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# DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST. TENTH QUARTERLY REPORT, NOVEMBER 7, 1992--FEBRUARY 7, 1993

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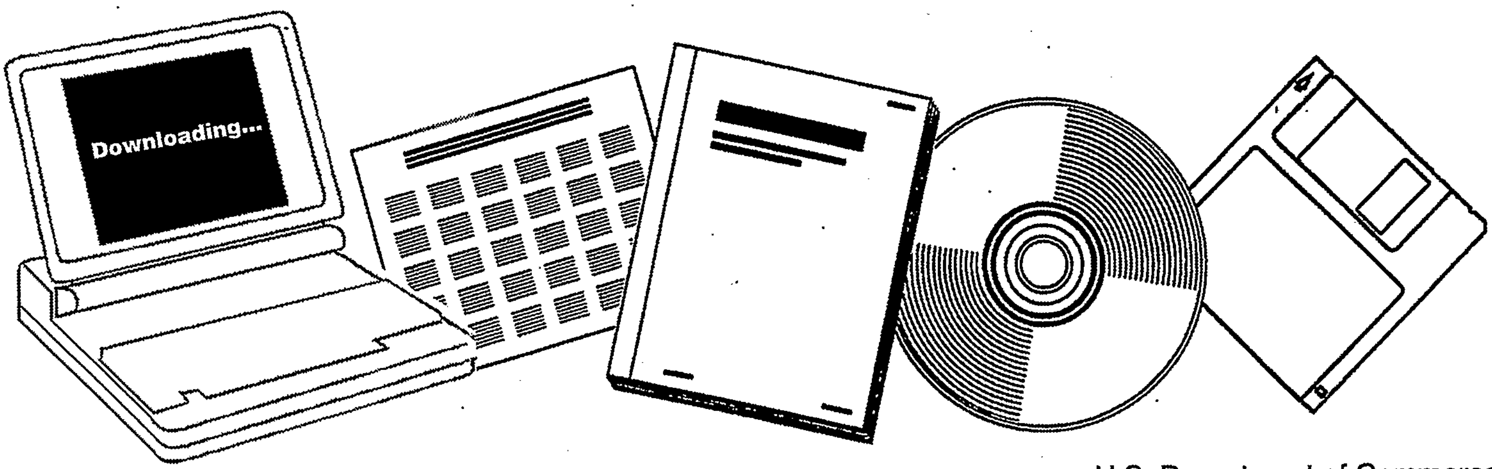

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# DESIGN OF A HIGH ACTIVITY AND SELECTIVITY ALCOHOL CATALYST

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Henry C. Foley and G. Alex Mills
Coprincipal Investigators

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

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## Ammonia TPD of Potassium Doped Rh-Mo/$\gamma$-$Al_2O_3$ Catalysts

To complement past work that examined the infrared (IR) spectra of adsorbed pyridine on our materials, we have constructed and brought on-line a unit for assessing total acid amount using ammonia temperature programmed adsorption (TPD). This unit is depicted in Figure 1 below.

