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The Effect of Carriers of MoO_3–CoO and MoO_3 Catalysts on the Activity for the Hydrocracking of Thiophene

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The catalytic activity for the hydrocracking of thiophene of molybdenum–cobalt catalysts mounted on SiO_2–Al_2O_3 of different compositions and the surface property of the carriers were studied. A correlation was found between the activity and the amount of MoO_3 mounted on the carriers. The amount of MoO_3 increased with the increase of the amount of anionic OH group on the carriers, which can be exchanged with fluorine ion. For a series of molybdenum catalysts mounted on various aluminas, magnesia–alumina, active carbon, etc., it was also found that the amount of MoO_3 correlated well with the amount of OH group. A MgO–Al_2O_3 carrier which has the largest amount of OH group supported the largest amount of MoO_3. The role of anionic OH group for the interaction between MoO_3 and carriers is discussed.

INTRODUCTION

A molybdenum–cobalt catalyst system has been extensively used as most effective hydrodesulfurization catalysts in petroleum industry. Recently, the surface property, bulk structure and activity of the catalysts and the adsorbed state of thiophene were studied by esr (*1–5*), uv (*6–7*), ir (*6–12*), ESCA (*13–17*), etc. (*18–25*). However, not much work has been done on the effect of the catalyst carriers. In the present work, the change in surface and catalytic properties of MoO_3–CoO and MoO_3 catalysts with change of the carriers has been studied with special reference to the amount and the nature of hydroxyl groups on the catalyst carriers.

EXPERIMENTAL METHODS

Catalysts and Reagents

Catalysts were prepared by the following two methods. In method I, a catalyst carrier was immersed in a mixture of aqueous solutions of cobalt nitrate and ammonium paramolybdate, evaporated to dryness at 120°C and calcined in air at 500°C. In this case, the concentrations of cobalt and molybdate ion in the mixture were adjusted so that the final amounts of MoO_3 and CoO become 6 and 1 wt%, respectively. In method II, a catalyst carrier was immersed in a much more concentrated mixture than in method I and allowed to stand for 2 days. The catalyst was washed with deionized water, followed by drying and calcining at 500°C. Since white precipitates were formed during the immersion of carriers having high acidity into a solution of ammonium molybdate, they were analyzed by an atomic-absorption spectrophotometer and the Kjeldahl method (Mo as MoO_3, 74.6%; NH_3, 4.4%; H_2O, 16.4%; unknown, 4.6%). It was ascertained by changing time of impregnation that Mo reached the saturation level

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in the case of method II. A series of SiO_2–Al_2O_3(I) having different compositions as catalyst carriers were prepared by mixing alumina sol ("alumina Sol-200" of Nissan Chemicals Co.) with silica sol ("Snowtex-O" of Nissan Chemicals Co.) followed by calcining in air at 500°C for 6 hr. A SiO_2–Al_2O_3(II) was Neobead D (10% $SiO_2 \cdot 90\%$ Al_2O_3) of Mizusawa Chemical Co. Al_2O_3(I) and (II) were alumina KHA and KHD of Sumitomo Chemical Co. Al_2O_3(III) and (IV) were prepared by hydrolysis of aluminum sulfate with 28% ammonia water followed by washing, drying and calcining at 500°C. Al_2O_3(V) and (VI) were a fibrous alumina of Showa Tansan Co. and Neobead C (100% Al_2O_3) of Mizusawa Chemical Co. Al_2O_3 (VII) was prepared by calcining alumina sol of Nissan Chemicals Co. A MgO–Al_2O_3 was prepared by mixing $Mg(OH)_2$ with alumina sol, drying and calcining at 500°C. An active carbon was carbon HGH-619 of Takeda Chemicals Co.

The contents of molybdenum and cobalt were determined by using a Hitachi 208 type atomic-absorption spectrophotometer for samples obtained by decomposing catalysts with a mixture of nitric acid and sulfuric acid. Thiophene was a guaranteed reagent of Kishida Chemical Co.

