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# Synthesis of Oxygenates from CO and Hydrogen over Supported Metal Clusters

Metal clusters serve as precursors to highly dispersed or unique supported metal catalysts (see, for example, Ref. (*1*)). While numerous studies describe the preparation and characterization of cluster derived catalysts, only a few describe their use for selective synthesis gas reactions. For these reactions, the product type (i.e., oxygenates or hydrocarbons) is generally similar to that produced on conventionally prepared catalysts (*2*).

We report here studies on supported metal cluster derived catalysts for CO hydrogenation that illustrate the differences between cluster precursors and conventional precursors. We show that cluster precursors can result in product types that are different than those produced by conventional catalyst preparations. We also show that the choice of cluster and support is critical in determining the product distribution.

Catalysts were prepared in the absence of air and water to avoid oxidation of the cluster. Reactor studies were carried out in tubular reactors with on-line gas chromatographic analysis of the products. Reactions were conducted at pressures of 300–900 psig with $H_2/CO$ ratios of 0.5–2. Catalysts were not reduced prior to exposure to synthesis gas. Two types of catalyst systems were studied: an anionic metal cluster based on Fe and Mn impregnated on MgO, $Al_2O_3$, or $ZrO_2/Al_2O_3$; and Ru carbonyl clusters on $TiO_2$.

*FeMn cluster catalysts.* $K[MnFe_2(CO)_{12}]$ was prepared as described in the literature (*3*). The cluster was dissolved in diethyl ether and aliquots of this solution were added to the support using the technique of incipient wetness. The solvent was evaporated after each addition. Metal loadings of 1.4–2.4% were obtained.

The $ZrO_2/Al_2O_3$ support was prepared by the addition of $[Zr(OC_3H_7)_4]$ to dried $Al_2O_3$ (Catapal SB). After addition of the Zr alkoxide, the solid was dried in vacuo at room temperature. The Zr loading was 10.1 wt%. This support was chosen to provide a source of high surface area $ZrO_2$.

Table 1 summarizes the results of clusters supported on $Al_2O_3$ and MgO (J. T. Baker Co.) as catalysts for the reaction of CO and $H_2$. The MgO (2.1% metal loading) and $Al_2O_3$ (2.4% metal loading) based catalysts exhibited product distributions typical for conventional Fe catalysts. The primary product under our reaction conditions was methane with selectivities of 55–58% for the MgO support. For $K[MnFe_2(CO)_{12}]$/MgO the oxygenate selectivity was initially zero. Increasing the temperature and lowering the $H_2/CO$ ratio resulted in the formation of alcohols. The selectivity to oxygenates was 19%, with methanol and ethanol as the only observable products. The oxygenate selectivity seemed to remain stable for at least 24 h. The hydrocarbons formed over the MgO catalyst showed the high olefin/alkane ratio than one would expect from an FeMn catalyst (*4*). Previous work with $K[MnFe_2(CO)_{12}]$ supported on $SiO_2$ and carbon showed enhanced olefin selectivities from synthesis gas (*5*, *6*).

Ichikawa showed that the use of basic supports, such as MgO, for clusters resulted in unusually high oxygenate selectivities from synthesis gas (*7*). Others, however, have shown that the use of Fe carbonyls supported on MgO resulted in

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TABLE 1

Results of CO Hydrogenation over $Al_2O_3$ and MgO Supported $K[Fe_2Mn(CO)_{12}]$[a]

| Support | $T$(°C) | $H_2/CO$ | TOS(h) | GHSV($h^{-1}$) | CO conv(%) | Selectivities (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_1$ | $C_2$–$C_4$ | $C_5$–$C_{11}$ | $C_{12}^+$ | DME | MeOH | EtOH | PrOH |
| MgO | 262 | 1 | 96 | 596 | 15.6 | 58.6 | 29.6 | 11.0 | 0 | 0 | 0 | 0 | 0 |
| MgO | 277 | 0.5 | 149 | 592 | 9.0 | 54.6 | 22.6 | 0 | 0 | 0 | 11.2 | 7.3 | 0 |
| $Al_2O_3$ | 265 | 1 | 24 | 590 | 44.5 | 25.9 | 39.3 | 18.6 | 12.8 | 1.0 | 0.8 | 2.0 | 0.5 |
| $Al_2O_3$ | 265 | 0.5 | 62 | 598 | 32.8 | 27.9 | 52.5 | 11.2 | 0 | 3.5 | 0 | 4.9 | 0 |

[a] Pressure = 300 psig, catalyst volume = 10 $cm^3$, bed length = 17.5 cm.

the selective formation of olefins (*2*). The $K[MnFe_2(CO)_{12}]/MgO$ catalyst appears to exhibit both of these features. Some oxygenates are observed with the remainder of the products being olefins.

