

REPORT ON THE CATALYTIC ACTIVITY OF 6-HETEROPOLYMOLYBDATES AS POTENTIAL FISCHER-TROPSCH SYNTHESIS CATALYSTS

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ABSTRACT

Unsupported and supported decomposition products of 6-heteropolymolybdates were tested as possible Fischer-Tropsch synthesis catalysts. Depending on the heteroatom, the activity changes significantly and the best supported catalysts have higher activity (based on total metal loading) than previously investigated MoO₂ and Mo₂C catalysts.

INTRODUCTION

Molybdenum catalysts are extensively used in hydrodesulfurization, hydrodenitration and selective oxidation reactions [1,2]. More recently high activity charcoal supported molybdenum Fischer-Tropsch (FT) catalysts were successfully prepared [3-5]. The advantages of using molybdenum based FT catalysts are their resistance to sulfur poisoning, the narrow product distribution (C₁ to C₆) and the ability to work with low H₂ to CO feed ratios without coking. These are balanced with high methane yields (30 to 50 wt% of the hydrocarbon products) and (for most molybdenum catalysts) moderate activity. Recent research has shown that both the activity and C₂⁺ selectivity of charcoal supported molybdenum compounds can be increased [3-5]. However, the increase in C₂⁺ selectivity comes about at the expense of a moderate decrease in activity.

We have recently begun investigating the possibility of increasing both the activities and selectivities of molybdenum catalysts simultaneously by starting with heteropoly compounds of molybdenum instead of ammonium heptamolybdate, the most commonly used starting compound in preparing supported catalysts. In this paper we report our results for both charcoal supported and unsupported catalysts prepared from 6-heteropolymolybdates.

The general formula of the 6-heteropolymolybdates is: (NH₄)_{6-n}[XMo₆O₂₄H₆].7H₂O where X is the heteroatom (Co, Al, Cr, Fe, Rh, Ga or Ni).

One example of the structure of the anion is shown in Figure 1. A central XO₆ octahedron is surrounded by six MoO₆ octahedra in a planar configuration. The

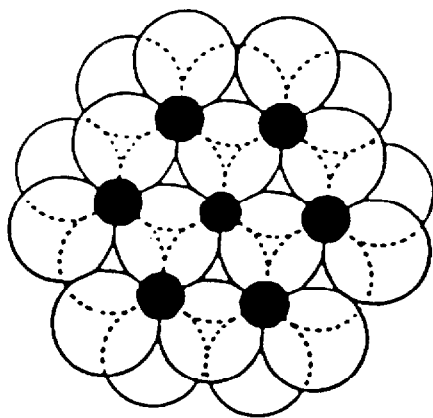


FIGURE 1 Diagram of the structure of the 6-molybdo-chromate (III) anion represented with atoms drawn to the scale of their ionic radii [6]. The central solid sphere is chromium ion, and the six solid spheres surrounding it are molybdenum ions. Open spheres represent oxygen ions.

ammonium salt also has seven molecules of water of hydration. The properties of all the 6-heteropolymolybdates were reviewed in detail by Tsigdinos [6]. Upon heating, water of hydration is lost first. Constituent water loss leading to decomposition begins at around 473 K.

Our goal in this research was to find out if we could modify the activity and selectivity of molybdenum catalyst in FT synthesis by varying the heteroatom and pretreatment conditions for these 6-heteropolymolybdates.

EXPERIMENTAL

Materials

Ammonium salts of 6-molybdo-nickelate, chromate, ferrate, cobaltate and aluminate were obtained from Climax Molybdenum Co., Ann Arbor Labs and were used without further purification. Calgon CPG charcoal was used as a support. According to the manufacturer, this charcoal has a BET surface area of $1100 \text{ m}^2 \text{ g}^{-1}$ and a bimodal pore size distribution with 50% of the pore volume being due to pores larger than 20 \AA in diameter. From the chemical analysis supplied by the manufacturer it contains low amounts (<0.1%) of Fe, K, Ca and Na impurities. Degussa P-25 Titania was used as a nonporous high exterior surface area support (BET surface area of $50 \text{ m}^2 \text{ g}^{-1}$) for one of our catalysts.