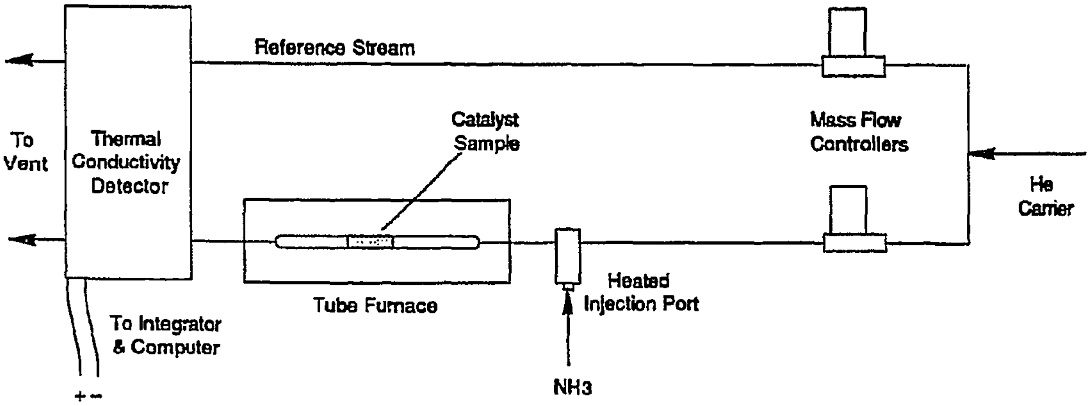


Figure 1. Ammonia TPD Unit

The unit's piping splits the He carrier gas. One stream goes directly to the thermal conductivity detector (TCD) to serve as a reference stream. The second stream passes through a heated injection port where ammonia is introduced and then passes into a sample tube in a tube furnace where adsorption on the catalyst sample occurs. In a typical experiment, the sample temperature is increased to 300 °C and the evolution of water off the surface is monitored by the TCD. The sample is then cooled to 50 °C and ammonia is injected in 100 - 1000 µl injections until the column is saturated. Preliminary analysis of a sample of $\gamma$-$Al_2O_3$ suggests that this protocol leads to the chemisorption of $NH_3$ equivalent to 24 active sites per 1000 $Å^2$. This value agrees well with the work of Peri [*J. Phys. Chem.*, **69**, 231 (1965)] which suggests that the sum of hydroxyl sites and various oxygen defect sites on alumina dehydrated to 800 °C amounts to 23 sites per 1000 $Å^2$. Based on the total temperature programmed desorption (TPD) to 300 °C, it appears that approximately 14 sites per 1000 Å$^2$ irreversibly adsorb $NH_3$ below 300°C., and these sites are then among the strongest acid sites. This system will be used to further examine both K-doped native alumina and K-doped Rh-Mo/$\gamma$-$Al_2O_3$ to assess total acidity.

## Bimetallic Catalyst Design Expert

Pursuant to our interest in improving the catalyst design process, we have undertaken to develop a computer-based expert system associated with the exploration of bimetallic catalysts for higher alcohol synthesis. Our prototype expert system is based on rules drawn from the experimental investigation of combinations of alumina-supported noble metals, namely Rh, Co, and Ru, promoted with either Mo or W [Foley, H.C. et al., *Appl. Catal.*, **61**, 351 (1990)]. These catalysts were synthesized from metal-carbonyl precursors to afford more carefully controlled active metal dispersion.

The motivation for this work stems from the recognized need within the field of catalysis engineering to (i) capture existing expertise in narrowly defined catalysis areas that may be evaporating due to retirement or attrition of long standing employees, (ii) free high level catalysis experts from mundane consultations, allowing them to focus on more creative problems, and (iii) increase the rapid dissemination of experimental results in a useful and practically accessible form. Furthermore, we contend that by employing the computer science tools of knowledge engineering at an early stage in the catalyst design process, an investigator can create an expert system which will (i) reveal key trends in experimental data which might otherwise be overlooked and (ii) help guide the investigation.

Our prototype system distills the results of a series of experiments on CO hydrogenation down to twenty-nine rules about activity and selectivity which guide the system toward the selection of a preferred combination of transition metal components. At the heart of these rules is a series of observations that suggest that, within the domain of the experimental parameters tested, Ru-based catalysts have the highest propensity for hydrocarbon production, Co-based catalysts have the highest olefin to paraffin ratio, and Rh-based catalysts have the highest propensity to form oxygenates. The rules make various intermediate conclusions about which promoter to use (either Mo or W) based on (i) reaction temperature, (ii) reaction pressure, and (iii) desired product slate. The system also can extrapolate results of alkaline metal doping tests on Ru-based catalysts to the Co and Rh-based systems should Co or Rh prove more appropriate for the desired set of products.

The next phase in our exploration of the use of expert systems technology will involve the application of an expert system to a series of experiments concerned with site isolation on a Rh-Mo/$\gamma$-$Al_2O_3$ catalyst. We have a set of provisional rules about Rh site isolation on the alumina surface; higher Rh dispersions seem to lead to increased oxygenate selectivity of the catalyst. In the context of testing a set of catalysts with a fixed Mo concentration and varying Rh site densities for oxygenate formation, we intend to test our provisional ideas. After running the experimental tests, we can then go back to the expert system and revise the provisional rules to make then more robust and broadly applicable. With this feedback cycle, we hope to revise and expand the database of site-isolation knowledge to a size that begins to guide the investigation—rather than simply represent the results in a novel way.