Measurement of Surface Acidity and Hydroxyl Group

Specific surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at −196°C. Surface acidity of catalysts was measured by titrating with *n*-butylamine, using 2-amino-5-azotoluene or neutral red as an indicator (*26*). The amount of surface hydroxyl group was measured by a modified Boehm's method (*27*). One gram of a sample (8–15 mesh) was put in 25 ml of an aqueous solution of ammonium fluoride (57.2 mmol/liter) and allowed to stand for 3–4 days with occasional shaking and then filtered. After the sample was washed with a definite amount of water, the fluorine content in the washings was analyzed by a thorium nitrate titration method (*28*). The amount of hydroxyl group was obtained by subtracting the amount of fluorine ion in the washings from the amount of fluorine ion in an initial fluorine solution. We employed ammonium fluoride instead of sodium fluoride, which was used by Boehm (*27*), in order to minimize the pH change caused by the exchange of hydroxyl ion with fluorine ion.

Reaction Procedure

The reaction of thiophene was carried out at 350°C by using a conventional flow method. Catalysts were treated with hydrogen and carbon disulfide at 450°C before the reaction. The molar ratio of hydrogen to thiophene was 10 and the contact time was 99.0 g·hr/mol. The amounts of thiophene and the reaction products were determined by gas chromatography with a 4 m column of tricresyl phosphate and a 6 m column of squalene on alumina, respectively. Toluene was used as an internal standard for the determination of thiophene.

Main reaction products were butenes and hydrogen sulfide. Besides, small amounts of *n*-butane and isobutane were formed. The selectivity of 1-butene, *cis*-2-butene and *trans*-2-butene was approximately 30, 40, and 30%, respectively, and the selectivity did not change much for various catalysts. The percentage conversion was calculated by the equation: (the amount of supplied thiophene − the amount of unreacted thiophene)/the amount of supplied thiophene × 100.

RESULTS AND DISCUSSION

Hydrocracking of Thiophene over MoO_3–CoO mounted on SiO_2–Al_2O_3 of Various Compositions

Table 1 shows the surface property of SiO_2–Al_2O_3(I) of various compositions, which were used as catalyst carriers. The catalytic activity of MoO_3–CoO mounted on the carriers by preparation method II

TABLE 1

Surface Property of SiO_2–Al_2O_3 (I) of Various Compositions

SiO_2–Al_2O_3 (I) (mol% of SiO_2)	Surface area (m^2/g)	Acidity (mmol/g)		Amount of OH (mmol/g)
		$H_0 \leqq 2.0$	$H_0 \leqq 6.8$	
0	313	Tr	0.06	0.75
10	238	0.01	0.07	0.75
20	279	0.03	0.09	0.76
40	193	0.03	0.13	0.71
60	172	0.10	0.12	0.67
80	245	0.20	0.24	0.37
90	238	0.16	0.21	0.57
100	242	Tr	0.07	0.10

and the amounts of MoO_3 and CoO are given in Table 2. The amounts of mounted MoO_3 and CoO change with the change of silica content in the carriers. The percentage conversion of thiophene varies largely depending on the amount of MoO_3. However, the percentage conversion per gram of MoO_3 are not the same. Since high conversions per gram of MoO_3 were observed when the ratios of MoO_3/CoO were low, the contribution of CoO to the activity cannot be neglected, though it is small. In the case where MoO_3–CoO–SiO_2–Al_2O_3 was prepared by preparation method I, the conversion per gram of MoO_3 showed a trend similar to the case where the catalyst was prepared by preparation method II. In general, the activity seems to depend mainly on the amount of MoO_3.

