



*S & T Chemical Catalysis*

DEPARTMENT OF CHEMISTRY  
PHONE: (414) 963-4411

*110mi  
Comment as desired*

October 4, 1973

Professor O. V. Krylov  
Deputy Director  
Institute of Physical Chemistry  
USSR Academy of Science  
Moscow, USSR

*Ray  
top of 30 Oct 73  
Ans by EXS 77-73  
dttd 20 Dec 73*

Re: Further Plans for Item 3, An In-depth Study of Selected Catalyst Systems

Dear Oleg Valentinovich:

First of all, let me send the sincere thanks of the American Delegation for the unmatched hospitality shown us during our recent trip to Moscow. Moreover, please extend my personal greetings and thanks to your good wife for the very enjoyable evening which we spent in your home. It is my hope that when you visit us here, we may be able to at least partially repay you for your kindness.

Next, I have some comments concerning our meeting in Moscow and the document which we signed. The meetings were quite beneficial to me; I feel that I now have a much better understanding of the research interests of various individuals. I particularly enjoyed those opportunities which we had to discuss research on an individual basis with the people actually doing the work. My chief regret is that the time required to generate the document prevented me from more such discussions. I also deeply regret that circumstances prevented our visit to Novosibirsk. Perhaps I can fill this gap in my knowledge on my next visit to the USSR.

I think that the agreement which we signed in Moscow is a good one which looks toward the future with optimism. Since my return here, I have been looking into ways and means of adding some ultra-high vacuum research on single crystals to our program. You will recall that in Moscow, Professor Turkevich agreed to use his good offices on a temporary basis to seek opportunities for junior Russian scientists to do post-doctoral research in the US. (Since there were no provisions made in our budgets for this purpose, the funding of such activities would necessarily have to come from other sources.) However, I agreed to try to add such a program to the US effort in the near future. Since my return here, I have had several conversations about this with Professor Baldeschwieler, and, whereas the matter is not completely settled, I am confident that it will become an accomplished fact before I receive an answer to this letter. I might add that we are taking these steps because of the great interest in this area in both your laboratory and that of Professor Boreskov. I'm sure that you are aware that I regard work in this area as a little remote from the central theme of understanding in some detail

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the mechanisms of few simple catalytic reactions. Nevertheless, I agree that this surface chemistry represents a challenging scientific problem and that it may contribute, in the long run, to the major themes agreed upon in our exchange of letters of October 31 and December 1, 1972.

In Moscow, I also promised that Professor Boudart would be added to our program as soon as funds became available. I have every reason to believe that this will also be accomplished in the immediate future. I will write you again about these two additions in the next several weeks, as I want you to have the information before you come to the US in November. Incidentally, I would appreciate it if you would write me in the immediate future concerning your plans for this trip. I will need some time to make suitable arrangements here and perhaps to help you visit certain other laboratories.

During 1974, I would like to collaborate directly with Professor V. B. Kazansky, and through him with Professor Kh. M. Minachev and Dr. G. M. Zhidomirov on the general problem of butene isomerization. I believe that this can be fruitful collaboration, with Kazansky studying the ground-state from which the carbonium ion is formed; Zhidomirov contributing quantum calculations to compare with my experimental data; and Minachev -- his wisdom and advice. I have written Kazansky separately concerning this proposal (copy attached). The following paragraphs contain a description of the work which I propose to carry out under this program. I am encouraging the other members of the American team to do likewise, and I hope that you will reciprocate by having our direct collaborators send us their detailed plans.

It is my view that for strong proton-donating catalysts, such as zeolites, the reaction schemes for hydrocarbon catalysis can be adequately described within the framework of carbonium ion chemistry. For these cases, the frontier lies in the direction of understanding some of the finer details of these processes. These details are no less important, however, because they include the isolation and understanding of the factors which control selectivity for the production of desired products at the expense of others.

The isomerization of the butenes has been used successfully as the tool in investigations of this kind. A definite and recognizable pattern of the behavior has been established for carbonium ion processes, and exceptions to this pattern have been noted for catalysts which may be characterized as poor proton donors. Catalysts which may be thought of as bases, e.g., MgO, and those that have dual acid-base sites, e.g., alumina, yield quite different product ratios than those found for carbonium ion reactions. Some evidence has been accumulated that in these latter instances, the reactions involve an intramolecular 1-3 hydrogen shift, whereas in the carbonium ion process, an intermolecular exchange process (via the

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catalyst protons) occurs. However, insufficient research has been done to date to make a categorical statement concerning the sequence of events which occurs in the non-carbonium ion reactions.