## High Surface Area Manganese Oxides Used as Catalysts in CO Hydrogenation to Methanol

### *Introduction*

Manganese is a frequently used transition-metal both for industrial technology and scientific research. For example, $MnO_2$ has been used in batteries for a long time; MnO has been employed as a component of one of the standard catalysts for high-pressure methanol and higher alcohol synthesis [Catalyst Handbook p454]. Manganese (oxide) promoted metal catalysts are also an active area of study as is evident in the current literature. For example, Luo et al. reported that Mn is an effective promoter for the Rh-catalyzed, direct synthesis of oxygenates from syngas [Appl. Catal. 38(2), 241(1988)]. The tilted Rh-C=O-Mn surface intermediate is considered to be the active species for CO hydrogenation on $SiO_2$-supported, manganese-promoted rhodium catalysts [reference of Lisitsyn: J.Mol. Catal. 63(2), 201(1990)]. There has been much research focused on Mn (oxide) promoted Co, and Fe catalysts for CO hydrogenation and the water-gas shift reaction [Gotts.:Appl. Catal. 51(1), 127(1989), Egiebor:Appl. Catal. 55(1) 47(1989)]. In each of these papers it was concluded that Mn is a important promoter. Furthermore, Mn oxide has been used in mixed oxides catalysts for oxidative conversion of hydrocarbons [Burch:Appl. Catal. 65(2) 259(1990)] and as the main component in catalysts for the oxidative coupling of methane to ethylene [Mamedov: Pet. Chem. USSR 31(3) 319(1991), Pereira:Preprints-Div. of Petrol. Chem. ACS vol37 No1, Judd:Catal. Today 13(2-3) 237(1992)].

However, not much attention has been paid to the intrinsic catalytic behavior of Mn oxides. As one of the transition metals with the most variability in its oxidation state, manganese should be very interesting. A deeper understanding of the intrinsic relationship between the properties of manganese oxides and their catalytic behavior will be helpful for developing new catalytic materials to meet different technological objectives. This kind of in-depth study of intrinsic catalytic behavior of the manganese oxide family of materials becomes possible due to the technology base of CHEMETALS, which can provide the different oxides with quite high surface area. These oxides are also promising materials to consider as catalyst support media, since they have variable surface area and quite variable intrinsic O/Mn ratios (bulk oxidation states.

So far this study has focused upon manganese-oxide catalyzed CO hydrogenation and the preliminary results are very interesting. On particular it was our goal to examine whether the activity and selectivity changes would accompany changes in the each oxidation state or O/Mn ratio of the precursor oxides. Surprisingly, this kind of systematic study of the intrinsic catalytic activities of the Mn oxides as catalysts for CO hydrogenation has not been reported in the literature. This fact especially encouraged us to initiate this research. In this report we discuss the preliminary results of our research and the future work that we plan to do.

## *Materials*

The series of manganese oxides examined in this work was provided by CHEMETALS. The physical properties of each sample is as follows:

Table 1. Physical properties of the Manganese oxides

| Sample | O/Mn | XRD | BET ($m^2/g$) | $N_2$ Pore Vol. (cc/g) |
|---|---|---|---|---|
| MnO | 1.00 | MnO | 2.2 | 0.004 |
| $Mn_3O_4$ | 1.16 | $Mn_3O_4$ | 7.7 | 0.011 |
| $Mn_2O_3$ | 1.50 | $Mn_2O_3$ | 29.5 | 0.240 |
| $MnO_2$ | 1.95 | $MnO_2$ | 98.0 | 0.152 |
| $MnO_2$-CuO* | 1.90 | $MnO_2$ | 74.0 | 0.150 |

* 1.9 wt%Cu

## *Experimental*

Manganese oxide catalyzed CO hydrogenation was carried out in a high pressure down-flow, fixed bed, tubular reactor. The dimension of the stainless steel reactor are: 7mm I.D.x10mm O.D.x 40cm L. Carbon monoxide and hydrogen (High purity, Matheson) were purified on line and metered into the reactor through separate mass flow controllers. Temperature and pressure of the reactor were controlled precisely by a thermal controller and back pressure regulator. The exit gas flow was transferred through heated line at 150°C to avoid product condensation and then to an auto sampling valves on TCD and FID gas chromatograghs. The concentrations of reactants and the products were calibrated using a standard gas. Carbon monoxide conversions were calculated from the ratio of the total number of moles of converted carbon to the total number of moles of carbon in the effluent gas. Products selectivities were calculated as: the fraction of number of mole of carbon in each product to the total number of mole of converted carbon, either with $CO_2$ included or excluded as a product.

