HYDROTALCITE CATALYSIS OF HYDROTREATING REACTIONS

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Magnesium-aluminum hydrotalcites have been tested for hydrotreating coal liquids. To understand the mechanism of the reactions that are catalyzed by the hydrotalcites, model compounds have been reacted with various potential hydrogen donors in the presence of several forms of the hydrotalcites. Aryl-heteroatom bonds are easily cleaved by hydrogen at temperatures below 350°C, not only with terephthalate-pillared hydrotalcite, but also with hydrotalcite carbonate. Evidence favors a Lewis acid catalysis mechanism for this process. Although molecular hydrogen is required for heteroatom cleavage, no activation of molecular hydrogen or any hydrogen donor molecule occurs on the hydrotalcite. Thiomolybdate-exchanged pillared hydrotalcite is converted to an active hydrogenation catalyst at these temperatures. However, higher temperatures are required for hydrocracking activity.

INTRODUCTION

Novel supports for metallic sulfide catalysts have been under investigation for their potential use in coal liquefaction. Conventional supported hydrogenation catalysts have encountered difficulties in coal liquefaction due to deactivation and coking (1-4). New catalysts may require more dispersed forms of catalytic sites or greater micropore dimensions to improve accessibility to catalytic sites. Hydrotalcites have been utilized in catalytic processing of various types (5-10), and recently, pillared hydrotalcites with large micropores were utilized in oxidation reactions (11).

This paper describes recent efforts to understand the effects of the hydrotalcite structure during hydrotreatment processing. Model compounds were treated with hydrogen and hydrogen donors in the presence of various pillared and nonpillared hydrotalcites.

EXPERIMENTAL

The following reagents: bibenzyl, cumene, 1-methylnaphthalene, diphenyl sulfide, 9,10-dihydroanthracene, and neopentylbenzene were obtained from Aldrich Chemicals, Co., Milwaukee, Wisconsin.

Preparation of Catalysts:

Hydrotalcites and molybdenum-exchanged hydrotalcites were prepared as described earlier (11,12). Instead of ammonium molybdate, ammonium tetrathiomolybdate was used for exchange into hydrotalcite. For the preparation of formate-pillared hydrotalcite, 160 mL of carbon dioxide-free distilled water were placed in a three-necked round-bottomed flask fitted with nitrogen inlet and outlet tubes and a dropping funnel. The system was purged with nitrogen for 30 minutes. Sodium formate (21.77 g) and sodium hydroxide (57.66 g) were placed into the reaction flask and stirred. When the dissolution of sodium formate was complete, a solution of 41.04 g of magnesium nitrate hexahydrate and 30.0 g of aluminum nitrate nonahydrate in 128 mL of carbon dioxide-free water was added dropwise into

the flask. The addition was completed after about one hour. A gel-like white precipitate was formed. The dropping funnel was then replaced by a reflux condenser and the reaction mixture heated to 75-85°C and allowed to stir overnight. After 9 hours had elapsed, about one third of the water had escaped from the container, so additional carbon dioxide-free water was added to bring the volume back to its original level and the reaction stirred for 9 more hours. The crude product was isolated by vacuum filtration and purified by resuspending in carbon dioxide-free water and centrifuging. The pasty white material was dried by heating in vacuum at 65°C until all the moisture had been driven off. The infrared spectum of the formate-hydrotalcite showed strong absorptions at 1593 and 1379-1406 cm^{-1} which are consistent with bands expected for the antisymmetrical and symmetrical vibrations of the COO^- structure (13).

Infrared spectra were obtained in KBr on either a Perkin Elmer Model 283 spectrometer or a Nicolet 20SXB FTIR spectrometer, equipped with a mercury cadmium telluride (MCTA) detector, and a Nicolet 1280 computer with a fast Fourier transform coprocessor. Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with Pectrocol column. Isooctane and n-octadecane were the internal standards. GC/MS was performed on a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron film of DB-5. A 15-m x 0.25-mm (ID), 0.25-micron DB-5 film capillary column was used for the analysis of high-boiling components. A Dupont Model 951 thermogravimetric analyzer module interfaced with a Dupont Model 1090 thermal analyzer was used to determine the thermal decomposition of the catalysts.

Hydrotreating Reactions:

In a typical run, 0.5 g of substrate and 0.25 g of catalyst were placed in a tubing bomb reactor. The reactor was sealed and pressurized with 68 atm of hydrogen or deuterium if needed, placed in a rocking autoclave heated to desired temperature, and heated for three hours. The reactor was cooled in dry ice-acetone slurry, degassed, and opened. The contents of the reactor were mixed with an appropriate internal standard and transferred into a centrifugation tube by washing with dichloromethane. The solid was separated by centrifugation. The liquid sample was analyzed by quantitative GC and GC/FTIR/MS. The solid was dried in vacuum at 110°C for 3 hours. The analytical data are given in Table 1.

