Fischer Tropsch Reaction over Reduced Molybdenum Catalysts Derived from Various Heteropoly Compounds

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The Fischer-Tropsch reaction was examined over reduced molybdenum catalysts using heteropoly compounds as catalyst precursors. Improvement in reducibility was realized by the use of heteropoly compounds. Metallic molybdenum powder with a very large surface area was obtained by the reduction of $H_3PMo_{12}O_{40}$. Its catalytaic activity was one order higher than conventional Mo catalysts. Using different salts of 12-molybdophosphoric acid, various additives were introduced under equivalent conditions and their addition effects were studied.

The catalytic hydrogenation of CO to form various hydrocarbons, the Fischer-Tropsch (FT) reaction, has been studied in detail for a long time. It is well known that group VIII elements such as Fe, Co, Ru, and Rh are active for this reaction, and most research regarding the FT reaction has been focused on these metal catalysts.[1—5] On the other hand, only a few studies have been reported for reactions over catalysts other than group VIII metals.[6—8]

The dissociation of CO is believed[9] to be an important process in the catalytic hydrogenation of CO. Fe and Ru have a great ability to dissociate CO, the reason for their high activity in the FT reaction. Among elements other than those from group VIII, molybdenum is reported[10] to have a high ability for CO dissociation and is worth noticing as a catalyst for the FT reaction. Saito and Anderson[7] examined CO hydrogenation over metallic molybdenum and several molybdenum compounds and found that reduced molybdenum is an active catalyst for the FT reaction. They reported the following order in activity: $Ni > Mo_2C > Mo(metal) > Mo_2N > MoO_2 > MoO_3$. Murchison and Murdick[11] reported that molybdenum catalysts containing potassium are selective in the formation of C_2—C_5 hydrocarbons (LPG) and have a relatively high torelance for sulfur poisoning.

However, these studies have been carried out within a reaction temperature range of 623 to 673 K (more than 100 K higher than the group-VIII metals), indicating the mild activity of molybdenum. Because MoO_3 is not easily reduced, Saito and Anderson reduced their molybdenum catalysts at 873K. In order to obtain a more active catalyst, we tried to lower the reduction temperature using more reducible compounds as the catalyst precursors. Niiyama *et al.*[12] studied the initial stage of the reduction of heteropoly compounds and found that $H_3PMo_{12}O_{40}$ (HPMo) and its transition-metal salts are more easilly accessible to H_2 reduction than MoO_3. Therefore, we examined heteropolymolybdates as precursors of molybdenum catalysts. In addition, the use of heteropoly compounds makes it easy to estimate the effect of various additives which are introduced as the counter cation of heteropoly acid since each cation is placed in an equivalent position of the precursors.

Experimental

Catalyst Preparation. Although each catalyst was reduced with hydrogen before use (and its form changed), the chemical formula before reduction is used to express each catalyst.

MoO_3. Reagent grade ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Wako Pure Chem.) was calcined in a flow of dry air at 773 K for 5 h. The resulting grey powder was submitted for catalytic studies. The grey MoO_3 was further purified following a method from the literature[13] and white powder was obtained. This MoO_3 was catalytically inactive and was used only as the raw material for heteropoly catalysts.

HPMo($H_3PMo_{12}O_{40}\cdot xH_2O$). According to the method of Tsigdinos[14] and Drechsel,[15] 12-molybdophosphoric acid was prepared as follows. 2.46 g of phosphoric acid (reagent grade, Wako Pure Chem.) was added to 150 ml of pure water and boiled with reflux for 30 min. 50 g of purified MoO_3 (white) was added stepwise and the mixture was allowed to boil for 6 h. After cooling, the insoluble contamination was removed by filtration. The objective compound was extracted with ether from the filtrate and dried. A yellow powder was obtained.