The amount of catalyst charged was 2g for each test. Before reaction, the catalysts were reduced at 300°C with 30-40sccm/min of $H_2$ for 3 hours. The CO hydrogenation reaction was carried out at 200 to 350°C and 300 to 500psi, and at a total flow rate of 40sccm/min ($CO/H_2=1/1$).

### *Results of Reaction Test and Discussion*

1. The effect of O/Mn ratio on methanol selectivity

Preliminary investigations of these manganese oxide materials show that the different oxides exhibit different selectivity toward methanol and other products. It seems that there is a correlation between the initial O/Mn ratio of the oxide and methanol selectivity. These conclusions are supported by the results displayed in Figures 1 and 2. The main product of the manganese oxide-catalyzed CO hydrogenation is methanol except on MnO, which shows the lowest methanol selectivity, but the highest $CO_2$ yield. Preliminarily, the results suggest that the higher the O/Mn ratio of the precursor oxide, the higher will be the methanol selectivity, while the $CO_2$ and methane selectivities will be lower. The higher $CO_2$ and $C_2$, $C_3$ and $C_4$ hydrocarbon selectivities over the MnO catalyst compared to the other manganese oxides tested, indicates that MnO acts more like a water-gas shift and Fischer-Tropsch catalyst.

**Figure 1a.** CO2-free selectivities for Various Manganese Oxide Catalysts (310°C, 500psi, CO/H2=1)

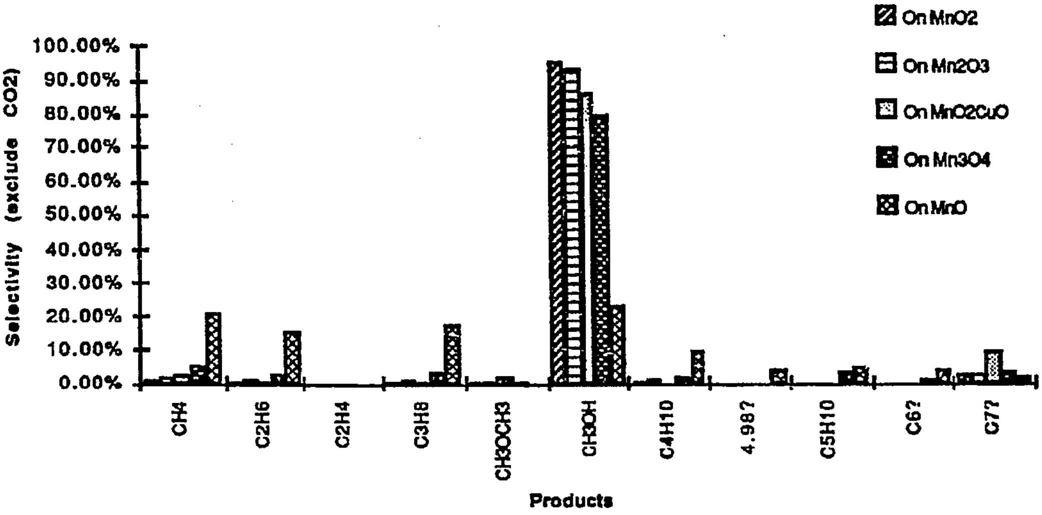


**Figure 1b.** Selectivities with CO2 included for Various Manganese Oxide Catalysts (310°C, 500psi, CO/H2=1)

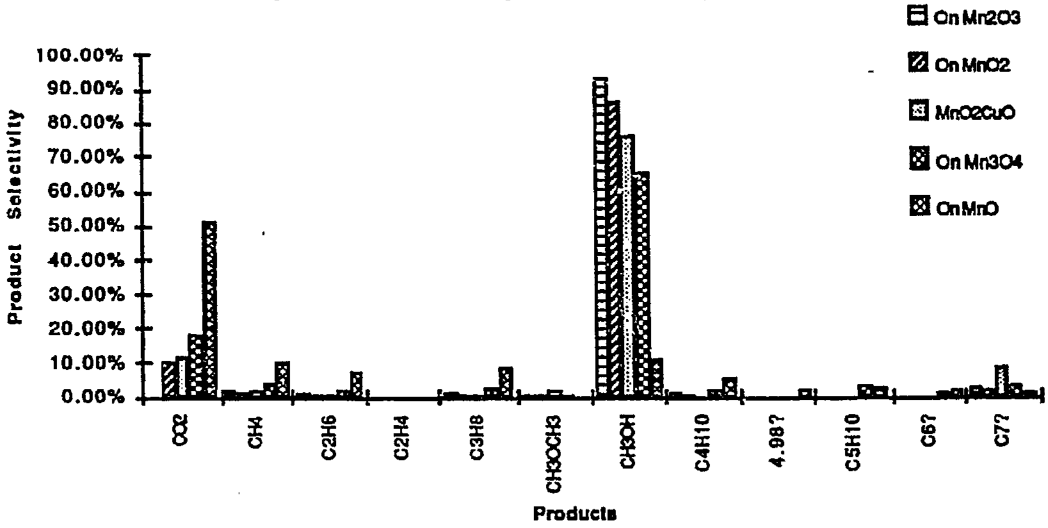
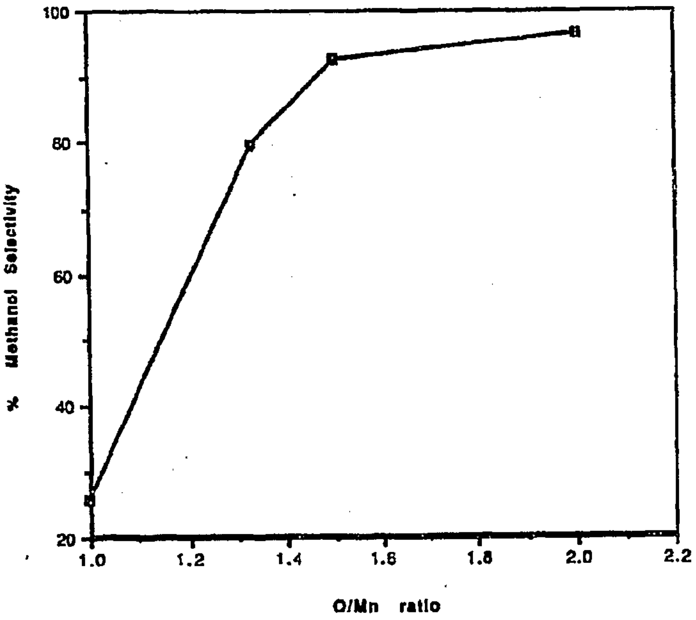


Figure 2. Methanol Slectivity Vs. O/Mn ratio



