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DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST. SEVENTH QUARTERLY REPORT, FEBRUARY 7, 1992--MAY 7, 1992

DELAWARE UNIV., NEWARK. CENTER FOR
CATALYTIC SCIENCE AND TECHNOLOGY

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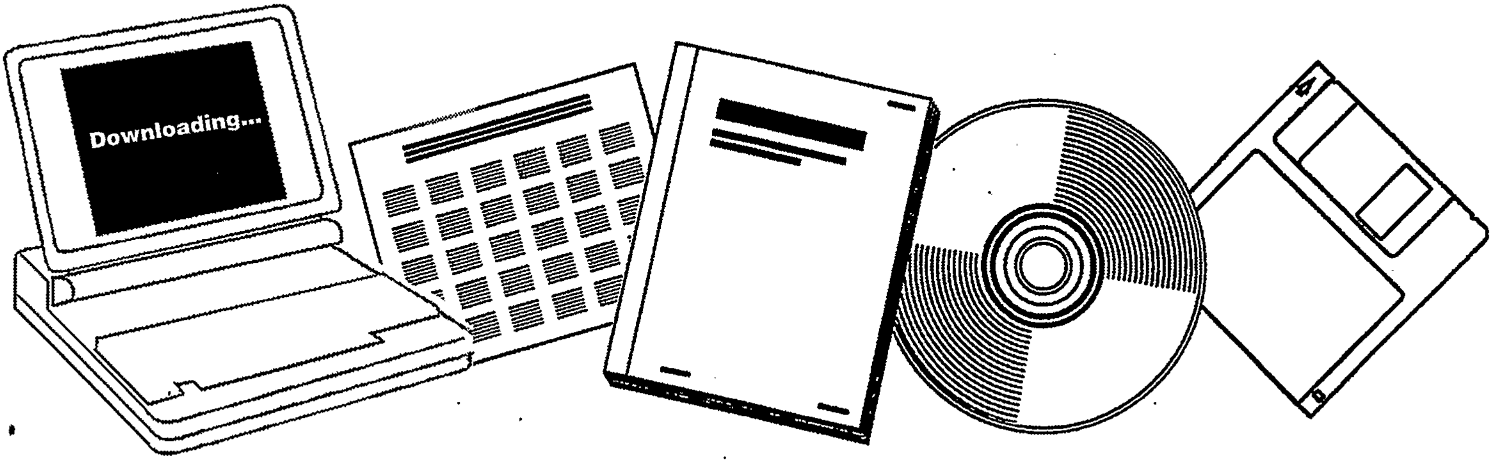

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DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST

Seventh Quarterly Report for Period
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Update on Methanol Dehydration Studies

In continuing to explore the secondary dehydration of methanol over our γ-Al_2O_3 support and over our bimetallic Rh-Mo/γ-Al_2O_3 catalyst, we have synthesized a new series of potassium-doped (K-doped) Rh-Mo/γ-Al_2O_3 catalysts. This new series has been prepared via aqueous impregnation of KNO_3 solution to pore volume saturation followed by calcining in air at 300 °C. In contrast, the series of K-doped Rh-Mo/γ-Al_2O_3 catalysts mentioned in our last update was prepared by contacting the catalyst with excess ion-exchange solution, filtering and finally calcining in air at 300 °C. In the former series, the ultimately achievable potassium loading was quite low, namely less than 1% by mass, and the presence of the potassium did not appear to materially effect the dehydration propensity of the surface. With this new series of catalysts, we seek to confirm our hypothesis that the higher potassium loadings achievable via aqueous impregnation will have, at most, only a minor influence on the dehydration activity of the catalyst. The genesis of this hypothesis stems from the pyridine adsorption-IR studies discussed in our last update, wherein IR spectra suggest that the transition metals in our system seem to interact with the Lewis acid sites on the native γ-Al_2O_3 surface, quashing acidity which might otherwise interact with K^+ cations from our ion exchange solution. We are currently evaluating this new series of samples for methanol dehydration activity in our low-pressure microreactor system.

Further work in this area will focus on the quantification of total "acid amount" on the surface via acid site titration by ammonia adsorption. In these experiments we (i) pack a stainless steel column with a sample of interest, (ii) inject controlled amounts of ammonia in a He carrier gas which flows through the column (experimental stimulus), and finally, (iii) evaluate the concentration of ammonia in the column effluent via a thermal conductivity detector. Assuming that the ammonia is irreversibly chemisorbed on the surface of the sample at a given temperature and given a small enough stimulus, the effluent will contain no ammonia until the surface acid sites are saturated. Once the surface sites are saturated *and an equilibrium level of physical adsorption is achieved*, the thermal conductivity detector will begin to respond, measuring the ammonia in the column effluent. After the detector returns to its baseline level, the difference between the cumulative stimulus and the cumulative detector response is proportional to the total of chemically and physically adsorbed ammonia at the temperature of the experiment. While this technique does not distinguish between the physisorbed and the chemisorbed species, if samples are evaluated with the same temperature treatment, comparisons of the relative acid amounts can be made. In the coming month, we hope to apply this technique to the various series of K-doped samples that we have synthesized in order to access total acidity across the samples as a function of potassium loading and transition metal content.

Bimetallic Cluster Synthesis

During the fall of 1991, we completed an extensive literature review of all homogeneous compounds containing Rh-Mo metal-metal bonds. This review established that several bimetallic compounds of Rh and Mo containing proposed dative Rh-->Mo interactions had been synthesized. Furthermore, in such compounds—given the presence of a Rh-Mo metal-metal interaction—the transition-metal centers were guaranteed to be in close proximity. These two notable features of the various bimetallic clusters in the literature have motivated us to attempt synthesize such compounds as precursors for a new Rh-Mo/γ-Al_2O_3 catalyst, with metals chemisorbed directly from the bimetallic precursor rather than sequentially chemisorbed from two independent metal-carbonyl precursors. Notably, Miessner et al. have successfully prepared a silica-supported Rh-Mo catalyst from a heteronuclear cluster and compared the reactivity of this catalyst with a Rh-Mo catalyst prepared from metal salts as well as an unpromoted Rh/SiO_2 catalyst [c.f. *Materials Chemistry and Physics*, **29**, 503-508 (1991)]. Miessner demonstrated that the heteronuclear cluster-derived catalyst had improved oxygenate selectivity in the hydrogenation of carbon monoxide. Given both the unique properties of such cluster-derived catalysts and the success of Miessner and his coworkers, we have set out to examine the potential of such cluster-derived catalysts both on alumina-supported materials and when derived from heteronuclear clusters of varying nuclearity and metal-metal bond distance. Pursuant to this goal, a visit scholar, Mr. Te Mure, from the Lanzhou Institute of Chemical Physics, Chinese Academy of Science has begun work (i) synthesizing various organometallic precursors needed to make the ultimate *bimetallic-catalyst* precursors for our new catalytic materials and (ii) has been successful in synthesizing what thus far appears to be one of the bimetallic Rh-Mo clusters reported in the literature. On-going efforts in this area will include:

- Perfecting various synthesis procedures;

- Synthesizing two to three distinct heteronuclear clusters of Rh and Mo;

- Catalyst preparation from such clusters via chemisorption onto γ-Al_2O_3;

- Reactor testing of such catalysts for the hydrogenation of CO to oxygenated products;
- Characterization of the ultimately produced materials via infrared spectroscopy and hydrogen and carbon monoxide chemisorption.

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