KPMo($KH_2PMo_{12}O_{40}\cdot xH_2O$).[14] A calculated amount of K_2CO_3 (reagent grade, Wako Pure Chem.) was added to an aqueous solution of HPMo so that the atomic ratio of K/Mo was 1/12. The solution was heated in a water bath until no more CO_2 was formed. After drying, a yellow powder was obtained.

MePMo($MeH_2PMo_{12}O_{40}\cdot xH_2O$; Me=Li, Na, Cs, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn). Alkali metal, alkaline earth and transition metal salts of HPMo were prepared in the same manner as the KPMo, following the method of Tsigdinos.[14] The atomic ratio Me/Mo was fixed at 1/12, except for CsPMo. In this case, the ratio was changed from 0.5/12 to 2/12.

Pretreatment. 1.0 g of catalyst was packed in a U-tube reactor attached with a 4-port valve, the weight of the reactor being measured in advance. After evacuating at room temperature for 10 min, the temperature was increased at a rate of 10 K/min. The temperature change was controlled by a temperature programmer, Ohkura PG 3001, and the evacuation continued at 453 K for 1 h. After the evacuation treatment, the water content of the HPMo was found to be 0.2% from the weight loss after evacuation at 823 K. After cooling to room temperature, the 4-port valve was closed and the weight was measured. In a flow of hydrogen (high purity grade, Showa Denko Co., passed through activated copper and molecular sieve) the catalyst temperature was increased at a rate of 10 K/min and kept at 773 K for 4 h. After cooling slowly to room temperature in hydrogen, the weight of the catalyst was again measured. From the weight loss during the reduction treatment, the degree of reduction was determined.

Activity Measurement. The reactor was attached to a flow system in order to examine the CO hydrogenation. A premixed gas ($H_2/CO=2.98$, Takachiho Chem. Co.) was used as a reactant gas. After increasing the temperature in a hydrogen flow, the reactant gas was (30 ml/min, atmospheric pressure) passed through the catalyst at 503 K until the activity was stabilyzed (for 6 h). Then the activity was measured at 473—573 K. Products (CO, CO_2, and C_1—C_7 hydrocarbons) were analyzed by gas chromatography.

X-Ray Diffraction. In order to keep the sample from being exposed to air, the reduced (or spent) catalyst was removed from the reactor to a glass sample holder in a nitrogen atmosphare, covered with mylar film, and then submitted to an X-ray diffraction process.

Results and Discussion

MoO_3. The reduction of purified MoO_3 (white) was examined, but it was difficult to reduce it to metallic molybdenum. Even when the reduction temperature was raised to 873 K, the degree of reduction was less than 40% and it was catalytically inactive for the FT reaction. Unpurified MoO_3(grey) was also difficult to reduce and catalytically inactive when the reduction temperature was 773 K. However, when it was reduced at 873 K, the degree of reduction increased to 97.8%. An X-ray diffraction study of the reduced catalyst suggested that metallic molybdenum was formed by reduction. In this case, a mild activity in the FT reaction was found, consistent with Saito and Anderson.[7)] In addition, the reduction of ammonium heptamolybdate (NH_4-Mo) was examined. NH_4-Mo was more easily reduced than MoO_3. Even at 773 K, the degree of reduction was 66%. Its catalytic activity was comparable to MoO_3 reduced at 873 K (Table 1).

HPMo. When HPMo was reduced in a hydrogen flow at 773 K, the degree of reduction was 98.1%. Apparently, the reduction of HPMo was easier than MoO_3. However, when HPMo was heated at 773 K *in vacuo* before reduction (so that the Keggin unit was destroyed), the reduction stopped at about 40%. Thus, not only the presence of phosphorus, but also the Keggin structure is required to improve the reducibility. The reduction temperature also affected the reducibility. The optimum temperature was 773 K and both higher and lower temperatures resulted in a lower degree of reduction (Fig. 1). The reduction of HPMo seems to proceed accompanied by the decomposition of the Keggin unit and at higher temperatures (when the rate of decomposition exceeds that of reduction), the reduction ceased before completion.

