vapors of PhOR were passed through a Pyrex tube, packed with glass fragments, and heated to 482-707° for PhOMe or 449-640° for PhOEt; PhOH was estd. in the effluent bromometrically, while the other products were isolated by fractionation. PhOMe yields 14% PhOH at 521° at space velocity 212 in an empty tube; the packed tube gave the following results (in the above order): 11.2%, 482°, 207; 22.8%, 521°, 300; 45.1%, 574°, 207; 51.7%, 640°, 257; 45.9%, 707°, 207. The off-gas ranged from 0.7 to 2.5 l. (from 14.85 g. PhOMe), parallel with the PhOH yields; the remaining material on distn. yielded C_6H_6, PhMe, unreacted PhOMe, and BzH; the ratio of PhOH to C_6H_6 was 15:1; the off-gas was free of C_2H_4 and contained CO, CH_4, and H. Addn. of steam to the feed (1.0-1.2 ratio) at 501-574° gave somewhat lower yields of PhOH at higher space velocities, but approx. the same as above at low space velocity (165). PhOEt is decompd. at lower temps. and appreciable reaction occurs at 449° (5.8% PhOH); the best yield (61.2%) occurs at 574° at space velocity 212. The off-gas contains but 10% C_2H_4 (the rest is as given above); the effluent contains alkylphenols (not isolated nor characterized), C_6H_6, and unreacted PhOEt; no PhMe or BzH was found.

G. M. Kosolapoff

10

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A. A. [illegible]

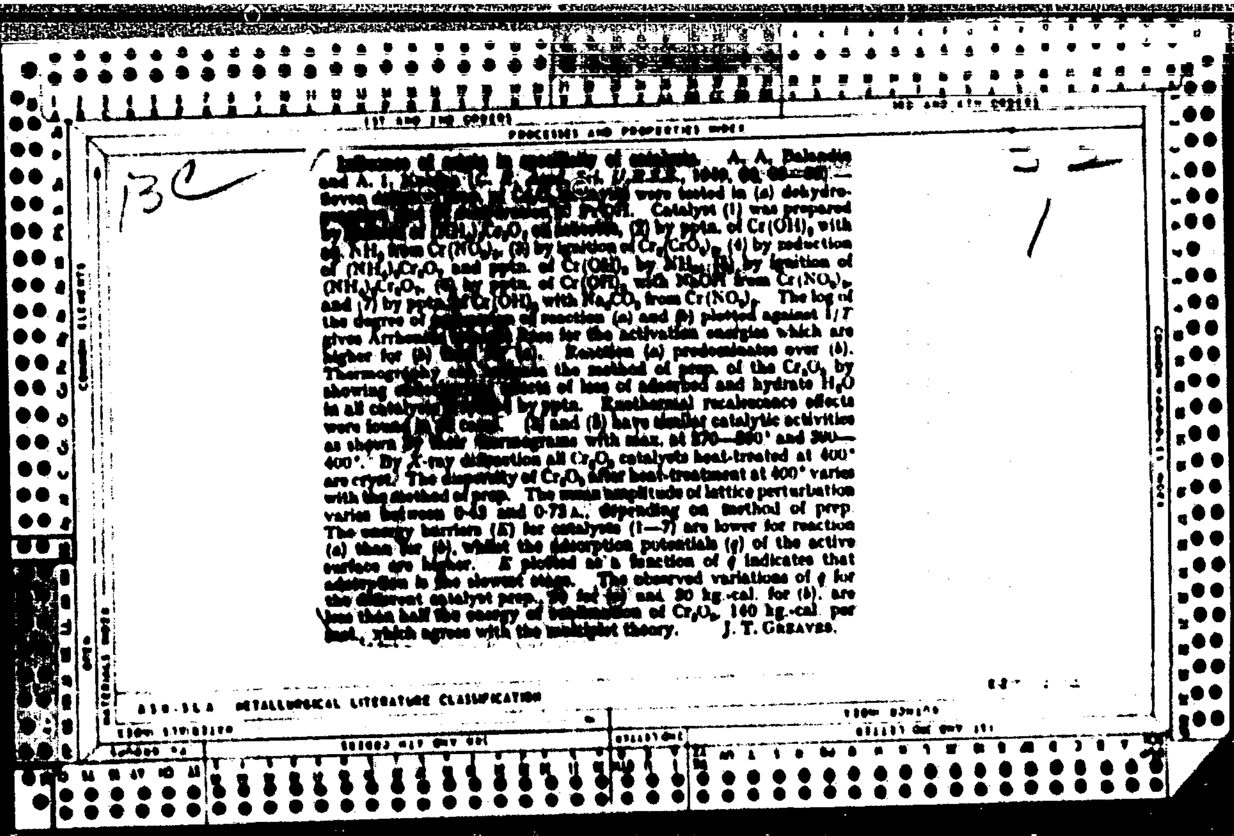
USSR/Chemistry -- Cyclohexane, Dehydrogenation Jan 49
Chemistry -- Naphthalene, Decahydro

"The Orientation of Decalin and Cyclohexane Molecules on Oxide and Metallic Catalyzers During Dehydrogenation," Acad A. A. Balandin, G. V. Isagulyants, 4 pp

"Dok Ak Nauk SSSR" Vol LXIV, No 2

Experimentally confirms that cyclohexane must dehydrogenate faster than decalin when their molecules are smoothly oriented on catalyzer's surface, which might be expected on basis of multiplet theory. Submitted 20 Nov 48.

