DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST

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Methanol Dehydration Studies

As mentioned in the last update, a new series of K-doped Rh-Mo/γ-Al$_2$O$_3$ has been prepared via aqueous impregnation of the samples to pore volume saturation. In contrast to past K-doped samples which had an ultimate K loading of less than 1% by mass, this new protocol lead to samples with K loading of up to 13% (approaching the theoretical monolayer coverage, based on 10 hydroxyl sites per nm^2). While these higher loadings of potassium do indeed effect the dehydration propensity of the support surface, as we suggested in the last update, the influence of this higher level of potassium was small compared to the change in the dehydration propensity of the surface resulting from low levels of potassium loading.

Consider first Figure 1 which depicts the influence on total conversion of methanol resulting from increasing the potassium loading on the surface. The most prominent feature of Figure 1 is that the consumption of methanol declines rapidly as the potassium loading increases—at approximately 6% potassium loading the rate of consumption of methanol has dropped by almost an order of magnitude over the undoped Rh-Mo/γ-Al$_2$O$_3$. More importantly, however, when the consumption of methanol for the Rh-Mo/γ-Al$_2$O$_3$ catalyst is compared to the point shown for native γ-Al$_2$O$_3$, the significantly enhanced methanol consumption for the transition-metal loaded samples comes to light. This enhanced methanol consumption is related to the dual-decomposition pathway for methanol in the presence of a Rh-Mo active phase on the catalyst which has been alluded to in past reports. Figure 2 sets forth a mechanistic schematic for this dual-decomposition pathway which has been verified by independent experiments wherein CO rather than He was used as a carrier gas. The CO was preferentially adsorbed on the Rh-Mo active sites essentially poisoning them for the decomposition of methanol as depicted in the lower half of the figure. The decline in methanol decomposition depicted in Figure 1, then, is due to the combined effect of the potassium oxide layer screening Lewis acid sites on the alumina as well as occluding the active Rh-Mo sites on the surface as the loading increases.

Given that this dual-decomposition pathway for methanol exists on the Rh-Mo/γ-Al$_2$O$_3$ and convolutes the information associated with the consumption of methanol, examining the rate of formation of dimethyl ether (DME)—rather than the rate of methanol consumption—proves more enlightening. Figure 3 depicts the rate of formation of DME as a function of potassium loading up to the levels achieved by aqueous impregnation. In Figure 3 we see that over the range of potassium loadings, the rate of formation declines rapidly at first and then more moderately, such that by 6% loading, yield of DME is negligible. The most dramatic decline highlighted by this chart occurs at loadings below 1% potassium. If we focus our attention on this section of Figure 3 and expand the scale in Figure 4, we see that by the time the loading is approximately 0.08% the rate of DME formation has been cut in half. We have suggested, based

on pyridine-adsorption infra red spectroscopy of these samples, that this dramatic decline is due to the inherent lack of Lewis acidity on the catalyst surface following the chemisorption of Rh during the synthesis of the catalyst. As the process of chemisorbing the Rh titrates the strongest Lewis acid sites, only an incremental level of potassium is then required to titrate the remaining Lewis sites on the surface strong enough to dehydrate methanol.

In summary, while higher potassium levels did, indeed, lead to a reduction in the dehydration propensity of the surface, at higher levels the potassium oxide layer formed after doping and calcining the surface interferes detrimentally with the Rh-Mo active metallic sites. The occlusion of such active sites under reaction conditions conducive to the production of oxygenates, namely high pressures in the presence of synthesis gas, would lead to reduced overall catalyst activity and hence is undesirable. However, low levels of potassium doping may prove advantageous in boosting alcohol yields under synthesis condition.

Bimetallic Cluster Synthesis

As set forth in the last update, given both the unique properties of cluster-derived Rh-Mo catalysts and the success of Miessner and his coworkers [c.f. *Materials Chemistry and Physics*, **29**, 503-508 (1991)] in both synthesizing such catalysts and testing their hydrogenation activity and selectivity, 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. The main emphasis of our efforts thus far focus on evaluating the potential for chemical and catalytic synergy in Rh-Mo catalysts synthesized from a homogeneous bimetallic precursor.

We have successfully synthesized one silica-supported and a second alumina-supported catalyst with approximately 0.5% Rh loading from $RhMo(CO)_3Cp(PPh_3)_2$. In order to assess the importance of starting with a bimetallic precursor, we have also synthesized similar catalysts via a coadsorption protocol wherein the support is simultaneously slurried with $RhH(CO)(PPh_3)_3$ and $[Mo(CO)_3Cp]_2$ in an organic solvent. Both series of catalysts were subsequently calcined in air at 200 °C prior to reduction and catalytic testing.

Table 1 depicts the range of results for these catalysts when tested for the hydrogenation of CO. Also listed in Table 1 are the results reported by Trunschke et al. for a trinuclear cluster-derived catalyst and a reference sample of Rh-Mo catalyst prepared by more traditional methods from inorganic salts. As the table demonstrates, our catalytic testing indicates that (i) all the metal carbonyl-derived catalysts have a higher propensity for oxygenate formation than the inorganic salt-derived catalysts, (ii) the bimetallic cluster-derived catalysts have higher total oxygenate selectivity than those that were prepared via a coadsorption protocol, and finally, (iii)

the bimetallic cluster-derived catalysts produce relatively more alcohols than ethers at similar reaction conditions and metal loadings on Al_2O_3. The data, then, suggest a measurable bimetallic synergy associated with the catalysts derived from bimetallic precursors. Furthermore, while we were concerned that the phosphine ligands present in the Rh precursors we employed would have a detrimental effect on ultimate selectivity and activity of the catalysts, calcining the catalysts prior to reduction and catalytic testing appears to have limited any poisoning effects associated with the phosphines.