It seems logical that the active component on all of the oxides may be a low or even zero valent of manganese species after reduction. This can be inferred from the fact that (1) the oxides show catalytic activity after reduction by $H_2$, or by $CO/H_2$ with longer times on stream, and (2) the color of most of the used catalysts is light green, which is obviously different from their original color. The color changed gradually when the used catalysts were contacted with air. Interestingly, when the used gray-colored $Mn_2O_3$ was contacted with air it reacted vigorously and exothermically. However, the lowest selectivity toward methanol, shown by MnO with the lowest O/Mn ratio, indicates that the active site for methanol formation on these catalysts may not be simply the lowest oxidation state, but rather may be an intermediate state, that can be derived readily from the reduction of the higher oxidation state manganese precursors.

## 2. Activity and Stability of the Manganese Oxides and Copper-manganese oxide

It can be seen from Fig. 3 that the higher O/Mn ratio single-oxides show very similar activities. But MnO show obviously lower activity, which may be partly because of its low surface area. The comparison of the total reaction rate of the single component manganese oxides indicates that $Mn_2O_3$ and $Mn_3O_4$ exhibit better activities than other two (Figure 4).

With regard to the mixed oxide catalyst $MnO_2$-CuO, it was expected that the presence of CuO would produce some improvement in the activity, since copper is one of the active components in the industrial methanol synthesis catalyst. As expected, copper does increase the activity of the catalyst (see Figure 3). $MnO_2$-CuO doubled the CO conversion of $MnO_2$ under exactly the same reaction conditions. At the same time the selectivity to methanol remains quite high, nearly as high as that of $MnO_2$ alone. Therefore, $MnO_2$-CuO is the most productive catalyst of the five oxides examined for methanol synthesis (see Table 2)