[redacted] 25/49T6



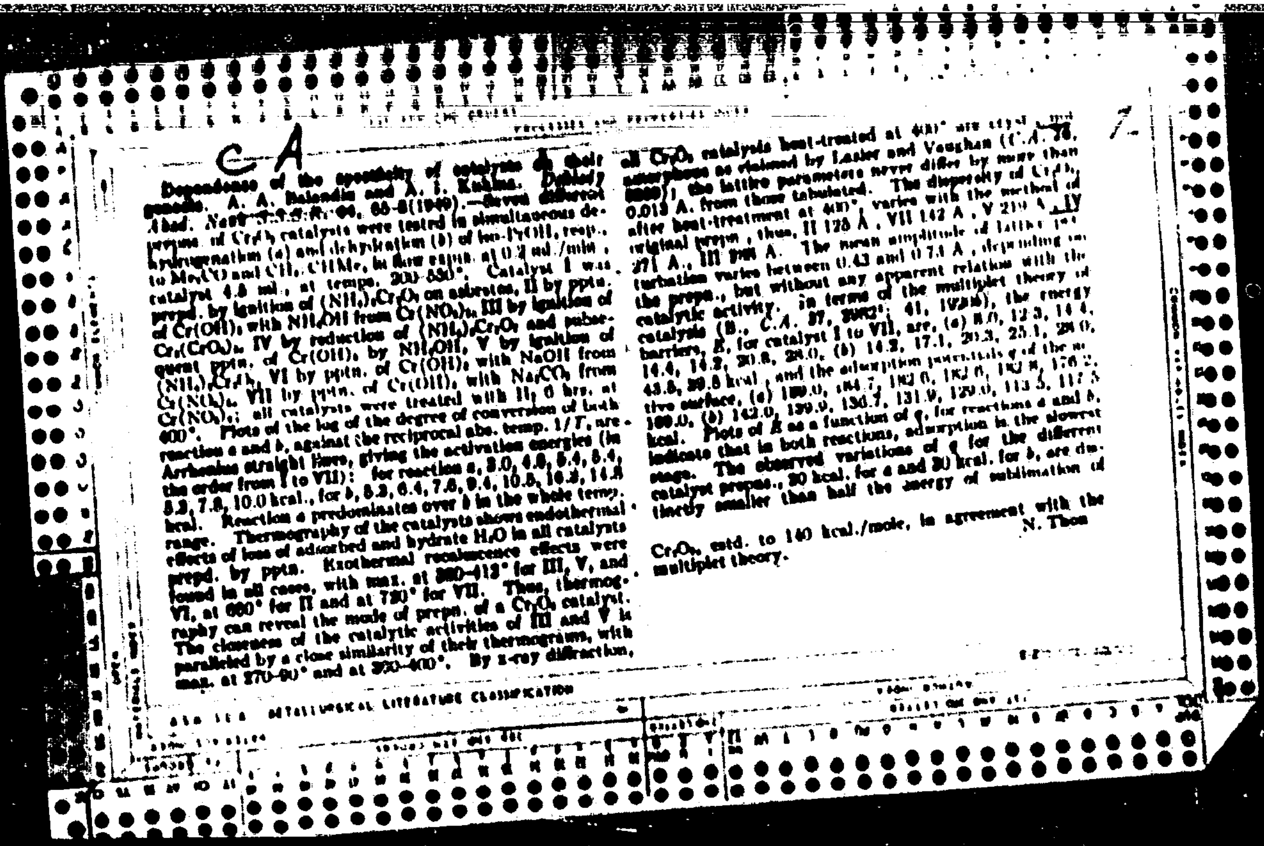
PROCESSES AND PROPERTIES INDEX

13C

1

Influence of [illegible] on specificity of catalysts. A. A. Balandin and A. I. [illegible] (C. R. [illegible] Sci. U.R.S.S., 1950, 64, [illegible]).—Seven [illegible] of Cr_2O_3 [illegible] were tested in (a) dehydrogenation and (b) dehydration of PrOH. Catalyst (1) was prepared by ignition of $(NH_4)_2Cr_2O_7$ at [illegible], (2) by pptn. of $Cr(OH)_3$ with aq. NH_3 from $Cr(NO_3)_3$, (3) by ignition of $Cr_2(CrO_4)_3$, (4) by reduction of $(NH_4)_2Cr_2O_7$ and pptn. of $Cr(OH)_3$ by NH_3, (5) by ignition of $(NH_4)_2Cr_2O_7$, (6) by pptn. of $Cr(OH)_3$ with NaOH from $Cr(NO_3)_3$, and (7) by pptn. of $Cr(OH)_3$ with Na_2CO_3 from $Cr(NO_3)_3$. The log of the degree of [illegible] of reaction (a) and (b) plotted against $1/T$ gives Arrhenius [illegible] lines for the activation energies which are higher for (b) [illegible] (a). Reaction (a) predominates over (b). Thermography [illegible] the method of prep. of the Cr_2O_3 by showing [illegible] effects of loss of adsorbed and hydrate H_2O in all catalysts [illegible] by pptn. Exothermal recalescence effects were found in all cases. (2) and (5) have similar catalytic activities as shown by their thermograms with max. at 270—[illegible]° and 300—400°. By X-ray diffraction all Cr_2O_3 catalysts heat-treated at 400° are cryst. The dispersity of Cr_2O_3 after heat-treatment at 400° varies with the method of prep. The mean amplitude of lattice perturbation varies between 0·[illegible] and 0·73 A., depending on method of prep. The energy barriers (E) for catalysts (1—7) are lower for reaction (a) than for (b), whilst the adsorption potentials (q) of the active surface are higher. E plotted as a function of q indicates that adsorption is the slowest stage. The observed variations of q for the different catalyst prep., [illegible] for (a) and 30 kg.-cal. for (b), are less than half the energy of [illegible] of Cr_2O_3, 140 kg.-cal. per mol., which agree with the multiplet theory. J. T. Greaves.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



CA

7-

Dependence of the specificity of catalysts on their genesis. A. A. Balandin and A. I. Kukina. Doklady Akad. Nauk S.S.S.R. 64, 65-8(1949).—Seven different prepns. of Cr_2O_3 catalysts were tested in simultaneous dehydrogenation (a) and dehydration (b) of iso-PrOH, resp., to Me_2CO and $CH_2:CHMe$, in flow expts. at 0.2 ml./min., catalyst 4.5 ml., at temps. 