The reduced catalyst was submitted to X-ray diffraction analysis and only the diffraction lines of metallic molybdenum were found. By means of X-ray fluorescence, it was found that the P/Mo ratio does not change during the reduction process (Table 2). On the other hand, the IR band of the P-O bond disappeared

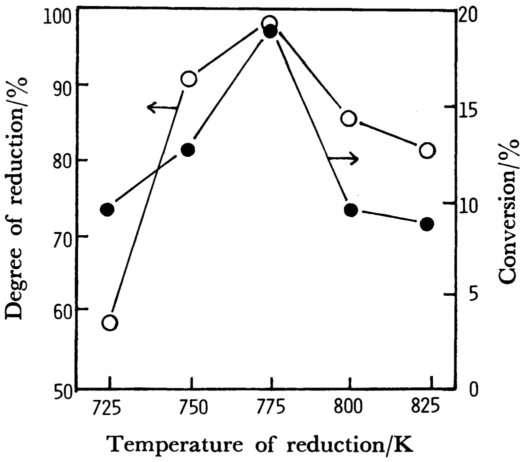

Fig. 1. Effect of reduction temperature on the degree of reduction and activity of HPMo.
-○-: degree of reduction, -●-: conversion (at 523K, amount of catalyst 1.0 g, flow rate 30 ml/min, $H_2/CO=2.98$).

Table 1. Reducibility and catalytic activity of various molybdenum compounds

Catal.	Reduction temp K	Degree of reduction (%)	Surface area (m^2/g)	X-ray Anal. (Diameter)*1 (Å)	Activity*2 523K	Activity*2 623K
MoO_3 (grey)	773	25.2	2.4	MoO_2	0.1	0.6
	873	97.8	11.8	Mo(440)	4.8	69.8
NH_4-Mo	773	66.0	5.9	Mo, MoO_2	5.6	—
HPMo	773	98.1	64.7	Mo(109)	74.1	—
MoO_3*3	873	(100)	7.5	Mo	—	61.5

*1: Particle size determined from the X-ray diffraction line broadening. *2: Rate of formation of hydrocarbons, µmol-C/min·g. *3: From Ref. 7 (Saito and Anderson).

Table 2. Results of the analysis of P/Mo ratio by means of X-ray fluorescence

Specimen	P/Mo (atomic ratio)
HPMo (before reduction)	1.1/12
HPMo (after reduction)	0.9/12
NiPMo (after reaction)	1.1/12

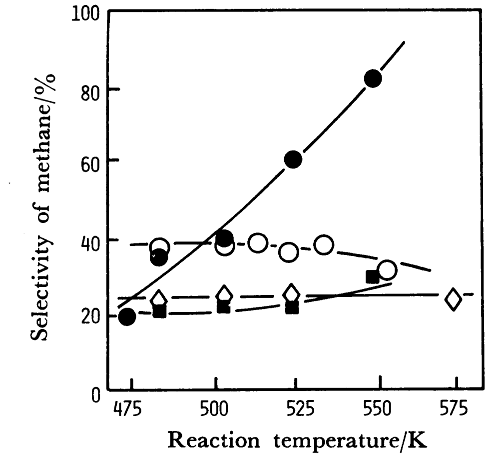

Fig. 2. Effect of reaction temperature on methane selectivity over Ru and various Mo catalysts.
-●-: Ru/alumina, -○-: HPMo, -◇-: CsPMo, -■-: CoPMo.