$K[Fe_2Mn(CO)_{12}]/Al_2O_3$ was more active than $K[Fe_2Mn(CO)_{12}]/MgO$, but produced a significantly different product distribution. The methane yield was only 18%, and the formation of oxygenated products was evident from the beginning of the run. The selectivity to oxygenates (dimethyl ether, methanol, ethanol, and propanol) was 24% at 265°C. The high olefin/paraffin ratio observed with the MgO support for the $C_2^+$ hydrocarbons was not observed on the $Al_2O_3$ support. The major products were alkanes.

Table 2 summarizes the results for synthesis gas conversion for $K[Fe_2Mn(CO)_{12}]/ZrO_2/Al_2O_3$ (1.4% FeMn loading). At 200°C, the catalytic activity was higher than expected for an Fe catalyst. Typically, temperatures of 250+°C are required for good activity. Conversions of 20% were obtained even at this low temperature. The product distribution obtained with $K[MnFe_2(CO)_{12}]/ZrO_2/Al_2O_3$ at 200°C was significantly different than the alumina or magnesia supported clusters. The formation of oxygenates predominated at all temperatures studied. The major products were dimethyl ether, methanol, ethanol, and propanol. The propanol was present only in the early stages of reaction and could have resulted from the decomposition of the alkoxide. The selectivities for oxygenate formation approached 81% at 280°C. The effect of temperature can also be seen in Table 2. Increasing the temperature from 250 to 280°C resulted in a shift in the oxygenate selectivity from $C_1$–$C_3$ alcohols to dimethyl ether. Higher temperatures favored the formation of methanol which then dehydrates to give the ether. At 280°C, the selectivity to dimethyl ether was 65% with the other major product being methanol. Surprisingly, the methane selectivity dropped to 7% on increasing the temperature. Changing the GHSV resulted in the expected drop in conversion with no change in the oxygenate selectivity. Even after 160 h on stream, the catalyst remained

TABLE 2

Results of CO Hydrogenation over $K[Fe_2Mn(CO)_{12}]/ZrO_2/Al_2O_3$[a]

| $T$(°C) | $H_2/CO$ | TOS(h) | GHSV($h^{-1}$) | CO conv(%) | Selectivities (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $C_1$ | $C_2$–$C_4$ | $C_5$–$C_{11}$ | $C_{12}^+$ | DME | MeOH | EtOH | PrOH |
| 203 | 1 | 13 | 598 | 20.0 | 12.8 | 20.6 | 10.6 | 0 | 14.9 | 31.2 | 3.4 | 6.6 |
| 251 | 1 | 45 | 299 | 48.0 | 7.9 | 6.5 | 3.9 | 0 | 46.8 | 19.7 | 0.6 | 13.0 |
| 247 | 0.5 | 132 | 612 | 34.7 | 18.0 | 18.9 | 0 | 0 | 42.8 | 20.4 | 0 | 0 |
| 280 | 1 | 158 | 299 | 58.4 | 6.9 | 13.3 | 0.7 | 0 | 65.7 | 13.5 | 0 | 0 |

[a] Pressure = 300 psig, catalyst volume = 10 $cm^3$, bed length = 17.5 cm.

stable with conversions of 50% while maintaining the high selectivity to dimethyl ether. The selectivity to hydrocarbons showed the expected high ratio of olefin to paraffins that are common for FeMn catalysts (*4*). At low temperatures (200°C) the only $C_2^+$ hydrocarbon products were olefins. At higher temperatures some paraffinic products are formed, but the high olefin/paraffin ratio was maintained.

In summary, for the $K[Fe_2Mn(CO)_{12}]$ catalyst systems, the MgO and $Al_2O_3$ supported catalysts gave typical Fischer–Tropsch (F–T) product distributions. Likewise, the product distribution and product type changed with time over these two catalysts. The MgO supported catalyst initially gave only hydrocarbon products, but after another 50 h oxygenates were observed. The $Al_2O_3$ supported catalyst initially resulted in a mixture of oxygenates and hydrocarbons. The oxygenate selectivity with the $Al_2O_3$ supported catalyst was minimal. The product distribution for the $ZrO_2 \cdot Al_2O_3$ was more stable. At all conditions studied, oxygenates were the major products, although there were changes in the distribution of the oxygenate products. This latter catalyst shows that long-lived selectivities for the synthesis of oxygenates can be obtained with a supported cluster catalyst.

*Ru cluster catalysts.* Ru is one of the most active Fischer–Tropsch catalysts (*8*). The product distributions over Ru catalysts generally consist of methane or higher hydrocarbons depending on the reaction conditions. Vannice reported that $Ru/TiO_2$, prepared by conventional techniques, was an extremely active F–T catalyst (*9*). His results showed that at low pressures (150 psig) the catalyst produced about 50–60% olefins with a fairly low selectivity to methane. He also reported that the catalyst produced exclusively hydrocarbons with no oxygenates, a product distribution typical of Ru catalysts. Our results using cluster derived catalysts result in substantial oxygenates.