300-550°. Catalyst I was prepd. by ignition of $(NH_4)_2Cr_2O_7$ on asbestos, II by pptn. of $Cr(OH)_3$ with NH_4OH from $Cr(NO_3)_3$, III by ignition of $Cr_2(CrO_4)_3$, IV by reduction of $(NH_4)_2CrO_4$ and subsequent pptn. of $Cr(OH)_3$ by NH_4OH, V by ignition of $(NH_4)_2Cr_2O_7$, VI by pptn. of $Cr(OH)_3$ with NaOH from $Cr(NO_3)_3$, VII by pptn. of $Cr(OH)_3$ with Na_2CO_3 from $Cr(NO_3)_3$; all catalysts were treated with H_2 6 hrs. at 400°. Plots of the log of the degree of conversion of both reactions a and b, against the reciprocal abs. temp. 1/T, are Arrhenius straight lines, giving the activation energies (in the order from I to VII): for reaction a, 3.0, 4.8, 5.4, 5.4, 5.2, 7.8, 10.0 kcal., for b, 5.2, 6.4, 7.6, 9.4, 10.5, 10.8, 14.8 kcal. Reaction a predominates over b in the whole temp. range. Thermography of the catalysts shows endothermal effects of loss of adsorbed and hydrate H_2O in all catalysts prepd. by pptn. Exothermal recalescence effects were found in all cases, with max. at 380-415° for III, V, and VI, at 600° for II and at 720° for VII. Thus, thermography can reveal the mode of prepn. of a Cr_2O_3 catalyst. The closeness of the catalytic activities of III and V is paralleled by a close similarity of their thermograms, with max. at 370-90° and at 390-400°. By x-ray diffraction, all Cr_2O_3 catalysts heat-treated at 400° are cryst. and not amorphous as claimed by Lasler and Vaughan (C.A. 38, 2060); the lattice parameters never differ by more than 0.013 A. from those tabulated. The dispersity of Cr_2O_3, after heat-treatment at 400°, varies with the method of original prepn., thus, II 125 A., VII 142 A., V 219 A., IV 271 A., III 398 A. The mean amplitude of lattice perturbation varies between 0.43 and 0.74 A., depending on the prepn., but without any apparent relation with the catalytic activity. In terms of the multiplet theory of catalysis (B., C.A. 37, 3002; 41, 1926), the energy barriers, E, for catalyst I to VII, are, (a) 8.0, 12.3, 14.4, 14.4, 14.2, 20.8, 28.0, (b) 14.2, 17.1, 20.3, 23.1, 28.0, 43.8, 39.8 kcal., and the adsorption potentials q of the active surface, (a) 189.0, 184.7, 182.0, 182.0, 182.8, 176.2, 100.0, (b) 142.0, 139.0, 136.7, 131.9, 129.0, 113.5, 117.5 kcal. Plots of E as a function of q, for reactions a and b, indicate that in both reactions, adsorption is the slowest stage. The observed variations of q for the different catalyst prepns., 30 kcal. for a and 30 kcal. for b, are distinctly smaller than half the energy of sublimation of Cr_2O_3, estd. to 140 kcal./mole, in agreement with the multiplet theory.