RESULTS AND DISCUSSION

A thermogravimetric method was used to determine the thermal decomposition of hydrotalcite and supported-hydrotalcite catalysts. Heating terephthalate-pillared hydrotalcite to 100°C resulted in 3.8% weight loss. This can be assumed to be the loss of interstitial water. For the tetrathiomolybdate-exchanged terephthalate-pillared hydrotalcite, the weight loss continued to 240°C. The additional loss may be due to the removal of sulfur from MoS_4 moieties. In the 240-300°C range, rapid loss was observed, which could be due to further loss of sulfur to form MoS_2 moieties. When the temperature was increased further, the weight loss was more or less continuous until 466°C. A 25% weight loss occurred in this temperature regime, which may be attributed to the decomposition of terephthalate. The weight loss is not consistent with that expected for decomposition of the hydrotalcite layer structure. Thus the hydrotalcite layer structure is stable at temperatures used for hydrotreating reactions.

In order to identify the selectivity and reactivity of hydrotalcite catalysts, the reactions of model compounds such as bibenzyl, 1-methylnaphthalene, cumene, neopentylbenzene, and dipheny sulfide were carried out with hydrotalcite, pillared

hydrotalcite, and molybdenum sulfide supported on hydrotalcite catalysts. Diphenyl sulfide was used as a test compound to investigate the catalytic activity of hydrotalcite catalysts for aryl-sulfur bond cleavages. The reaction of diphenyl sulfide with terephthalate-pillared hydrotalcite at 300°C for 3 hours in the presence of 68 atm of hydrogen gave 86.4% conversion of the substrate into products (Table 1). Reaction products were mainly benzene and H_2S, along with a small amount of benzenethiol. When the same reaction was carried out in the absence of catalyst, the conversion was very small (1%). A trace amount of benzene was the only product. The reaction of diphenyl sulfide with tetrathiomolybdate-exchanged terephthalate-pillared hydrotalcite at 300°C for 3 hours in the presence of 68 atm of hydrogen gave a high conversion (88.9%) of diphenyl sulfide. The major product from this reaction was benzene. Small amounts of cyclohexane, thiophenol, cyclohexanethiol were also formed. Nonpillared hydrotalcite (carbonate) gave conversion and product distributions

TABLE 1. CATALYTIC HYDROTREATING OF DIPHENYL SULFIDE (DPS)

Reaction Temp. = 300°C, Reaction Time = 3 hrs
Catalyst wt./Substrate wt. = 0.5, H_2 = 68 atm

Catalyst (g)	Substrate (mmol)	Conv. (%)	Major Products (mmol)
None	DPS (2.68)	1	Benzene (trace)
Mg-Al-HT (0.25)	DPS (2.73)	81.7	Benzene (4.5) Benzenethiol (0.13)
Zn-Cr-HT (0.25)	DPS (2.64)	60	Benzene (2.9) Benzenethiol (tr.)
PH-HT (0.25)	DPS (2.95)	86.4	Benzene (4.4) Benzenethiol (0.12)
F-HT (0.25)	DPS (2.71)	83.4	Benzene (4.0) Benzenethiol (0.2)
MgO (0.25)	DPS (2.67)	2	Benzene (trace)
Calcined Mg-Al-HT (0.25)	DPS (2.74)	40	Benzene (1.9) Benzenethiol (0.15)
Mo-PH-HT (0.25)	DPS (2.79)	88.9	Benzene (4.5) Cyclohexane (0.1)

Mg-Al-HT = Magnesium aluminum hydrotalcite carbonate
Zn-Cr-HT = Zinc chromium hydrotalcite nitrate
PH-HT = Terephthalate-pillared hydrotalcite
F-HT = Formate-exchanged hydrotalcite
Mo-PH-HT = Molybdenum-exchanged terephthalate-pillared hydrotalcite

similar to the terephthalate-pillared hydrotalcite described above. Thus neither the molybdenum (sulfide) nor the pillared structure are required for carbon-sulfur bond cleavage; the hydrotalcite itself is sufficient for catalysis of hydrogenolysis of these bonds. The active sites for this catalysis were hypothesized to be electron deficient aluminum sites in the hydrotalcite layer. The hydrotalcite-carbonate was calcined at 450°C to dehydrate and decompose carbonate. The hydrotalcite layer structure is significantly altered at higher temperatures. The calcined hydrotalcite was then used to catalyze the hydrogenolysis reaction of diphenyl sulfide. The conversion was low, but activity was not totally lost. Magnesium oxide was, however, completely inactive as a catalyst for diphenyl sulfide hydrogenation. These oxides are, of course, basic, but the calcined hydrotalcite may still contain active Lewis acid sites corresponding to trigonal Al atoms.