Catalyst preparation and testing

Details of the standard procedure for preparing the supported catalysts and testing of their performance has been given elsewhere [5].

X-ray spectra taken initially verified that all the catalysts had the previously

reported structures [6]. In order to identify the actual phases present in the catalysts under the reaction conditions, X-ray spectra of the reduced and used catalysts were also taken. Before being taken to a Philips X-ray diffractometer, these samples were allowed to cool down to room temperature in flowing hydrogen and then exposed to air. This process should lead to only surface oxidation of the unsupported catalysts. (It is difficult to decide whether the supported catalysts were also surface oxidized or not). To our surprise only MoO_2 was found to be present but quite a few of the peaks were asymmetric, indicating the presence of strains. Since the X-ray spectra were taken in air we suspect that some lower oxidation state Mo compound was converted to MoO_2 . For the charcoal supported catalysts, the average MoO_2 crystallite size was found to be $200 \pm 40 \text{ \AA}$. For the unsupported catalysts, crystallite sizes were too large to be reliably measured by X-ray line broadening (i.e. larger than 1000 \AA).

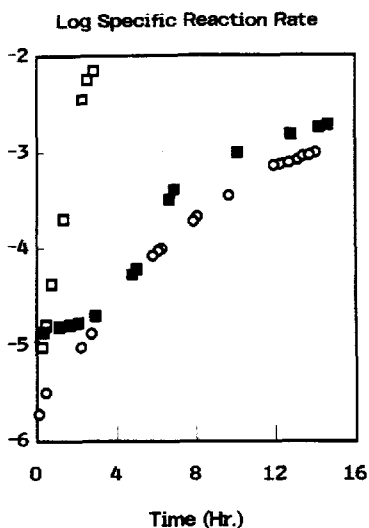


FIGURE 2 Self-reduction and activation of several 6-heteropolymolybdate catalysts. Reaction conditions: 573 K, 0.12 MPa, $\text{H}_2/\text{CO} = 3$. Specific rates are in the units of the moles of CO reacted to form hydrocarbon/mole of moly atom-min. Symbols: □, Mo,Ni; ■, Mo-Co; ○, Mo-Cr.

RESULTS AND DISCUSSION

In our first attempt, 0.15 g of unsupported ammonium 6-molybdo-nickelate was loaded into the reactor and tested after drying in flowing helium at 423 K for only two hours. At the reaction conditions of 473 K and a feed $\text{H}_2/\text{CO} = 3$ the catalytic activity was too low to produce detectable amounts of hydrocarbons. The only detectable products were CO_2 and water, at a low conversion of only 0.2%. Upon heating the reactor to 573 K we noticed that the hydrocarbon production increased

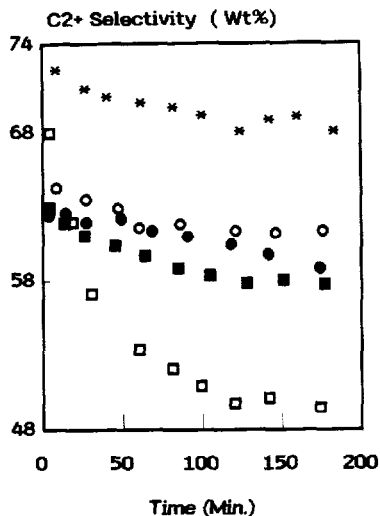


FIGURE 3 Specific rates of unsupported 6-heteropolymolybdate catalysts. Specific rate units and the reaction conditions are the same as that given in Figure 2. All catalysts are reduced at 773 K for four hours. Symbols: \square , Mo-Ni; \blacksquare , Mo-Co; \circ , Mo-Cr; \bullet , Mo-Al; $*$, Mo-Fe.

with time as shown in Figure 2. This, we believe, is due to the nickel catalyzed self-reduction of the catalyst. By activating the hydrogen, nickel catalyzes the reduction of Mo^{+6} to Mo^{+4} or possibly even lower oxidation states which may in turn catalyze hydrogenation of carbon monoxide. This increase in activity continued for several hours before peaking. Similar but slower autocatalyzed reduction and activation was also observed with the cobalt and chromium heteropolies, as shown in Figure 2. We see that the ease of reduction for these heteropolies is in the order of $\text{Ni} > \text{Co} > \text{Cr}$. On the other hand, Al and Fe heteropolies showed no detectable activity at this temperature and are therefore not shown in the figure.