N. Thon

METALLURGICAL LITERATURE CLASSIFICATION

CA

2

Orientation of decahydronaphthalene and of cyclohexane molecules in dehydrogenation on oxide and on metallic catalysts. A. A. Balandin and G. V. Isagulyants. *Doklady Akad. Nauk S.S.S.R.* 64, 207-10(1949).—(1) On 1.5 g. (8 cm.) of a Cr_2O_3 catalyst on asbestos (20% Cr_2O_3 by wt.), at a flow rate of 0.0023 mole/10 min., the rates of dehydrogenation of decahydronaphthalene (I) (approx. equimol. mixt. of *cis* and *trans*) and of cyclohexane (II), measured by the amt. of (97-98% pure) H_2 evolved in 10 min., and expressed by the percentage of conversion *p* in 10 min., are very nearly equal at the same temp. The Arrhenius straight lines log *p* against 1/*T* for I and II are not only parallel (which fact indicates equal activation energies) but almost coincide. In the light of the multiplet theory of catalysis (B. and Brusov, *Zhur. Obshchei Khim.* 7, 18(1937); C.A. 31, 6107), this is consistent with an "edge" orientation of the hydrocarbons on the surface of the Cr_2O_3 catalyst (doublet model), the rate-detg. step in the dehydrogenation of II being the elimination of the 1st H_2 mol. (2) By the same theory, plane orientation on the (111) face of a face-centered cubic catalyst (sextet model), calls for different rates of dehydrogenation of I and of II. In this orientation, I occupies 6, II occupies 10 atoms of the catalyst; moreover, the d. of coverage decreases strongly with increasing no. of catalyst atoms occupied by a mol. of the adsorbed hydrocarbon (Langmuir, *C.A.* 34, 4322⁴). This leads to an calcd. rate 2-3 times as great for I, and the conclusion remains valid also for a nonhomogeneous catalyst surface. It was confirmed in dehydrogenation expts. on a Ni catalyst (20 g., 20 cm.), at approx. the same rate of flow as on Cr_2O_3. Between 200 and 300°, the Arrhenius lines for I and for II are parallel (activation energy of 12.5 kcal./mole), but the rate of dehydrogenation of I is roughly twice that of II.

N. Thon

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A. A., L. Kh. Freydlin, and E. A. Lokhanova

Interaction of Acid Anhydrides with Formates. II. Effect of the Nature of the Anhydride, page 350
Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol I, Moscow-Leningrad 1953, pages 762-766

Inst of Organic Chemistry, Acad, Sci USSR

FREYDLIN, L.Kh.; RUDNEVA, K.G.; BALANDIN, A.A., akademik.

Investigation of the nature of activity of a skeleton iron catalyst. Dokl. AN SSSR 91 no.5:1171-1174 Ag '53. (MLRA 6:8)

1. Akademiya nauk SSSR (for Balandin). 2. Institut organicheskoy khimii Akademii nauk SSSR (for Freydlin and Rudneva). (Catalysis)

FREYDLIN, L.Kh.; RUDNEVA, K.G.; BALANDIN, A.A., akademik.

Reduction of the metal-hydrogen composition of the active surface of a skeleton nickel catalyst. Dokl.AN SSSR 91 no.6:1349-1352 Ag '53. (MLRA 6:8)

1. Akademiya nauk SSSR (for Balandin). 2. Institut organicheskoy khimii Akademii nauk SSSR (for Freydlin, Rudneva).
(Reduction, Chemical) (Catalysts)

BALANDIN, A. A.

"The Free Energy of Adsorption on Dehydrogenation for a heterogeneous surface." Dokl. Akad. Nauk SSSR, 93, 55-58, 1953.

The adsorption of substances on a heterogeneous dehydrogenation catalyst is discussed and equations are given for the free energy of adsorption on such a surface.

BALANDIN, A. A.

"The Nature of activity centers of Dehydrogenation catalysts." Dokl. Akad. Nauk SSSR, 93, 475-8, 1953 (cf. ibid. 273)

A tentative phys. explanation is offered for the 2 laws of dehydrogenation catalysis, namely: (1) that the changes of environment of the active center of quasi-uniform centers act alike on the attraction of various mols., as a result of which their adsorption coeffs. remain unchanged; and (2) that the catalytic overvoltage (E') is proportional to the adsorption overvoltage (A') with a neg. sign, or $E' = nA'$

ISAGULYANTS, G.V.; GOLOVINA, O.A.; BALANDIN, A.A., akademik.

Synthesis of acetaldehyde and ethyl alcohol tagged with radiocarbon C^{14}.
Dokl.AN SSSR 93 no.4:659-661 D '53. (MLRA 6:11)

1. Akademiya nauk SSSR (for Balandin).
(Acetaldehyde) (Ethyl alcohol) (Carbon--Isotopes)

USSR/Chemistry - Fuels FD-1144

Card 1/1 Pub. 129-8/23

Author : Slovokhotova, T. A.; Sovalova, L. I.; Kazanskiy, B. A.; Balandin, A. A.