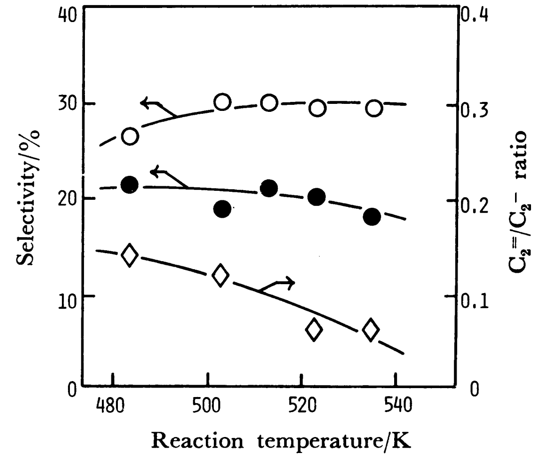

Fig. 3. Effect of reaction temperature on C_2 and C_3 selectivity and $C_2^=/C_2^-$ ratio over HPMo.
-○-: C_2 selectivity, -●-: C_3 selectivity, -◇-: $C_2^=/C_2^-$ ratio.

after reduction. Nozaki *et al.*[16] reported that the formation of nickel phosphides such as Ni_3P or Ni_7P_3 was observed by the hydrogen reduction of $Ni_3(PO_4)_2$. Probably the phosphorus in HPMo is also reduced and is included in the metallic molybdenum phase.

The BET surface area after reduction was 64.7 m^2/g, which was in agreement with the particle size calculated from the X-ray line broadening (Table 1). This surface area was more than five times larger than MoO_3 (reduced at 873 K). The presence of phosphorus seems to inhibit the crystal grouth of molybdenum. As a metal powder obtained by the hydrogen reduction of an oxide at high temperatures, this metallic molybdenum has a very small particle size.

The catalytic activity of HPMo was much higher than MoO_3, owing to its large surface area. The reaction rate was even higher than for molybdenum carbide, which was reported[7] to be the most active among Mo compounds. However, the product distribution for HPMo was in agreement with that of MoO_3 (Fig. 4), suggesting that the presence of phosphorus had little effect on selectivity. The product distribution followed the Schulz-Flory distribution, with a propagation coefficient 0.44.

One of the features of the Mo catalysts (HPMo and MoO_3) compared with the group-VIII metals (such as Ru) is that the former produces CO_2 as an oxygen compound, whereas the latter forms H_2O. Another is that Ru changes the product distribution extensively with reaction temperature (Fig. 2), whereas Mo changes it only a little. As shown in Figs. 2 and 3, the selectivities of C_1—C_3 were almost constant for Mo at 483—533 K. Only the olefin/paraffin ratio changed with temperature. Such a stability in selectivity against reaction temperature is advantageous in practical operation because this reaction is exothermic and the heat of reaction tends to disturb the reaction.

We also tried to estimate the turnover frequency of this reaction over HPMo on the basis of the number of surface Mo atoms calculated from the BET surface area supposing that 1.73×10^{19} atoms are exposed per square meter.[17] The resulting turnover frequency was 2.6×10^{-3} s^{-1} at 523 K, a value comparable to that of Ir (2.6×10^{-3} s^{-1} at 523 K)[18] which was the least-active metal among group-VIII elements.

Alkali Metal and Alkaline Earth Salts. HPMo has three protons per heteropolyanion which can be exchanged with various cations. We prepared three Cs salts, changing the content of Cs from 0.5 to 2 per polyanion. The degree of reduction of $Cs_{0.5}$ and Cs_1 catalysts was 81—82%, in contrast to Cs_2 which was reduced only 52%. The activity of Cs_2 was also lower than $Cs_{0.5}$ and Cs_1, although no significant change in the product distribution was found for the Cs_1 and Cs_2 catalysts. Thus, the optimum content of an alkali metal seemed to be one cation per heteropolyanion.