Figure 3 shows the initial deactivation rates for the unsupported catalysts. The shape of the deactivation curve seems to be a characteristic of the particular catalyst. The initial rate of deactivation is highest for the nickelate and lowest for aluminate and ferrate. According to the initial deactivation rates indicated, nickelate and chromate would have approximately equal steady state activity. On the other hand, cobaltate and aluminate would have roughly the same steady state activity which is about one third of that of the nickelate and chromate. Figure 3 also indicates that ferrate catalyst is not active at these conditions.

Table 1 shows the specific reaction rate for the bulk catalysts after various reduction treatments. We see that after reduction at 573 K only Ni, Co and Cr heteropolies have significant activity. After four hours of reduction at 673 K

TABLE 1

Specific reaction rates^a of unsupported 6-heteropolymolybdates in Fischer-Tropsch synthesis

Hetero atom	Specific rate ^b			
	Reduction conditions			
	573 K, 4 h	673 K, 4 h	773 K, 4 h	773 K, 12 h
Ni	0.0092	0.0089	0.0118	0.0288
Co	0.0037	0.0232	0.0049	0.0087
Cr	0.0024	0.0168	0.0119	0.0055
Al		0.0069	0.0031	0.0041
	8.7×10^{-5}			
Fe				0.0044
	5.3×10^{-6}	3.7×10^{-4}	9.3×10^{-4}	

^aReaction conditions used: 573 K, 0.12 MPa, $H_2/CO = 3$.

Rate values are taken at time equal to 2 h.

^bSpecific reaction rate is defined as the moles of CO reacted to form hydrocarbon/mole of moly atom-min.

the activity of the Ni-containing catalysts stays the same but all other catalysts are significantly more active. We note that after this reduction treatment both the cobalt and chromium containing catalysts are quite active. Our specific reaction rate is based on the bulk molybdenum amount and has the units of: moles of CO reacted to form hydrocarbon/mole of moly atom-min. These rates may be compared to the previously reported values of 0.0014 for the bulk molybdenum oxide, 0.0042 and 0.0029 for the bulk molybdenum carbide [7-9] and 0.0040 and 0.0044 for charcoal supported molybdenum oxide and carbide respectively [10]. Considering the fact that these are low surface area ($5-10 \text{ m}^2 \text{ g}^{-1}$) unsupported catalysts these specific rates are quite high. Increasing the reduction temperature to 773 K brings about more drastic changes. Nickelate based catalyst is 30% more active, chromate and aluminate show 30% and 55% drop in activity respectively. The most dramatic decrease is exhibited by the cobaltate based catalyst: a 370% drop in activity. Lengthening the reduction time at 773 K from four hours to 12 hours results in increased rates for all the catalysts tested except the chromate which shows a decrease of more than twofold. The increases and decreases observed with the increased reduction temperature and time are due to two opposing processes going on simultaneously: as the temperature is increased the increased reduction is also accompanied by sintering. Increased reduction results in higher activity while sintering results

TABLE 2

Specific reaction rates^a of 6% supported 6-heteropolymolybdates in Fischer-Tropsch synthesis

Hetero atom	Specific rates ^b			
	Reduction conditions			
	573 K, 4 h	673 K, 4 h	773 K, 4 h	773 K, 12 h
Ni	0.0141	0.0162	0.0137	0.0123
Co	0.0112	0.0238	0.0392	0.0142
Cr		0.0069	0.0137	0.0148
	6.7×10^{-4}			
Al	0.0011	0.0042	0.0105	0.0049
Fe		0.0107	0.0121	0.0168
	2.9×10^{-4}			
AHM		0.0101	0.0231	0.0238
	9.1×10^{-4}			
Co ^c		0.0095	0.0061	0.0118
	9.0×10^{-4}			

^aReaction conditions used as that given in Table 1.