TABLE 2

Catalytic Activity of MoO_3–CoO–SiO_2–Al_2O_3 for Hydrocracking of Thiophene

Catalyst				Activity	
Mol% of SiO_2 in SiO_2–Al_2O_3 (I)	Amount (wt%) of		Ratio of MoO_3/CoO	Conversion (%)	% conversion/g of MoO_3
	MoO_3	CoO			
0	11.6	1.95	6.0	64.0	0.83
10	12.3	1.73	7.1	64.9	0.79
20	12.6	1.89	6.7	67.0	0.80
40	11.6	1.95	6.0	62.2	0.81
60	7.2	1.68	4.3	60.4	1.26
80	2.3	1.11	2.1	19.3	1.29
90	6.1	1.45	4.2	42.8	1.06
100	1.5	0.25	6.0	5.7	0.59

It is apparent from Tables 1 and 2 that there is no correlation between the amount of MoO_3 and the specific surface area of the carriers. There was found an inverse relation of the amount of MoO_3 with the acidic property of the carriers. Namely, comparatively smaller amounts of MoO_3 are mounted on the SiO_2–Al_2O_3(I) containing 60–90 mol% of SiO_2 whose acid amounts are comparatively larger. The silica–aluminas containing 0–20 mol% of SiO_2, which have comparatively smaller or no acid amounts hold comparatively larger amounts of MoO_3. The fact that white precipitates were formed during the immersion of carriers having high acidity seems to indicate that acid sites react with ammonium molybdate to form the precipitates and hence the acidity of carriers causes the amount of MoO_3 to decrease. However, a small amount of MoO_3 was mounted on 100% SiO_2 in spite of the low acidity of the support. On the other hand, a fairly good correlation was found between the amount of MoO_3 and the amount of surface hydroxyl groups, as shown in Fig. 1. The surface OH groups measured by the fluoride exchange method are probably *anionic*. Certainly, the OH concentration of 100% SiO_2 is very much lower than the total actually present. Thus, the correlation between the amount of anionic hydroxyl group and the hydrocracking activity is better than the inverse relation between the acidity and the hydrocracking activity.

Correlation between the Amount of MoO_3 and the Amount of OH over Various Carriers

The correlation tested by employing various carriers is shown in Fig. 2. The larger the amount of anionic OH on the carriers, the larger the amount of MoO_3

which can be mounted. The largest amount of MoO_3 was observed for a $MgO–Al_2O_3$ carrier which has the largest amount of anionic OH.

In order to examine further the correlation, aluminas (VI) and (VII), which have different amounts of surface OH, were prepared by immersing the aluminas into an aqueous solution of ammonium fluoride of different concentrations for different times of immersion and the amounts of mounted MoO_3 were determined. As shown in Fig. 3, a good correlation was obtained between the amount of MoO_3 and the amount of OH. The amount of MoO_3 decreased with the decrease of the amount of OH accompanied by treating with fluorine ions. From these results, the amount of anionic OH which can be exchanged by fluorine ion is concluded to play an important role for controlling the amount of mounted MoO_3 which governs the catalytic activity for the hydrocracking of thiophene.

Interaction of MoO_3 with Carriers

It is pointed out by the experiments on reduction with hydrogen (*29*) and the measurements of electrical conductivity (30–31), esr (*2*) and ir (*7*) spectra that some chemical interactions exist between MoO_3 and Al_2O_3. According to esr study, Dufaux *et al.* (*2*) reported that MoO_3 interacts with γ-Al_2O_3 through the process of

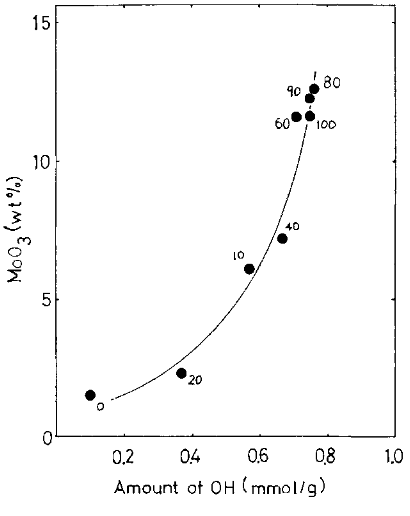


FIG. 1. The correlation between the amount of MoO_3 in MoO_3–CoO–SiO_2–Al_2O_3 and the amount of OH on SiO_2–Al_2O_3(I). The numerals show the mol% of SiO_2 in SiO_2–Al_2O_3(I).

