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HIGH ACTIVITY OF MoO_3-SnO_2 FOR HYDROCRACKING OF DIPHENYL ETHER AND DIPHENYLMETHANE

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Of four newly synthesized catalysts designed for coal liquefaction, MoO_3-SnO_2 was superior for use with diphenyl ether and diphenylmethane with either H_2 or CO + H_2O. This agrees with the results of using these catalysts with a sub-bituminous coal. Carbon monoxide and H_2O is superior to H_2 for ether cleavage, whereas H_2 is better for hydrocarbon cleavage.

The MoO_3-CoO and MoO_3-CoO-Al_2O_3 are known as active catalysts for the liquefaction of coal. Recently, those catalysts have been used for the hydrocracking of model compounds of coal to understand the liquefaction mechanism.[1)] Since MoO_3-SnO_2 was found to show highest activity among a series of complex molybdenum oxide catalysts for the hydrocracking of a sub-bituminous coal,[2)] we tried to use MoO_3-SnO_2 as a catalyst for the hydrocracking of diphenylmethane and dephenyl ether as model compounds of coal to see the cleavage of aliphatic and ether linkages between aromatics. For comparison, the activity of newly synthesized Fe_2O_3-SiO_2, Fe_2O_3-TiO_2, Fe_2O_3- ZrO_2, and commercially available MoO_3-CoO catalysts were also studied. The gases, CO + H_2O were also used as reducing agents to determine the potential of using the lower cost synthesis gas as a substitute for H_2.

The MoO_3-SnO_2 catalyst was prepared by hydrolysis of a mixed solution of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and tin tetrachloride with ammonia water, the final pH being 8. The precipitate was aged over a water bath for 2 h, then washed with deionized water, dried at 120°C for 24 h, and finally calcined at 500°C for 3 h in air. The atomic ratio of Mo/Sn was 1/1. The Fe_2O_3-SiO_2, Fe_2O_3-TiO_2, and Fe_2O_3-ZrO_2 catalysts were prepared by impregnation of $Fe(NO_3)_3$ on each support from the aqueous solution, followed by calcination at 500°C in air. The supports, SiO_2, TiO_2, and ZrO_2, were prepared by hydrolyses of ethyl orthosilicate, $TiCl_4$, and $ZrOCl_2$, respectively, followed by calcination at 500°C in air. The contents of Fe in the catalysts were 1/9 in atomic ratio of Fe to the metallic components of supports in all cases. The cobalt molybdate catalyst is commercially available one (Ht-400 E 1/16 of the Harshaw Chemical Company).

The reactions using H_2 as a reducing agent were done in 12 ml stainless steel reactors at 425°C for 2 h on a rocking heater mount. The diphenylmethane and diphenyl ether were used at 0.0025 moles each. Hydrogen was used at 0.0259 moles (5.17×10^6 Pa) in each reactions. The oxide catalysts were used at 10 wt% of the starting material in all reactions. In all the reactions, 0.2 ml of water was used to avoid a lot of charring at 425°C. Argon was added to make up the starting pressure to 1.03×10^7 Pa at room temperature. Glass beads were put in the reactors to ensure homogeneous mixing of the gases at the reaction temperature. After 2 min of heating time and 2 h of reaction, the reactions were quenched by immersing the reactors in acetone-dry ice mixture to avoid any possible loss of volatile products. The contents of the reactors were then taken out with ether. The ether solutions were dried over anhydrous magnesium sulfate and analyzed with a GC Varian 2100 using 1.8 m 3 % OV 17 column.

The reactions using CO + H_2O as a source of hydrogen were done similarly as in the case of diphenylmethane. The starting materials were used at 0.0025 mole. The CO was used at 0.0259 mole (5.17×10^6 Pa) and H_2O at 0.015 mole.

All reactions are duplicated and values in Tables 1-4 are averaged. The results in all the Tables are shown in weight percent of the starting material. The conversion is based on recovered starting material.

Table 1. Hydrocracking of Diphenylmethane with H_2

Catalyst	PhH, %	$PhCH_3$, %	$PhCH_2CH_2Ph$, %	Others, %	Conversion, %
none	5.2	4.6	Trace	Trace	14.9
$CoO \cdot MoO_3$	11.5	12.8	Trace	6.5	39.5
$Fe_2O_3 \cdot SiO_2$	15.6	13.7	2.6	12.0	48.4
$Fe_2O_3 \cdot TiO_2$	8.6	7.5	0.8	2.0	26.5
$Fe_2O_3 \cdot ZrO_2$	11.2	8.3	1.3	5.0	28.6
$MoO_3 \cdot SnO_2$	13.7	12.2	2.9	12.5	45.0

Table 2. Hydrocracking of Diphenylmethane with CO + H_2O

Catalyst	PhH, %	$PhCH_3$, %	$PhCH_2CH_2Ph$, %	Others, %	Conversion, %
none	Trace	Trace	---	---	Trace
$CoO \cdot MoO_3$	2.5	3.2	Trace	3.1	9
$Fe_2O_3 \cdot SiO_2$	1.3	2.1	Trace	2.0	5.5
$Fe_2O_3 \cdot TiO_2$	Trace	Trace	---	---	Trace
$Fe_2O_3 \cdot ZrO_2$	Trace	Trace	---	---	Trace
$MoO_3 \cdot SnO_2$	7.1	6.8	1.2	3.3	18.4

The results of the hydrocracking of diphenylmethane with H_2 are shown in Table 1. The conversion effectiveness of the catalysts was in the order of Fe_2O_3-SiO_2≈MoO_3-SnO_2>CoO-MoO_3>Fe_2O_3-ZrO_2≈Fe_2O_3-TiO_2. The main products were benzene and toluene. The weight percentages of benzene were almost the same as those of toluene.