The introduction of various alkali metals and alkaline earth cations into HPMo caused a decrease in the degree of reduction from 98.1% (HPMo) to 60(NaPMo)—82% (CsPMo). The catalytic activity also decreased, compared with HPMo. However, no correlation was found between the degree of reduction and activity. In order to increase the degree of reduction of KPMo, we prepared KNiPMo (which contain each one K^+ and Ni^+ per polyanion) and examined its catalytic activity. Although the degree of reduction of KNiPMo increased to 91% (compared with KPMo (74%)),. the activity was lower than KPMo. Therefore, the change

Table 3. Results of the FT reaction over MoO_3, HPMo, and alkali metal or alkaline earth salts of HPMo

	MoO_3	HPMo	LiPMo	NaPMo	KPMo	CsPMO	MgPMo	CaPMo	KNiPMo
Temp/K	523	523	573	573	573	573	523	523	573
selectivity (%)									
C_1	36.9	36.1	31.6	18.1	21.0	24.5	26.8	28.3	29.6
C_2	25.0	27.0	25.2	30.8	35.0	33.5	28.0	30.0	32.5
C_3	16.1	16.7	17.7	26.5	24.8	23.0	27.5	24.4	19.0
C_4—C_7	22.0	20.1	25.4	24.6	19.2	19.0	17.8	17.4	18.9
$C_2^= + C_3^=$	3.1	2.0	4.4	29.9	29.6	32.7	6.5	13.9	28.3
Conv. (%)	2.4	31.3	29.4	14.4	21.5	10.3	11.8	1.3	15.0

Table 4. Results of the FT reaction over transition metal salts of HPMo at 523K

	MnPMo	FePMo	CoPMo	NiPMo	CuPMo	ZnPMo
C_1	30.1	21.5	20.9	25.3	25.5	24.8
C_2	30.5	22.6	26.1	27.9	32.6	25.8
C_3	23.5	33.5	21.1	28.0	27.6	30.6
C_4—C_7	15.8	22.5	32.0	18.8	14.6	18.8
$C_2^= + C_3^=$	4.6	8.3	12.2	7.9	8.3	11.2
Conv.	6.6	10.9	27.6	23.4	4.5	4.5

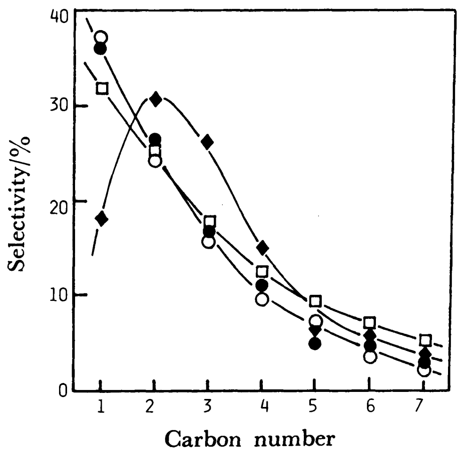

Fig. 4. Products distribution over MoO_3, HPMo, LiPMo and NaPMo.
-○-: MoO_3, -●-: HPMo, -□-: LiPMo, -◇-: NaPMo.

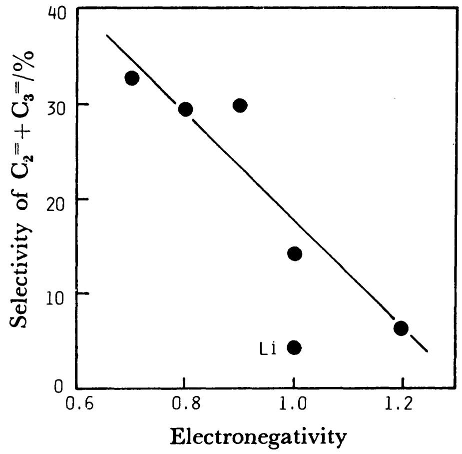

Fig. 5. Relation between electronegativity of alkali metals and alkaline earth metals and olefin selectivity over each salt of HPMo.

in the degree of reduction is not the main reason for activity loss by the introduction of K^+ and other alkali metal cations. Rather, the intrinsic interaction of cations and Mo seems to cause the effect.