With zinc-chromium hydrotalcite (nitrate) as the catalyst, the conversion was significantly lower (60%). The product distribution was the same as that with magnesium-aluminum hydrotalcite carbonate. The conversion and product distributions from the reaction of formate-exchanged hydrotalcite were also comparable with that of terephthalate-pillared hydrotalcite. Unlike reactions with solid acid catalysts, no coking, oligomeric products, or dibenzothiin were observed in any of the reactions (14).

Reactions of diphenyl sulfide with terephthalate-pillared hydrotalcite (no molybdenum) in the absence of hydrogen gas indicated a very small conversion (3%) of diphenyl sulfide into products. A trace amount of benzene was the only product from this reaction (Table 2). Thus molecular hydrogen is required for carbon-sulfur bond cleavage in the hydrotalcite reactions. This was not the case in the reactions of various model compounds with strong acid catalysts, where products such as benzene were observed even when molecular hydrogen was not present. These products could be derived from proton addition to the ipso position of the benzene ring (Brönsted-acid mechanism) followed by cleavage of the substituent groups and probably hydride donation from Scholl intermediates. No condensation to oligomeric or polymeric material or coke was observed for any of the hydrotalcite reactions carried out in the absence of molecular hydrogen. This fact and the requirement for molecular hydrogen are inconsistent with a Brönsted acid mechanism for the hydrotalcite reaction.

When hydrogen was replaced by deuterium, the conversion of diphenyl sulfide was considerably smaller. The decreased conversion could be attributed to isotope effects. The majority of the benzene product was singly labeled, but multiple labeling was also observed. No deuterium was incorporated into the recovered diphenyl sulfide.

The reaction of molecular hydrogen with 1-methylnaphthalene was investigated with the hydrotalcite to determine if the hydrotalcite structure can catalyze the addition of hydrogen. The conversion of 1-methylnaphthalene was only 9% with the phthalate-pillared hydrotalcite, whereas the tetrathiomolybdate-exchanged phthalate-pillared hydrotalcite gave 95% conversion. Only a small amount of cracking to naphthalene occurred in either reaction. It is clear that the tetrathiomolybdate in the interstitial layer was converted to a form that was highly active for catalyzing the addition of molecular hydrogen to aromatics. It is not yet known what the form of molybdenum is: MoS_2 microcrystals, MoS cluster, or some monomeric form.

TABLE 2. REACTIONS OF DIPHENYL SUFIDE

Reaction Temp. = 300°C, Reaction Time = 3 hrs
Catalyst wt./Substrate wt. = 0.5

Catalyst (g)	Substrate (mmol)	Reduc. (psi/g)	Conv. (%)	Major Products (mmol)
PH-HT (0.25)	DPS (2.77)	None	3.0	Benzene (tr.)
PH-HT (0.25)	DPS (2.95)	Hydrogen 68 atm	86.4	Benzene (4.4) Benzenethiol (0.12)
PH-HT (0.25)	DPS (2.67)	Deuterium 68 atm	21.1	Benzene (0.4) Benzenethiol (tr.)
PH-HT (0.25)	DPS (2.75)	CO/H_2O 68 atm 0.22 g	10.2	Benzene (0.3) Benzenethiol (tr.)
PH-HT (0.25)	DPS (2.77)	DHA 1.00 g	9.0	Benzene (0.3) Benzenethiol (tr.)
PH-HT 0.25	DPS (2.83)	Methanol 1.00 g	7.1	Benzene (0.2)
F-HT (0.25)	DPS (2.79)	None	4.0	Benzene (tr.) Benzenethiol (tr.)