^bSpecific reaction rate is defined as that given in Table 1.

^cMo-Co supported on titania.

in a lower surface area catalyst. For the ferrate based catalyst the decrease in the surface area is more than made up by the increased degree of reduction at all temperatures used, therefore resulting in a continuous increase in activity. We should note that this catalyst has the lowest activity of all and clearly is the most difficult one to reduce. The nickelate based catalyst also shows similar trend of increased activity at increasing reduction temperature and time. On the other hand, the other three catalysts exhibit the maximal activity at medium reduction temperature and time.

In order to decrease the sintering problem and to increase (if possible) the active surface area we prepared 6 wt% (by molybdenum) charcoal supported catalysts. The results of reaction rates at different reduction conditions are shown in Table 2. The effect of the support can be seen by comparing Table 2 with Table 1. We see that for the nickelate based catalyst supporting on charcoal results in a twofold activity increase after reduction at 673 K but there is a continuous decrease in activity with increased reduction time and temperature, the maximum activity being about 55% of the unsupported catalysts. This indicates that sintering

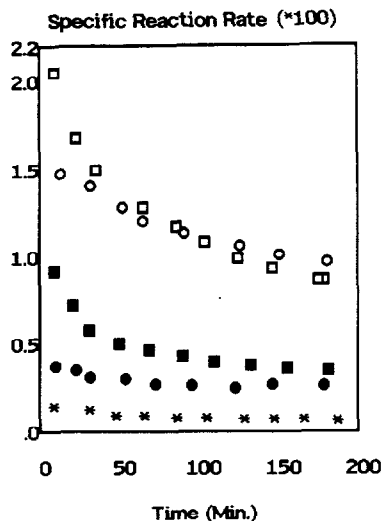


FIGURE 4 C_2^+ selectivity of unsupported 6-heteropolymolybdate catalysts. Selectivity is defined as nC_n/nC_n . Reaction and reduction conditions as that given in Figure 2. Symbols: □, Mo-Ni; ■, Mo-Co; ○, Mo-Cr; ●, Mo-Al; *, Mo-Fe.

occurs more readily than reduction for this supported catalyst. The cobaltate based catalyst increases its activity at higher reduction temperature and reaches its maximum activity after four h of reduction at 773 K. This maximum value is about 70% higher than the maximum of the corresponding unsupported catalysts. Unlike the unsupported catalyst, the supported chromate catalyst's activity increases continuously but the maximum is slightly lower. The supported ferrate based catalyst shows the most increase in activity as compared to the unsupported one, with the maximum being four times higher. This clearly indicates that the supported ferrate based catalyst is more readily reduced. The aluminate based catalyst exhibits the effect of sintering after the 12 h reduction of 773 K. It is also the lowest activity supported catalyst. For comparison, we have also listed a supported catalyst prepared from a pure ammonium heptamolybdate (AHM) solution and a titania supported cobaltate based catalyst. As a contrast to 6-heteropolies, we find that the AHM catalyst has its highest activity after the 12 h reduction at 773 K. The titania supported catalyst is inferior to the charcoal supported catalyst, showing the importance of the support.

Figure 4 shows the C_2^+ selectivities of all the unsupported catalysts after 4 h of reduction at 773 K. It is found that this reduction condition gives the maximum in desired C_2^+ selectivity. We see that ferrate based catalyst exhibits the highest while nickelate based catalyst gives the lowest C_2^+ selectivity. Of the higher hydrocarbons about half is ethane, with the balance being propane and