Japanese workers have recently established a direct correlation between the activity of  $\text{SnO}_2\text{-MoO}_3$  catalyst for the production of acetone, by oxidation of propylene, and their activity. Similarly, Soviet scientists have found evidence of the intervention of acid properties in catalytic oxidation. These findings suggest a new area for investigation, viz., the effect of the acidity of the catalysts on their activity and selectivity in oxidation reactions. Therefore, the catalysts which we are preparing for part of the joint collaboration dealing with catalytic oxidation reactions will be evaluated as acid (or base) catalysts. Soviet contributions to the catalysts banks will be examined in a similar fashion.

Three problem areas have been mentioned above: (1) the understanding of the finer details of carbonium ion reactions and the origin of selectivity in these reactions; (2) systematizing and classifying the characteristics of the non-conforming reactions with a view to establishing their mechanisms; and (3) characterizing the surfaces of the catalyst made for oxidation research in terms of their acidic or basic character. This is about all that can be accomplished during the first year and perhaps that is optimistic. There are, however, two other large and important problems which should be undertaken in the near future. These are: (1) the determination of the surface density and distribution of catalytically active centers and (2) the characterization of these sites (kind and strength), perhaps by spectroscopic means. I would envision that these would be done in collaboration with Professor K. V. Topchieva and Professor G. K. Boreskov.

Catalysts prepared for this work will be entered into the catalysts banks. Attempts will be made to devise model catalyst systems such as alumina or germania built onto the surface of silica at below monolayer coverage. Some pure oxides will also be examined and an attempt will be made to prepare these in such a way that they will have a respectable surface areas. These will include  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ . I would also like to include some selected zeolites. Perhaps Professor Minachev can furnish some of these.

The next stage in our collaboration must involve an exchange of personnel. Time is becoming critical in this connection. It is my understanding that, because of the vacation schedule in the Soviet Union, it is desirable that our people arrive there not later than February 1. Ordinarily this is not a problem in the US, but during the summer of 1974, Professor Keulks and I will be moving our laboratories to a new building. This will undoubtedly disrupt work for a week or two, so that we also would like to have the Soviet junior scientists at an early date. My personal situation is still

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more complicated in that I moved here only a month ago and it will take several more months to get the necessary equipment set up for my project. On the other hand, we have problems which you don't. As I understand it from the USSR the junior scientists will be coming from your several Institutes. Presumably, these people have fairly stable, permanent employment. In the US, both post-doctoral students and graduate students have termination dates which occur at times known some months in advance. Our problem then is to arrange for them to visit the Soviet Union at times which coincide with their termination dates. If this cannot be done, the individual moves on to another position and usually becomes lost from the program forever. Another problem is that most of our candidates have several alternatives including industrial employment, which at times can be tempting because of the high salaries which are paid. In a word, for each particular junior scientist, we have only a narrow window in time in which we can get him to commit himself to accept an appointment in the Soviet Union before he accepts another option. I tell you these things so that you can better appreciate our situation. Presently our hands remain tied until we learn what the salary will be for our junior scientists in the Soviet Union. You will recall that we discussed this matter in your office and that Professor Boreskov said that the approval of a committee will be necessary on our proposal to pay them the equivalent of \$750 per month in Rubles. As soon as this information is available, please let us know so that we can make definite offers to our people. Otherwise, some of our best prospects may escape us.

As I see it, there is one other major problem. This is the appropriate matching of junior scientists with positions. The development of the program in the US was based on premise that the USSR would send a junior scientist to work with each of the principal investigators and that we would reciprocate by sending an equal number to the corresponding principal investigators in your country, i.e., an exchange of people to fill positions. In point of fact, I see pressures developing on both sides to create positions that fit the needs of the people who are available. This creates a dilemma which must be resolved in the near future. I mention it at this time so that you can give it some consideration before you visit the US later this fall and so that we can discuss it at that time.

Finally, I have from Professor Weinberg, a copy of a letter from Professor Yu. Yermakov in which he states "money will be paid by Professor Turkevich from the fund of the USA government in accord with the program of scientific collaboration between our countries" (for the support of a junior Soviet scientist in the laboratory of Professor Weinberg). This is a misunderstanding. Professor Turkevich could not and did not commit funds earmarked for research in his laboratory for this purpose. He promised only to look for a suitable position in a laboratory where ultra-high vacuum research is being carried out; the financial support could necessarily come from either

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the USSR or other sources in this country. In addition, however, I stated that I would take steps to add another principal investigator to our side of the program at the earliest possible moment. And, as I noted above, this is being done.

With kindest personal regards, I am

Sincerely yours,

W. Keith Hall  
Distinguished Professor of Chemistry

WKH:nd  
Enclosures

cc: Prof. Boreskov  
Prof. Minachev  
Prof. Kazansky  
Prof. Keulks