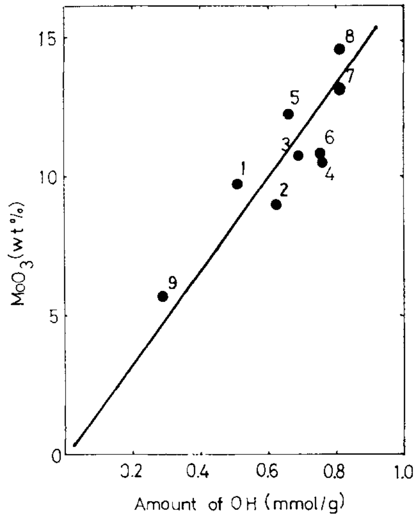


FIG. 2. The correlation between the amount of MoO_3 in MoO_3-carriers and the amount of OH on various carriers. (1) Al_2O_3(I), (2) Al_2O_3(II), (3) Al_2O_3(III), (4) Al_2O_3(IV), (5) Al_2O_3(V), (6) Al_2O_3(VI), (7) SiO_2–Al_2O_3(II), (8) 10% MgO–Al_2O_3, (9) active carbon.

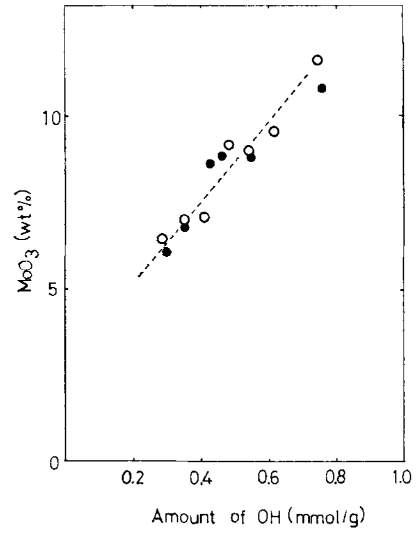
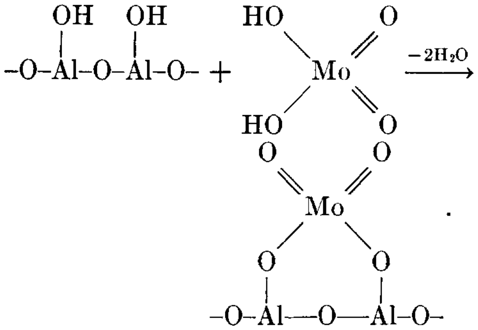


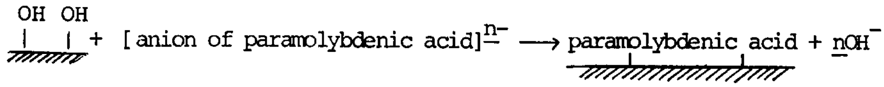
FIG. 3. The correlation between the amount of MoO_3 in MoO_3–Al_2O_3(VI) and MoO_3–Al_2O_3(VII) and the amount of OH on partially fluorinated carrier surfaces. (●) MoO_3–Al_2O_3(VI), (○) MoO_3–Al_2O_3(VII).

immersion and calcination as shown by scheme I.



(I)

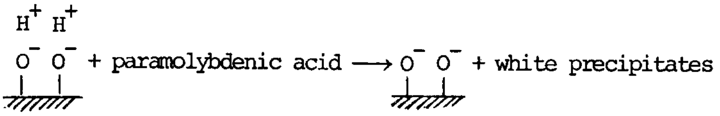
Thus, the amount of OH over Al_2O_3 is important for the formation of the binary oxide. Our observation that the amount of MoO_3 correlates with the amount of anionic OH supports the validity of scheme I and persists the anionic nature of the OH groups. However, it seems to be more valid to assume the exchange of OH group with the anion of paramolybdenic acid, because MoO_3 is in the form of molybdenum salt during the immersion, as shown below:



(II)

The exchanged paramolybdenic acid makes stronger bonds with alumina by drying and calcination.

On the other hand, acidic OH groups which leave oxygen anions on the carrier react with paramolybdenic acid to form white precipitates. In this case, the amount of MoO_3 becomes less.



(III)

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