Title : Catalytic conversion of isomeric octanes with water over a nickel and kieselguhr catalyst

Periodical : Vest. Mosk. un., Ser. fizikomat. i yest. nauk, 9, No 7, 65-72, Oct 1954

Abstract : Saturated hydrocarbons react with water over a nickel and kieselguhr catalyst forming products of gradual demethylation of the original hydrocarbon. The degree of conversion depends on the structure of the hydrocarbon. 2, 2, 4-Trimethylpentane reacts slower than the 2, 2, 3 isomer. Eight curves. Ten references (five USSR).

Institution : Chair of Organic Chemistry

Submitted : February 1, 1954

BALANDIN, A. A.

"Catalytic Hydrogenation: I, Kinetic Equation of Hydrogenation and Dehydrogenation over Nickel Catalyst; II, Catalytic Hydrogenation over Nickel and Platinum. Hydrogenation by Deuterium; III, Further Development of the Theory. Hydrogination over Copper and Palladium; IV, Modification of the Hydrogen Surface. Selective Hydrogenation of Mixtures," A.A. Balandin, Acad Sci, USSR, Moscow

"J Gen Chem (USSR)" Vol. 15, 1954, pp 608-18, 619-27, 770-80, 781-90

A new theory of catalytic activity is proposed, according to which hydrogenation requires different areas of Ni catalyst for activation of the hydrogenating substance and for activation of H. The absorption on the active points of either type occurs according to the Langmuir isotherm. The kinetic equations deduced from these considerations explain the quantitative relations observed in hydrogenation of toluene over a Ni catalyst on the Al_2O_3 carrier. This theorty is applied in the explanation of variation of temperature effect with pressure, and the change of reaction order in catalyst poisoning by CO; the order of reaction in the liquid phase differs from that in the gaseous phase. Hydrogenation by D is discussed. The application of the new concept depends purely on the chemical process involved and on adsorption, diffusion effects have no importance. Mathematical relations are developed for the equilibria between the gaseous and adsorbed forms for the material to be hydrogenated.

So: V-336, 31 March 1948

5

USSR.

I Components of the activation energy and the problem of choosing catalysts [illegible]

[illegible]

generation [illegible] The catalyst was [illegible]

[illegible] Leach

USSR/Chemistry

Card : 1/1

Authors : Balandin, A. A., Academician

Title : Multiple theory and principle of minute equilibrium. The mechanism of hydro- and dehydrogenation

Periodical : Dokl. AN SSSR, 97, Ed. 3., 449 - 452, July 21, 1954

Abstract : The multiple theory and principle of minute equilibrium, which in hundreds of cases indicate the sequence of reactions of complex molecules and make it possible to determine the energy of bonds between the molecules and the catalyst, are explained. The results, derived from the application of the basic principle of the multiple theory - superimposition of molecules on the lattice surface of the catalyst, are described. The mechanism of hydro- and dehydrogenation is elucidated. Seventeen references: 15-USSR and 2-USA. Graph, drawings.

Institution : Acad. of Sc. USSR, the N. D. Zelinskiy Inst. of Org. Chem. and the M. V. Lomonosov State University, Moscow

Submitted : May 22, 1954

USSR/Chemistry - Catalysis

Card 1/1 : Pub. 22 - 25/46

Authors : Balandin, A. A., Academician

Title : Catalytic layers and their effect on the activation energy

Periodical : Dok. AN SSSR 97/4, 667-670, Aug 1, 1954

Abstract : The effect of catalytic layers (five basic layers in intermediate state), on the activation energy of a heterogeneous catalysis, is elucidated. The effect of catalyst atoms, which are not included in the active center of layer I, on the atoms of layer II is identical to the effect of surface micro-roughness or nature of sometimes separated atoms (carriers and admixtures). Equations are presented which indicate the elements constituting the activation energies of expanded catalysis reactions. Fifteen USSR references (1930-1954). Drawing.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Inst. of Org. Chem. and the M. V. Lomonosov State University, Moscow

Submitted : June 1, 1954

USSR/Chemistry - Dehydrogenation

Card 1/1 Pub. 22 - 23/47

Authors : Balandin, A. A., Academician, and Klabunovskiy, E. I.

Title : Kinetics of butanol-2 dehydrogenation over nickel

Periodical : Dok. AN SSSR 98/5, 783-786, Oct 11, 1954

Abstract : The kinetics of butanol-2 dehydrogenation over nickel was investigated in a vaporous phase of a flowing system. The rate constants were determined from the general kinetic equation of the catalytic mono-molecular reactions occurring in the flow. Equations determining the relative adsorption coefficient, change in free energy and entropy during the adsorption on catalytically active centers are included. The heats of adsorption displacement were found to be very high and exceed the activation energy. The actual hydrogenation activation energy for butanol-2 is presented in a table. Eleven references: 8-USSR; 1-English; 1-French and 1-Belgian (1925-1954). Tables; graphs.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : July 29, 1954

L-701597 TREASURE ISLAND BOOK REVIEW AID 817- S

BALANDIN, A. A. (Institute of Organic Chemistry, Academy of Sciences, USSR). DISKUSSIYA (Discussion). In Problemy kinetiki i kataliza (Problems of Kinetics and Catalysis), vo. 8. Izdatel'stvo Akademii Nauk SSSR, 1955. Section II: General Problems of the theory of catalysis. p. 155-156.