**Figure 3. CO conversion VS time on stream**
**(310°C, 500psi, CO/H2=1)**

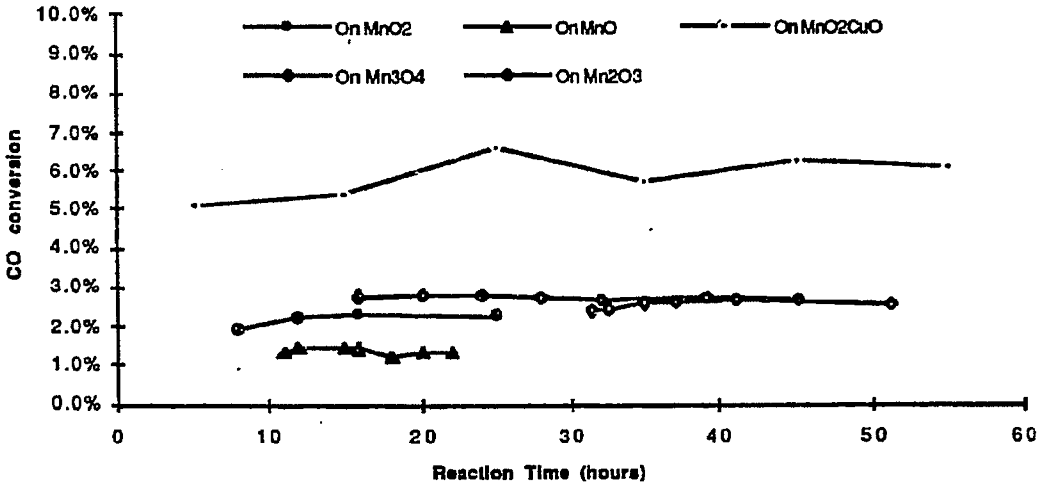


Table 2. Methanol Productivity and total reaction rate on the Manganese Oxide Catalysts

| Manganese Oxide | $MnO$ | $Mn_3O_4$ | $Mn_2O_3$ | $MnO_2$ | $MnO_2$-$CuO$ |
|---|---|---|---|---|---|
| Methanol Productivity[a] | 0.402 | 4.43 | 6.72 | 5.39 | 11.3 |
| Total reaction rate[b] | 3.56 | 6.77 | 7.13 | 5.69 | 14.9 |

a. $10^4$moles of MeOH produced/g oxide/hour

b. $10^4$moles of converted CO/g oxide/hour

It is well established that copper metal is the active phase in the industrial methanol synthesis catalysts [Catalyst Handbook]. The improved activity of CO hydrogenation on $MnO_2$-$CuO$ catalyst indicates that some reduced copper species must be formed on the surface.