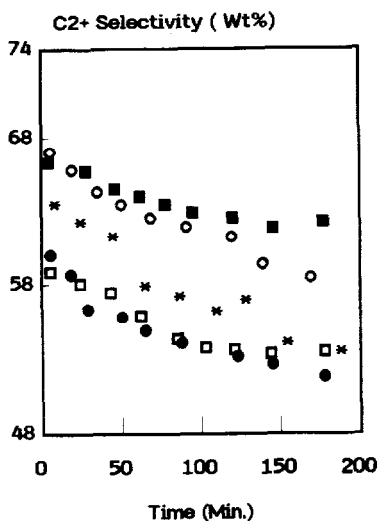


FIGURE 5 C_2^+ selectivity of 6% charcoal supported 6-heteropolymolybdate catalysts. Selectivity is defined as nC_2/nC_n . Reaction and reduction conditions as that given in Figure 2. Symbols: □, Mo-Ni; ■, Mo-Co; ○, Mo-Cr; ●, Mo-Al; *, Mo-Fe.

small amounts of ethylene, butane and pentane. However, it is interesting to note that, with the exception of the nickelate, the variation in selectivity is only $\pm 10\%$ among all catalysts.

Figure 5 shows the C_2^+ selectivity of the supported catalysts. The variation in steady state C_2^+ selectivity is only $\pm 5\%$ among all catalysts. Unlike the unsupported catalysts, two thirds of the C_2^+ fraction is ethane with the balance being largely propane. Small amounts of butane and ethylene were observed only for the more active catalysts.

Reactivity with CO_2 feed

Instead of using CO, we also tested our catalysts using CO_2 feed. The results are shown in Table 3 and Table 4 for the activity and C_2^+ selectivity respectively. We note here that only the unsupported nickelate based catalyst is significantly more active than that of using CO feed at the reduction of 673 K and four h. In every other case the activities obtained are far less than their corresponding activities with CO feed. This is not surprising since previous studies have shown the activity from using CO_2 feed of many methanation and Fischer-Tropsch synthesis catalysts, such as Ni, Fe, Ru and Co based catalysts are significantly lower than that of CO feed (for example, ref. [11-26]). For comparison, literature activity and selectivity values for bulk molybdenum based catalysts reported by Anderson et al. [15] are also included in these tables. Since these literature values are

TABLE 3

Specific reaction rates^a of our t-heteropolymolybdates catalysts in comparison with previously reported bulk molybdenum catalysts using CO₂ feed

Hetero-atom	Specific reaction rates ^b *10 ⁺⁴		
	Reduction conditions		
	673 K, 4 h	773 K, 4 h	773 K, 12 h
Unsupported			
Ni	195.0	26.6	25.2
Co	24.5	11.1	12.1
Cr	2.7	6.8	9.3
Al	1.6	1.7	2.4
Fe	< 1.0	< 1.0	< 1.0
Charcoal			
Supported			
Ni	18.7	3.0	3.9
Co	27.7	10.0	8.6
AHM	6.1	2.9	2.7
Reaction at			
Bulk catalyst			
from ref. [11]	623 K ^c	573 K ^d	
MoO ₃	0.0	0.0	
MoO ₂	10.8	1.9	
MoS ₂	1.8	0.3	
Mo	3.5	0.6	
Mo ₂ C	44.3	7.6	
Mo ₂ N	1.2	0.2	

^aReaction conditions used as that given in Table 1.

^bSpecific reaction rate is defined as that given in Table 1.

^cThese are initial rate at reaction conditions of: 623 K, 1 ATM, H₂/CO = 3.7, from ref. [11].

^dThese rates are converted from rates at 623 K to 573 K, assuming an apparent activation energy of 25 kcal mol⁻¹ for all catalysts.

taken at 623 K and not at 573 K, the temperature we used, they are not directly comparable to ours. For simplicity in converting their values we have assumed a reasonable apparent activation energy of 25 kcal mol⁻¹ for all catalysts they

TABLE 4

C_2^+ selectivity^a of our t-heteropolymolybdates catalysts in comparison with previously reported bulk molybdenum catalysts^b using CO_2 feed.