Discussion of the classification of catalytic reactions given by S. Z. Roginskiy namely: 1) oxidation-- reduction reactions and 2) proton reactions. The author considers this classification incomplete, since surface reactions may be of ionic or atomic nature. He proposes the following classification:

I. Non-ionic (atomic) reactions
II. Ionic reactions
    1. oxidation - reduction reactions
    2. acid-base (proton) reactions

To non-ionic reactions belong: catalytic dehydrogenation and hydrogenation of hydrocarbons on metals and on some oxides; dehydrogenation of alcohols and amines; hydrogenation of alcohols, ketones, aldimines and ketimines; nitriles, etc. To ionic reactions belong: catalytic oxidation (with O_2) of hydrogen sulfide, ammonia, hydrocarbons. To acid-base (proton) reactions belong: hydrolysis, BALANDIN, A. A., Diskussiya AID 817 - S

hydration and dehydration with acids, isomerization, cracking, and numerous condensation and polymerization reactions. Although there are specific catalysts for each type of reaction, some of the catalysts may be used in several reactions.

Vasserberg, V.E.

BALANDINA,V.A. [translator]; BOGDANOVA,O.K.[translator]; VASSERBERG,V.E., [translator]; KIPERMAN,S.L.,[translator]; BALANDIN,A.A., akademik, redaktor; RUBINSHTEYN,A.M., professor, redaktor; SATAROVA,M.V., redaktor; OGANDZHANOVA,N.A., redaktor; IOVLEVA,N.A., tekhnicheskiy redaktor

[Catalysis, catalysts for,organic reactions; translated from the English] Katalis, katalizatory organicheskikh reaktsii. Perevod s angliiskogo Balandinoi i dr. Moskva, Izd-vo inostrannoi lit-ry, 1955. 336 p. (MLRA 9:2)

(Catalysts)

AF701597 TREASURE ISLAND BOOK REVIEW AID 834 - S

BALANDIN, A. A. (Institute of Organic Chemistry, Academy of Sciences, USSR)
DISKUSSIYA (Discussion). In Problemy kinetiki i kataliza (Problems of Kinetics and Catalysis), vol. 8. Izdatel'stvo Akademii Nauk SSSR, 1955. Section IV. Nature of the active surface. p. 233-234.

With reference to the paper by G. M. Zhabrova, Balandin points out that on many catalysts both dehydration and dehydrogenation belong to non-ionic reactions, i.e., they occur without formation of free ions. The dehydration of alcohols may be conducted as an ionic reaction under the action of acids (e.g., addition of phosphoric acid to activated carbon.) In experiments with isopropyl alcohol, Balandin found that on addition of chloroform to alcohol (25% chloroform + 75% isopropyl alcohol) at temperatures exceeding 300°C (in the presence of chromic oxide); the dehydration of alcohol is markedly increased. HCl shows a still greater effect. One reference (Russian) (1954)

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[illegible]

ZELINSKIY, Nikolay Dmitriyevich, 1861-1953 [deceased] KAZANSKIY, B.A., akademik; BALANDIN, A.A., akademik; KOCHESHKOV, K.A.; SHUYKIN, N.I.; KAVERZNEVA, Ye.D, doktor khimicheskikh nauk; LEVINA, R.Ya., doktor khimicheskikh nauk; PLATE, A.F., doktor khimicheskikh nauk; RUBINSHTEYN, A.M., doktor khimicheskikh nauk; YUR'YEV, Yu.K., doktor khimicheskikh nauk; KISELEVA, A.A., tekhnicheskiy redaktor.

[Collected works] Sobranie trudov, Moskva, Izd-vo Akademii nauk SSSR. Vol. 2. 1955. 743 p. (MLRA 8:11)

1. Chlen-korrespondent AN SSSR(for Kocheshkov and Shuykin)
(Hydrocarbons) (Petroleum)

The mechanism and kinetics of heterogeneous catalysis in organic chemistry. A. A. Balandin and N. I. Shuikin (Voprosy Khim. Kinetiki, Kataliza i Reaktsionnoi Sposobnosti, Akad. Nauk S.S.S.R. 1955, 44[illegible]). A historical review of the development of heterogeneous catalysis. 85 references.

W. M. Sternberg

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✓ **The characteristics of the active state in heterogeneous catalysis.** A. A. Balandin. *Voprosy Khim. Kinetiki, Kataliza i Reaktsionnoi Sposobnosti, Akad. Nauk* [illegible] 1955, 461-83.—Several layers must be distinguished in an intermediate analytical complex. A diffusion layer, a layer of and substituents, a reacting [illegible] center layer, and the surrounding [illegible]. The various competing opinions on catalysis refer most frequently to different layers, or to different phases of catalysis and can be unified. The correspondence of structure and energetics must be observed in catalysis. The correspondence of structure refers to the combination of the principal data that prove the existence of catalysis and the consideration of conditions in which the multiplet theory conforms to the principle of detailed equil. A long list of earlier work (83 references) is given in the discussion of the energetic correspondence, and new exptl. data are discussed in connection with the theory of catalyst selection. The Semenov new theory of catalysis (*Some Problems of Chemical Kinetics and Reactivity*, 1954) (C.A. 49, 12948h) is discussed.