The product distribution also changed with the introduction of these cations. Alkali metal salts produced less C_1 (methane) than HPMo or MoO_3 except LiPMo, which showed a product distribution similar to HPMo (Fig. 4). An increase in the C_2—C_3 selectivity was accompanied by a decrease in the C_1 selectivity. MgPMo and CaPMo showed an intermediate property between the two groups in selectivity. A sharp increase in olefin selectivity was observed for Na-, K-, and CsPMo. For CsPMo, the selectivity of the lower olefins (ethylene+propylene; $C_2^=+C_3^=$) was one order higher than that of HPMo. An increase in olefin selectivity was also observed for CaPMo, however it was only small for Li-and MgPMo. The formation of trace amounts of alcohols (mainly methanol) was found for na-, K-, and CsPMo.

Such a tendency of change in the product distribution caused by alkali metals (decrease in C_1 and increase in olefins) has also been observed for group-VIII metals such as Ru[19] and Fe.[20] As shown in Fig. 5, a correlation between the electronegativities of the cations and the olefin selectivity was found with the exception of LiPMo.

Transition Metal Salts. Various transition metal salts (Mn, Fe, Co, Ni, Cu, Zn) of HPMo were prepared and submitted to FT reactions. The amount of the bivalent cations introduced was fixed to one cation per heteropolyanion. The activities of these catalysts were inferior to HPMo. A significant decrease in activity was observed after the introduction of Mn, Zn, and Cu. On the other hand, there was only a small decrease over Fe, Co, and Ni salts. The degree of reduction exceeded 90% (except Mn; 89%), and so the transition-metal salts appear to be easily reduced. (Especially, Fe-, Ni-, and CuPMo were almost completely reduced.) Perhaps these transition metals were reduced first and activated the hydrogen to accerelate the reduction of Mo.

A decrease in the C_1 selectivity was also observed as clearly as for the alkali metal salts. The C_1 selectivity of CoPMo (20.9%) was comparable to that of KPMo (21.0%). In the case of the alkali metal salts, the effect to suppress the C_1 selectivity was obtained at the expense of an activity loss, but Fe- and CoPMo realized the same effect with only a slight loss of activity. For Na-, K-, and CsPMo, a significant increase in the olefin selectivity was accompanied by a decrease of C_1. However, for the transition metal salt, olefin selectivity was less than half of that of the alkali metal salts even though the C_1 selectivity was in the same range. The relation between the C_1 selectivity and the olefin ($C_2^= + C_3^=$) selectivity is illustrated in Fig. 6. A clear correspondence between the two factors was observed except for Na-, K-, Cs-, and CaPMo.

If both a decrease in the C_1 selectivity and an increase in the olefin selectivity are brought about by a single driving fource (for example the electron donation from added elements to Mo), there must be a correspondence between the two selectivities. The behavior of the catalysts which fit on the curve of Fig. 3 seems to be such a case. On the other hand, Na-, K-, Cs-, and CaPMo also significantly promote olefin formation. The characteristic that distinguish these elements from others is that they have a strong common basicity. When basic sites are formed on a catalyst surface, they will abstract hydrogen from the surface alkyl group, which is formed by the surface polymerization of CH_2, and promote the formation of olefins.[19]

Mo Compounds Containing Co. In order to compare the additional effect of Co with CoPMo (which proved to be active and selective to C_2—C_3 among various heteropoly compounds) other Mo compounds containing Co were examined. Co-Mo-O (Co/Mo=1/12) was prepared by drying a mixture of aqueous solutions of cobalt nitrate and ammonium heptamolybdate. The product was calcined in air at 773 K for 5 h. X-Ray diffraction showed that it was a mixture of $CoMoO_4$ and MoO_3. $(NH_4)_3H_6[CoMo_6O_{24}]$ contains Co as a heteroatom, and is a different type of heteropoly compound from HPMo or CoPMo. We prepared it following a method described in the literature.[21]

The degree of reduction of Co-Mo-O was only 45.2%, and its activity for CO hydrogenation (conversion 1.8% at 523 K) was one order lower than CoPMo. The product distribution for Co-Mo-O was (as shown in Fig. 7) almost equal to that of HPMo or MoO_3, showing a poor addition effect of Co. Even though the ratio of Co and Mo is the same, CoPMo shows a more clear effect of Co than Co-Mo-O. This is because CoPMo (before reduction) contains Co and Mo in uniform concentrations in atomic level which results in a close interaction between the two elements after reduction. On the other hand, Co-Mo-O is a mixture of $CoMoO_4$ and MoO_3 and, thus, the ratio of Co/Mo is not uniform. Thus, the advantage of using heteropolymolybdates as the raw materials for a Mo catalysts is again suggested.