Hetero-atom	C_2^+ selectivity		
	Reduction conditions		
	673 K, 4 h	773 K, 4 h	773 K, 12 h
Unsupported			
Ni	3.0	32.6	26.6
Co	3.5	34.3	33.0
Cr	7.7	27.8	31.8
Al	0.0	2.0	11.9
Fe	0.0	1.8	10.8
Charcoal			
Supported			
Ni	11.7	1.6	1.4
Co	0.1	0.1	0.1
AHM	0.1	0.2	0.1
	Reaction at		
Bulk catalyst			
from ref. [11]		623 K	
MoO_3		0.0	
MoO_2		2.0	
MoS_2		0.0	
Mo		2.0	
Mo_2C		24.3	
Mo_2N		0.0	

^a C_2^+ selectivity are based on the values at time equal to 2 h. Reaction conditions as that given in Table 1.

^bLiterature C_2^+ selectivity values are based on the initial values.

tested. The converted activity values are listed in Table 3 together with the unconverted values. We see that, with the exception of Mo_2C , our more active catalyst (nickelate, cobaltate and chromate based catalyst) are in general an order of magnitude more active than their bulk catalysts. Their Mo_2C catalyst is about the same activity as our nickelate and cobaltate based catalysts. The C_2^+ selectivity values show some interesting points. We see that our more active catalysts exhibited

about 30% C_2^+ selectivity after being reduced at 773 K while all their bulk catalysts except Mo_2C show a negligible C_2^+ selectivity. Since higher temperature favors the formation of methane for molybdenum catalysts, the C_2^+ selectivity of their catalysts would be somewhat higher if they were tested at 573 K. However, considering the negligible C_2^+ selectivity of these catalysts, reaction at 573 K would not bring their C_2^+ selectivity to as high as 30%. Again, their Mo_2C catalyst would have a comparable C_2^+ selectivity to our catalysts. It is apparent our catalyst has the advantage of relatively high C_2^+ selectivity even with the CO_2 feed. As indicated in the work by Anderson et al, our catalysts may have some amorphous lower valence Mo species dispersed in the MoO_2 matrix.

The role of the heterometal atoms

The ratio of the heterometal atoms to molybdenum is one to six. Thus if the heteroatoms were a separate phase having activity comparable to their individual FTS activities the overall activities of our bulk catalysts should have been significantly different. Higher activities (more than two orders of magnitude higher) for catalysts with heteroatoms Ni, Co and Fe should have been observed. The fact that we could not detect the presence of the heterometal atoms by X-ray rules out the possibility of having separate large heterometal crystallites. The absence of X-ray peaks can be due to very small crystallites (less than 20 Å) or atomic dispersion of the metal atom in the MoO_2 lattice. The low activities we observed seem to favor the latter explanation. If the heterometal atoms are in the MoO_2 lattice they could not be easily reduced and would not affect the overall activity. However there is some evidence that the heterometal atom does make a difference. Ni and Co containing catalysts are activated at lower reduction temperatures than catalysts prepared using pure AHM. On the opposite side Fe and Al containing catalysts are much harder to activate and therefore have lower activities. Perhaps these atoms form highly stable oxides with molybdenum.

The activity pattern with CO_2 feed gives significant evidence that the heterometal atoms are participating in converting CO_2 to methane and higher hydrocarbons. Ni and Co by themselves are quite active in converting CO_2 to hydrocarbons [15,20, 26]. As seen in Table 3 the activities of Ni and Co containing catalysts are significantly higher than the AHM based catalysts. This is explicable if it is assumed that a small fraction of the heterometal atoms are on the surface of molybdenum oxide crystallites.

CONCLUSIONS

We have found that the decomposition products of 6-heteropolymolybdates are moderately active Fischer-Tropsch synthesis catalysts. The presence of the heteroatom cannot be detected by X-ray analysis, indicating that it is uniformly dispersed in the MoO_2 matrix. While the effect of the heteroatom on the activity of the decomposition product is significant, the selectivity appeared to be largely determined by the MoO_2 phase and does not change much for all the catalysts.

We also found that in general the charcoal supported catalysts are somewhat harder to reduce (when compared to the unsupported ones), but are more active and sinter less. Feeding with CO₂ instead of CO decreased the activity of most of our catalysts, but the C₂⁺ selectivity is relatively high at 30 wt%.

ACKNOWLEDGEMENTS

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