We prepared $TiO_2$ (Degussa) supported Ru catalysts by impregnating the support to incipient wetness with a hydrocarbon solution of clusters such as $[Ru_3(CO)_{12}]$ and $[H_4Ru_4(CO)_{12}]$. Metal loadings were 0.2% for $[Ru_3(CO)_{12}]/TiO_2$ and 0.9% for $[H_4Ru_4(CO)_{12}]/TiO_2$.

Results for the conversion of synthesis gas are summarized in Table 3. The effect of pressure and $H_2/CO$ ratio was examined for the $[Ru_3(CO)_{12}]/TiO_2$ while $[H_4Ru_4(CO)_{12}]/TiO_2$ was only examined at two different temperatures. $[Ru_3(CO)_{12}]/TiO_2$ showed fairly good activity for the conversion of synthesis gas but only at temperatures greater than 300°C. Conversions at $T < 300°C$ were too low to measure accurately in our system. A these temperatures, the conversions at 900 psig were 30–80% with the product distribution showing some surprising results. The distribution of the products was not the expected hydrocarbon distribution normally observed for Ru

TABLE 3

Results of CO Hydrogenation over $TiO_2$ Supported Ru Clusters[a]

| Cluster | $T$(°C) | $H_2/CO$ | GHSV | $P$(psig) | CO conv | Selectivities (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_1$ | $C_2$–$C_4$ | $C_5$–$C_{11}$ | $C_{12}^+$ | DME | MeOH | EtOH | PrOH |
| $Ru_3(CO)_{12}$ | 316 | 1 | 305 | 860 | 78.9 | 25.7 | 25.0 | 6.5 | 0 | 0 | 41.9 | 0.9 | 0 |
| $Ru_3(CO)_{12}$ | 316 | 1 | 609 | 900 | 30.0 | 23.6 | 26.4 | 4.7 | 0 | 0 | 44.2 | 1.1 | 0 |
| $Ru_3(CO)_{12}$ | 320 | 1 | 305 | 300 | 10.2 | 54.6 | 19.7 | 3.6 | 0 | 0 | 22.0 | 0 | 0 |
| $Ru_3(CO)_{12}$ | 320 | 2 | 298 | 300 | 19.8 | 47.6 | 17.4 | 1.8 | 0 | 0 | 33.2 | 0 | 0 |
| $H_4Ru_4(CO)_{12}$ | 260 | 1 | 309 | 300 | 25.4 | 48.6 | 39.6 | 6.8 | 0 | 0.9 | 1.3 | 2.4 | 0.4 |
| $H_4Ru_4(CO)_{12}$ | 301 | 1 | 604 | 300 | 28.8 | 44.7 | 29.5 | 7.6 | 0 | 0 | 11.5 | 1.4 | 0 |

[a] Catalyst volume = 10 $cm^3$, bed length = 17.5 cm.

catalysts. Instead, the products consisted of a mixture of hydrocarbons and oxygenates. At 900 psig, the methanol selectivities were 40–45 wt% of the total product. Lowering the pressure to 300 psig resulted in the expected drop in conversion and a drop in the methanol selectivity. At 300 psig, raising the $H_2/CO$ ratio to 2 resulted in an increase in the conversion and an increase in the methanol selectivity. This result was rather surprising. We would expect methanol to decompose on reaction with Ru metal at 300+°C. Others have shown significant methanol synthesis activity at temperatures of 300°C (*8*). Earlier we suggested that methanol forms by a CO insertion mechanism that involves an intact metal cluster (*10*). An increase in the $H_2$ partial pressure should result in the formation of a higher concentration of Ru metal and a loss in the methanol selectivity. Likewise, if the pressure is increased the cluster should be more stable and the methanol selectivity will be higher.

The use of the $[H_4Ru_4(CO)_{12}]$ resulted in essentially the same catalyst behavior as the $[Ru_3(CO)_{12}]$. The methanol selectivities were somewhat lower, but the pressures and temperatures studied were different. Interestingly, at 300°C the methanol selectivity was significantly higher than at 260°C, contrary to what is usually observed for methanol synthesis catalysts.

In comparison with the literature, our work shows some striking differences between these catalysts and other supported Ru catalysts. Generally, Ru produces hydrocarbon products with high molecular weight products being common. Vannice (*9*) and Kugler (*11*) showed that Ru supported on reducible oxides results in the formation of olefins from synthesis gas. Vannice also showed this for $TiO_2$ supported catalysts. Although the reaction conditions used in Vannice's work were different than those studied here, the differences in product distribution cannot simply be explained by these differences. Our results show that metal clusters can be used to prepare active, stable catalysts for the conversion of synthesis gas. Although the product distribution changes, the product type stays fairly constant with time. Therefore, through the appropriate choice of cluster and support, one can alter the selectivities for synthesis gas reactions. Anionic clusters, in particular, seem to provide interesting catalytic properties for CO hydrogenation reactions (*12*).

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