$(NH_4)_3H_6[CoMo_6O_{24}]$ is also a kind of heteropoly compound, but it was not as easily reduced as HPMo or CoPMo (the degree of reduction was 59.2%). The conversion of CO was only 5.2% at 523 K, perhaps due to the low degree of reduction. The product distribution (Fig. 7) showed the effect of Co, *i.e.* a decrease in

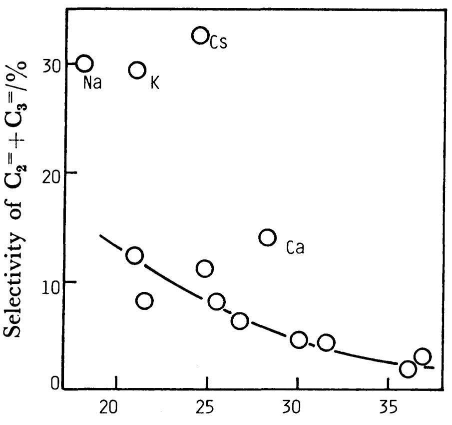

Fig. 6. Relation between methane selectivity and olefin selectivity over various salts of phosphomolybdate.

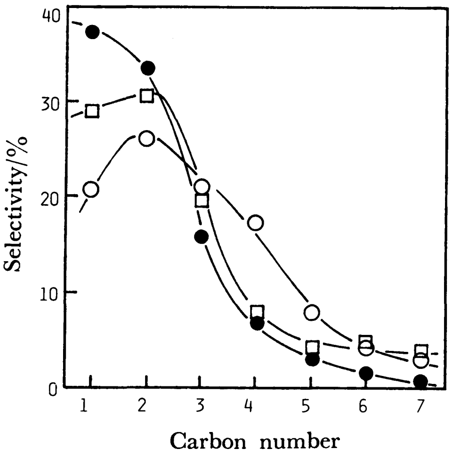

Fig. 7. Product distribution over Mo catalysts containing Co.
-○-: CoPMo, -●-: Co-Mo, -□-: $(NH_4)_3H_6[CoMo_6O_{24}]$.

the selectivity of C_1. It was not as clear as the case of CoPMo. Therefore, the effect of Co is more clearly observed when Co is the counter cation rather than the heteroatom.

Conclusions

1) 12-molybdophosphoric acid is an excellent precursor of metallic molybdenum owing to its reducibility. Thus, we could get a Mo catalyst with a very large surface area. Its activity for CO hydrogenation was one order higher than the conventional Mo catalyst. It was more active than Mo_2C, which was reported to be the most active among various molybdenum compounds.

2) It is possible to introduce various cations as additives using their salts of molybdophsphoric acid, and enables us to estimate their addition effect in equivalent conditions. Alkali metal and alkaline-earth cations suppressed the activity, but improved the selectivity for C_2—C_3 hydrocarbons, especially in the olefin formation.

3) Transition metal salts were reduced as easily as HPMo but the activity was lower than HPMo. By the addition of transition metals, the selectivity of methane decreased in the same manner as for the alkali metals. However, the addition effect was not so clear on the olefin formation as the alkali metals. Correlation was found between C_1 selectivity and olefin ($C_2^{=}+C_3^{=}$) selectivity except the salts of strong base cations (Na^+, K^+, Cs^+, and Ca^+).

4) The addition of cobalt was most effective on selectivity when cobalt was introduced as the counter cation of heteropoly acid.

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