Building upon our results thus far, we are currently conducting CO hydrogenation experiments meant to assess kinetic parameters of these sample such as activation energy and power-law rate dependence on feed concentration. In addition, we are testing the activity and selectivity of the catalysts for CO_2 hydrogenation.

MeOH Consumption as a Function of K Loading for 2.8% Rh-3.4% Mo/Gamma-Alumina
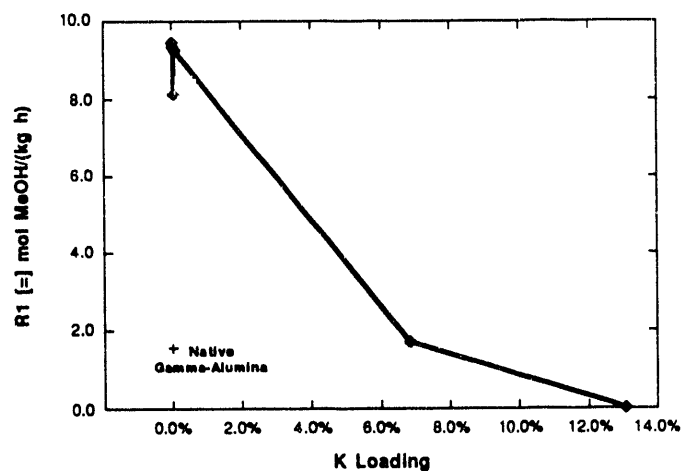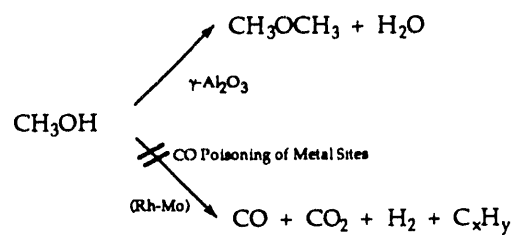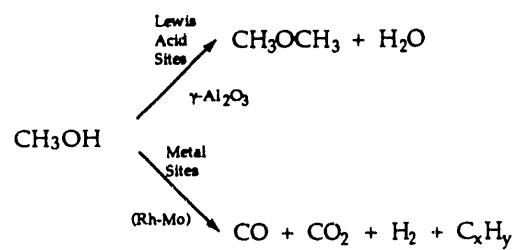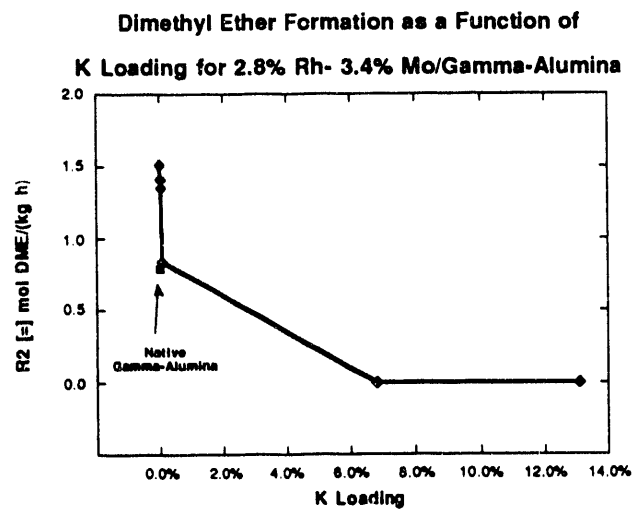

Figure 1

Figure 2

Dimethyl Ether Formation as a Function of

K Loading for 2.8% Rh- 3.4% Mo/Gamma-Alumina

Figure 3

DME Formation as a Function of K Loading for

2.8% Rh-3.4% Mo/Gamma-Alumina: ION EXCHANGE DOPING

Figure 4

SELECTIVITY OF Rh-Mo BIMETALLIC CATALYSTS

Catalyst	Rh wt%	Rh/Mo	H_2/CO	T °C	P(MPa)	C_xH_y	MeOH	Me_2O	$EtOH_+$	Total Oxy.	Ref.
RhMo/SiO$_2$	0.5	1	2	300	2.0	21.6	73.5	0.3	4.4	78.2	
Rh,Mo/SiO$_2$	0.5	1	2	300	2.0	48.0	41.5		10.5	52.0	
RhMo/Al$_2$O$_3$	0.5	1	2	250	1.87	24.8	17.8	44.9	12.4	75.1	
Rh,Mo/Al$_2$O$_3$	0.5	1	2	300	2.0	37.4	19.9	42.7	/	62.5	
RhMo$_2$/SiO$_2$	1.4	0.5	2	250	1.0	45.5	38.6	/	15.9	54.5	1
Rh-MoO$_3$/SiO$_2$	1.6	0.5	2	250	1.0	68.5	19.3	/	12.2	31.5	1

Note

RhMo represent RhMo(CO)$_3$Cp(PPh$_3$)$_2$ derived catalyst

Rh,Mo represent the catalyst derived from the mixture of RhH(CO)(PPh$_3$)$_3$ and [Mo(CO)$_3$Cp]$_2$

RhMo$_2$ represent RhMo$_2$(CO)$_5$Cp$_3$ derived catalyst

Rh-MoO$_3$ indicates the catalyst made from salts

1.) A.Trunschke et al., J.Mol.Catal., 56,95(1989).

Table 1

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