Figure 4. Total CO converting rate versus O/Mn ratio

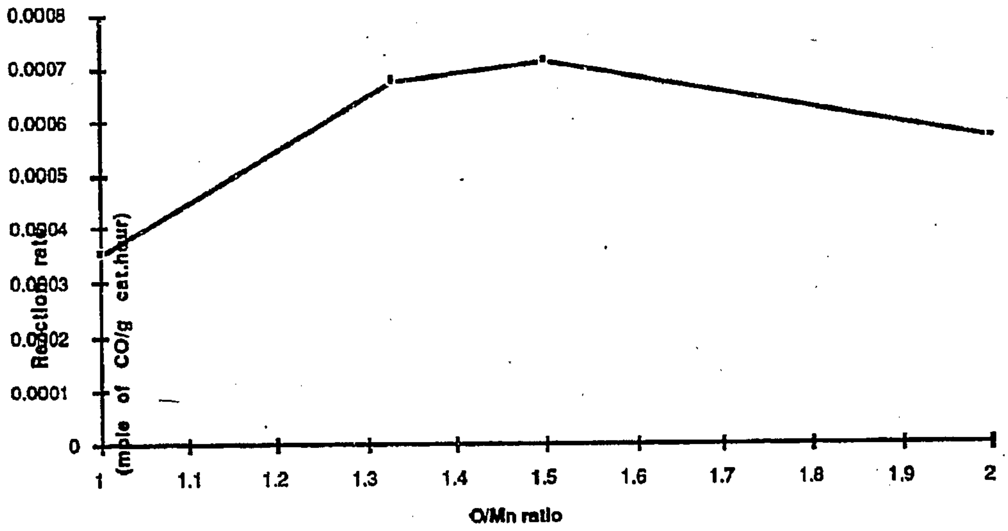


**Figure 5. Reaction arte versus BET surface area of manganese oxides**

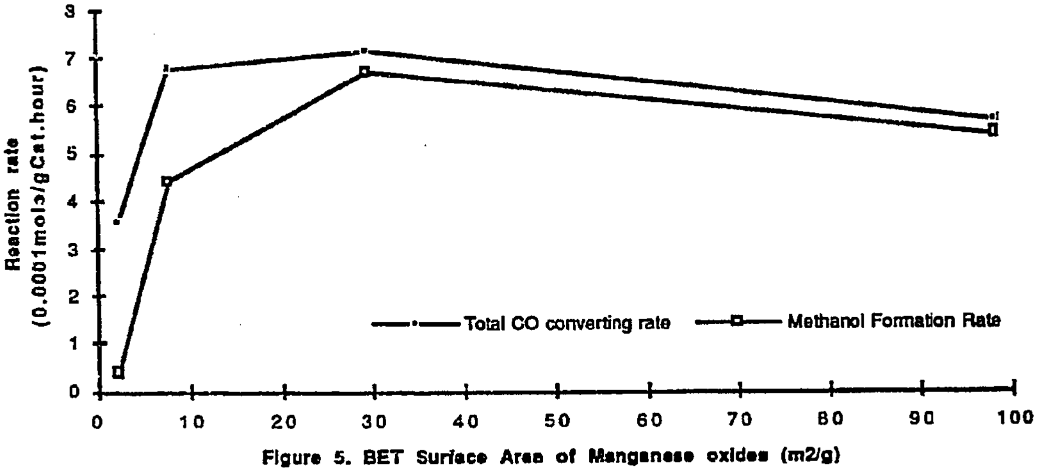
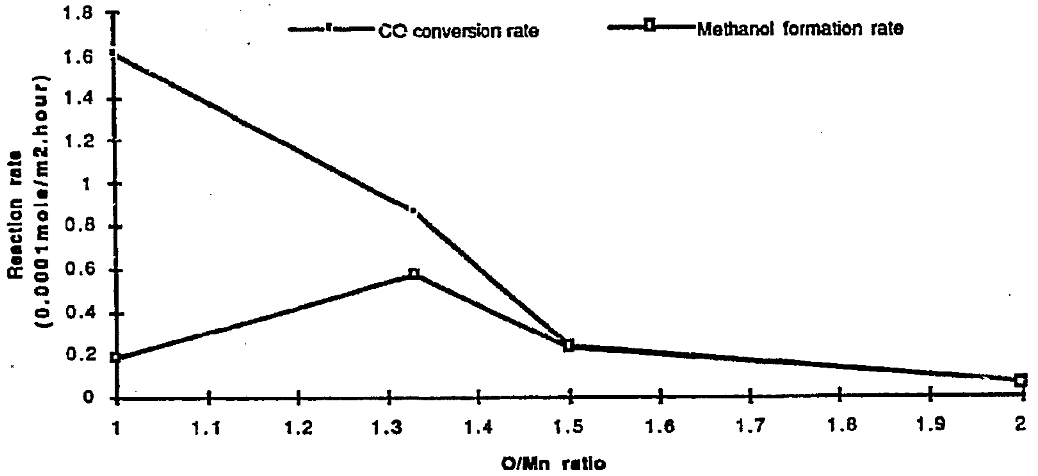


**Figure 6. Reaction rate per square meter of BET area versus O/Mn ratio**



## *Preliminary Conclusions and Future Work*

The results show both interesting and promising aspects of the manganese oxide catalysis. All of the manganese oxides show remarkably stable activities for CO hydrogenation to methanol. $Mn_2O_3$ and $MnO_2$ display unexpected high selectivities to methanol. The correlation between O/Mn ratio of the bulk oxide precursors and methanol selectivity was wholly unexpected. It indicates that the higher the O/Mn ratio of the precursor oxide, the higher the selectivity toward methanol. Promotion of $MnO_2$ with copper at 1.9 wt% lead more than doubled the activity of $MnO_2$ but the selectivity to methanol remained high. This motivates further work.

The future work will be focused on extensive reaction tests and characterizations of the manganese oxides and catalysts derived from these materials. In outline form will go as follow:

(1) Measure the activation energy for CO conversion and product formation over the various oxides;

(2) Determine CO and H2 chemisorption on each oxide sample after reduction in order to calculate turnover frequencies;

(3) XRD and BET surface area measurements to determine the extent of phase and surface area changes;

(4) Develop manganese oxide-supported Rh and Ir catalysts for CO hydrogenation to oxygenates, especially for higher alcohols, test their catalytic characteristics.

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