W. M. Sternberg

BALANDIN, A.A.

Present state of catalysis and theoretical principles of catalyst research. Izv.AN SSSR. Otd.khim.nauk no.4:624-638 Jl-Ag '55.
(MLRA 9:1)

1.Institut organicheskoy khimii imeni N.D.Zelenskogo Akademii nauk SSSR. (Catalysis)

V. The free energy of the adsorptive displacement of [illegible] ene by water on a catalytic surface. A. A. Balandin, V. [illegible] and [illegible]

[illegible]

USSR/Chemistry - Catalytic chemistry

Card 1/1 Pub. 124 - 3/32

Authors : Balandin, A. A., Academician

Title : Problems and perspectives in the development of catalytic chemistry

Periodical : Vest. AN SSSR 25/6, 19-23, June 1955

Abstract : The advantages and great importance of cataysis and catalysts in modern organic and inorganic chemical industry are discussed. The role which catlaytic chemistry will have to assume in realising the basic tendencies of modern organic technology - derivation of materials from water, air, coal, petroleum, and petrol-gases - is explained. The problems concerning the proper selection of active and suitable catalysts needed for various chemical-technological processes are analyzed.

Institution : .....

Submitted : ....

[illegible]

R [illegible] CH₂)OH), RCH CHCH [illegible]
[illegible] H)Ma. RCP CHCH CHOO [illegible]
[illegible] H)Br, RCH CHCH CH₂C [illegible]

[illegible]

[illegible] HMg [illegible]
[illegible] R [illegible]
[illegible] 2-phenyl [illegible]
[illegible] Raney Ni [illegible]

[illegible]

[illegible] R [illegible]
heptane, RCH₂CH₂OH [illegible]
[illegible] Ni [illegible] 30° [illegible] butane [illegible]
octane

7

1. **Catalytic dehydrogenation of amines with formation of ketimines.** A. A. Balandin and N. A. Vasyunina (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 103, 831-4(1955).—Passage of 2-aminoheptane over Pt-on-asbestos at 325° gave 25.1% H and no NH_3; hydrolysis of the catalyzate gave MeCOAm, b. 150.2°, indicating that the original reaction was merely that of dehydrogenation with formation of a *ketimine*. Over Ni-Al_2O_3 at 350° 41.2% H was similarly obtained; over Pt at 320° were formed 30.5% H and 18.1% NH_3, indicating partial deamination. *$H_2NCHMeCH_2CHMe_2$*, b. 106-7°, n_D^{20} 1.4095, d_{20} 0.8192, passed over Pd at 320° gave 32.5% H without any NH_3, and the catalyzate hydrolyzed to iso-BuAc; over Ni-Al_2O_3 at 324° the yield of H was 30.2% without any NH_3. *$H_2NCH(CHMe_2)_2$*, b. 125-7°, d_{20} 0.7882, over Pd at 318° gave 28.4% H without NH_3, and hydrolysis of the catalyzate gave iso-Pr_2CO; over Ni-Al_2O_3 at 325° the yield of H was 27.9% without any NH_3. *$H_2NCHEtCMe_3$*, b. 102.5°, [illegible] d_{20} 0.7668, dehydrogenated only feebly over Pd [illegible] at [illegible] gave 83.3% H and 25.9% NH_3; hydrolysis of the catalyzate gave pinacolone and some $EtCMe_3$ was isolated from the original catalyzate. EtCHPhNH₂ over Pd at 340° gave 35.6% H and 10.2% NH_3; over Ni-Al_2O_3 at 340° the yield of H was 44.9%, with 16.8% NH_3; over ThO_2 38% H with 18.2% NH_3 resulted; hydrolysis gave EtBz, while the catalyzate also gave some phenylpropene. This is the 1st example of dehydrogenation of aliphatic amines to ketimines (cf. C.A. 29, 2865). G. M. Kosolapoff

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5006

Catalytic transformations of cyclohexane hydrocarbons on aluminosilicate catalyst. A. A. Balandin, M. B. Turova-Polyak, and Syui Kan. *Doklady Akad. Nauk S.S.S.R.* 105, 716-19 (1955). 3