Table 3. Hydrocracking of Diphenyl Ether with H_2

Catalyst	PhH, %	PhOH, %	Conversion, %
none	Trace	Trace	Trace
CoO·MoO_3	5.8	5.1	11.8
Fe_2O_3·SiO_2	Trace	Trace	Trace
Fe_2O_3·TiO_2	Trace	Trace	Trace
Fe_2O_3·ZrO_2	Trace	Trace	Trace
MoO_3·SnO_2	5.5	4.8	10.5

Table 4. Hydrocracking of Diphenyl Ether with CO + H_2O

Catalyst	PhH, %	PhOH, %	Others, %	Conversion, %
none	Trace	Trace	Trace	Trace
CoO·MoO_3	6.1	5.1	2.5	14.0
Fe_2O_3·SiO_2	2.5	3.8	4.0	10.0
Fe_2O_3·TiO_2	4.9	3.5	2.6	12.0
Fe_2O_3·ZrO_2	Trace	Trace	Trace	Trace
MoO_3·SnO_2	6.2	4.7	3.8	15.0

In the hydrocracking of diphenylmethane with CO + H_2O, the MoO_3-SnO_2 catalyst exhibited a very high activity as shown in Table 2. The activity of MoO_3-SnO_2 is much higher than that of Fe_2O_3-SiO_2. The activity is considered to be governed by the activity for the water gas shift reaction, $CO + H_2O \longrightarrow CO_2 + H_2$, i.e., the reaction is controlled by hydrogen evolution from CO and H_2O. The product distribution provides no additional clarification of the process, since the amounts of benzene and toluene were almost the same. For comparison, the hydrocracking of 1,2-diphenylethane (bibenzyl) with CO + H_2O was carried out under the same reaction condition. The conversion was 52 % in the absence of catalyst and the effect of catalyst was small. The result that bibenzyl is more reactive than diphenylmethane is in agreement with the conclusion that the longer the carbon chain which combines aromatics, the easier the cleavage of the aliphatic carbon-carbon bond.1)

The hydrocracking of diphenyl ether with H_2 or CO + H_2O are shown in Tables 3 and 4. For the hydrocracking with H_2, only two catalysts, CoO-MoO_3 and MoO_3-SnO_2, were active, but the other three iron catalysts were inactive. For the hydrocracking with CO + H_2O, however, Fe_2O_3-SiO_2 and Fe_2O_3-TiO_2 became active. The catalytic activity for CO + H_2O is in the order of MoO_3-SnO_2 $\simeq$ CoO-MoO_3 > Fe_2O_3-TiO_2 $\simeq$ Fe_2O_3-SiO_2 $\gg$ Fe_2O_3-ZrO_2. The main reaction products in the hydrocracking of diphenyl ether were benzene and phenol, the amount of each product was almost the same.

The % conversion in the hydrocracking of diphenyl ether with H_2 is lower than that in the hydrocracking of diphenylmethane with H_2 (cf. Tables 1 and 3). This contradicts with the conclusion that the cleavage of ether bond is easier than that of carbon-carbon bond$^{1)}$, indicating that the conclusion depends on the reaction condition and nature of catalyst. It is interesting that the ether conversions are higher with CO + H_2O than with H_2.

In any cases, MoO_3-SnO_2 was found to show high catalytic activity. This is considered due to the high ability of $SnO_2$$^{3)}$ to reduce MoO_3 to form active species. The order of catalytic activity (% conversion) for the hydrocracking of a sub-bituminous coal (Taiheiyo coal) was MoO_3-SnO_2 (84) > Fe_2O_3-ZrO_2 (73) > MoO_3-CoO-Al_2O_3 (<68) > Fe_2O_3-SiO_2 (60 %)$^{2)}$. Neither the diphenylmethane results nor the diphenyl ether results alone predict the relative order of catalytic activity for Taiheiyo coal; however, the results taken together predict the MoO_3-SnO_2 catalyst to be equal or better than CoO-MoO_3. Therefore, the cleavage of carbon-carbon bond of diphenylmethane and carbon-oxygen bond of diphenyl ether plays an important role but not an exclusive one for the hydrocracking of the sub-bituminous coal.

Carbon monoxide and water appears to be superior to hydrogen for ether cleavage, whereas hydrogen is better for hydrocarbon cleavage. Therefore, synthesis gas has the potential as a superior reducing gas mixture to either alone.

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