chem

—Passage of substituted cyclohexanes over aluminosilicate catalyst at 540° gave the following yields of products from indicated starting materials (% yield of liquid catalyzate, gaseous products in ml./g., % yield of coke, gaseous hydrocarbons, liquid olefins, isomerization products, total aromatics, C_6H_6, MePh, xylenes, higher aromatics): cyclohexane 82, 171, 2.0, 13, 4, 4.1, 12.3, 1.4, 2.7, 2.5, 5.7; methylcyclohexane 69.5, 250, 2.3, 24.9, 9.2, 7.5, 15.5, —, 8.1, 2.4, 5.0; ethylcyclohexane 68.0, 254, 2.4, 21.9, 9.9, 7.2, 16.1, —, —, 13.2, 2.9; 1,4-dimethylcyclohexane 64.8, 311, 2.6, 28.1, 11.1, 4.2, 19.9, —, 2, 14, 3.9; 1,1-dimethylcyclohexane 74.1, 300, 1.3, 19.3, 9.5, —, 14, —, 8.8 (including xylenes), 5.2; 1,3,5-trimethylcyclohexane 59.1, 309, 4.3, 33.9, 11.5, 2.5, 21.2, —, —, 15.8, 5.4; isopropylcyclohexane 63.4, 276, 4.1, 21.6, 16.3, 8.7, 18.2, —, —, 14.3, 3.9. The longer the time of contact, the greater is the proportion of gaseous products, particularly CH_4, the above set of values obtained at space velocity 0.29 l./l./hr. Elevation of temp. from 500° to 568° raises the total conversion, the yield of gases, and amt. of MePh formed. The apparent activation energy was found from gas evolution to be 27,700 cal./mole for methylcyclohexane and 39,600 cal./mole for [illegible]

G. M. Kosolapoff

FREYDLIN, L.Kh; BALANDIN, A.A., akademik; NAZAROVA' N.M.; YEGOROV, Yu.P.

Alkylation of propane and n-pentane with propylene at high temperatures, under high pressures, and in presence of aluminum oxide. Dokl. AN SSSR 105 no.6:1270-1273 D '55. (MLRA 9:4)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Alkylation) (Hydrocarbons)

COTTRELL, T.L.; DYATKINA, M.Ye. [translator]; BALANDIN, A.A., akademik, redaktor; OGANDZHANOVA, N.A., redaktor; SHAPOVALOV, V.I., tekhnicheskiy redaktor

[The strength of chemical bonds. Translated from the English] Prochnost' khimicheskikh sviazei. Perevod s angliiskogo M.E. Diatkinoi. Pod red. A.A.Balandina. Moskva, Izd-vo inostrannoi lit-ry, 1956. 281 p. (MLRA 9:8)

(Chemistry, Physical and theoretical)
(Valence (Theoretical chemistry)

BALANDIN, A.A.

[illegible]

USSR/ Chemistry - Organic chemistry

Card 1/1 Pub. 40 - 23/25

Authors : Freydlin, L. Kh.; Balandin, A. A.; and Borunova, N. V.

Title : Effectiveness of catalysts prepared from nickelous oxide treated in water vapors under pressure

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 128-130, Jan 1956

Abstract : It was established experimentally that by employing different aging conditions for NiO on the carrier by treating with water vapors it becomes possible to control the activity of nickel catalysts. It was found that nickel catalysts treated in such a manner lose the ability of hydrogenating the aromatic bond but still retain their activity for the hydrogenation of the C = C and C ≡ C bonds. Two USSR references [illegible]

Institution : Acad. of Sc., USSR, Inst. of Organ. Chem. im. N. D. Zelinskiy

Submitted : July 20, 1955

BALANDIN, A.A.

USSR/Kinetics - Combustion. Explosions. Topochemistry. Catalysis. B-9

Abs Jour : Referat Zhur - Khimiya, No 6, 1957, 18625

Author : L.Kh. Freydlin, A.A. Balandin, N.V. Borunova, A.Ye. Agronomov.

Inst : Academy of Sciences of USSR.

Title : Mechanism of Deactivation of Nickel Catalysts by Steam Under Pressure.

Orig Pub : Izv. AN SSSR, Otd. khim. n., 1956, No 8, 913-922

Abstract : Unreduced catalysts of the composition 35% of NiO and 65% of Al_2O_3, as well as Ni-catalysts prepared from them after reduction were treated at 350° with amixture of H_2 (700 atm) and steam (100 atm) 5 hours in a special high pressure reactor. It was found that their activity in the reaction $C_6H_6 + 3H_2$ and in the reverse reaction decreased strongly after the treatment, especially if the samples had been treated thus before the reduction. In this case, the magnitude of the specific surface of

Card 1/2

Zelinskiy Inst. Organic Chem, AN USSR.

USSR/Kinetics - Combustion. Explosions. Topochemistry. Catalysis. B-9

Abs Jour : Referat Zhur - Khimiya, No 6, 1957, 18625

samples decreases (from 170 and 80 to 10 and 30 sq.m/g respectively), which the authors explain by recrystallization of nickel lower oxide, as well as of the carrier. The authors think that the bibliographically recorded deactivation of reduced Ni-catalysts (and, as it seems, also of Fe-catalysts) by steam during the process of work is explained by the appearance of a surface film or a phase of NiO, which recrystallizes rapidly and the reduction process of which is hampered and results in the formation of little dispersed Ni.

Card 2/2

BALANDIN, A.A.; TOLSTOPYATOVA, A.A.

Kinetic determination of bond energies as an approach to the theory of the selection of catalysts. Part 2. Comparison of results with chromia [with English summary in insert]. Zhur.fiz. khim. 30 no.7:1636-1646 Jl '56. (MLRA 9:11)

1. Akademiya nauk SSSR, Institut organicheskoy khimii imeni N.D. Zelinskogo, Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova, Moskva.
(Chromium oxides) (Catalysts)