Thus, the hydrotalcite structure itself (no molybdenum) possesses significant capability for hydrodesulfurization. Since only minimal hydrogenation was observed with 1-methylnaphthalene, we conclude that hydrotalcite does not activate hydrogen, but hydrogen is required for the conversion of diphenyl sulfide with hydrotalcite. The question of how the C-S bonds are cleaved in the presence of hydrogen is very interesting and deserves further study. Since molecular hydrogen is evidently not activated directly by the hydrotalcite catalyst for addition to aromatics, the use of hydrogen sources other than molecular hydrogen was examined to determine whether the hydrotalcite catalyst could catalyze the transfer of hydrogen from these hydrogen sources to a sulfur-containing species, thereby catalyzing reductive cleavage of the C-S bond. The interlayer space of hydrotalcite contains basic species that could be involved in the formation of hydride-donor intermediates that would affect the reduction. Since carbon monoxide and water generate potential hydride donor species in the presence of a base, the reaction of diphenyl sulfide in this system was investigated (no molecular hydrogen added). Conversion was very small (10%). Hydrotalcite (formate) gave a similar poor conversion in the absence of hydrogen. Methanol has been shown to be an effective reductant in basic conditions, but it also gave a poor conversion of diphenyl sulfide in the reaction with hydrotalcite. A radical hydrogen transfer mechanism is another route for reduction of the C-S bond. The reaction of diphenyl sulfide was carried out in the presence of 9,10-dihydroanthracene. If the mechanism involved homolytic cleavage of the C-S bond to give a radical intermediate, this radical intermediate should be able to abstract hydrogen from dihydroanthracene. However, the conversion in the experiment was,

again, very poor (9%). Since the conversions in these experiments are a bit higher than in the case with no hydrogen or no reductant, there may have been some small amount of hydrogen generated in the experiments as a result of a water-gas reaction or dihydroanthracene decomposition to hydrogen.

No evidence for phenol was found in any reaction. The formation of phenol would have indicated that the basic species directly attacked the C-S bond. Catalysis of the C-S bond cleavage appears to be associated with the hydrotalcite layers, rather than basic species. Because of the aluminum atoms in the layer structure, many electron deficient sites (Lewis acids) are available for catalysis. The reactions observed with hydrotalcites are significantly different from reactions with other solid acid catalysts, however, since condensations and formation of dibenzodithiin were not found.

The hydrocracking activity of hydrotalcite and molybdenum supported on hydrotalcite was investigated by reacting bibenzyl, cumene, and neopentylbenzene with this catalyst. The reaction of bibenzyl with molybdenum supported on hydrotalcite at 300°C for 3 hours and in the presence of 68 atm of hydrogen gave a small percent conversion. Traces of benzene and toluene were the only products. Increasing the temperature (350 and 400°C) resulted in an increase in the percent conversion of bibenzyl (25 and 40%, respectively). Benzene, toluene, and ethylbenzene were major products of this reaction. Previous studies with solid acid catalysts gave mostly benzene and ethylbenzene via the Brönsted acid-ipso cleavage mechanism. The large amount of toluene formed from bibenzyl indicates that a major pathway for hydrocracking in the HT-catalyzed reaction is cleavage of the bond adjacent to the ring (α-β cleavage). A similar cleavage was observed for the reaction of cumene with HT catalyst, which gave ethylbenzene as the major product. Other products resulted from Lewis acid-catalyzed rearrangement and alkyl addition reactions of the cumene. Neopentylbenzene exhibited similar α-β cleavage to give toluene.

A mechanism involving the Lewis acid HT sites is shown in Figure 1. Al in the figure represents an electron deficient Lewis acid site that bonds to the aryl ring.

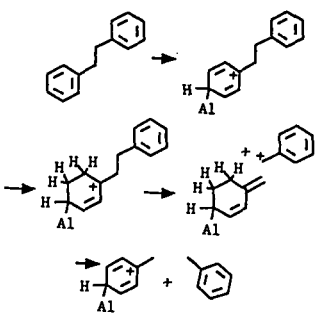

Figure 1. Hydrotalcite-catalyzed mechanism.

TABLE 3. CATALYTIC HYDROTREATMENT OF MODEL COMPOUNDS

Reaction Time = 3 hrs, Hydrogen = 68 atm
Catalyst wt./Substrate wt. = 0.5

Catalyst (g)	Substrate (mmol)	Temp. (°C)	Conv. (%)	Major Products (mmol)
PH-HT (0.25)	1-MENP (3.66)	350	9	Methyltetralins (0.1) Naphthalene (0.06)
MO-PH-HT (0.25)	(1-MENP) (3.67)	350	94.6	Methyltetralins (2.8) Decalin (0.2) Naphthalene (0.06) Tetralin (0.12)
PH-HT (0.25)	BB (2.69)	300	8	Benzene (tr.) Toluene (tr.)
Mo-PH-HT (0.25)	BB (2.76)	350	25	Benzene (0.04) Toluene (0.1) Ethylbenzene (0.2)
MO-PH-HT (0.25)	BB (2.75)	400	40	Benzene (0.2) Toluene (0.4) Ethylbenzene (0.2)
PH-HT (0.25)	Cumene (4.10)	400	14	Ethylbenzene (0.3) Benzene (0.1) n-Propylbenzene (0.1)
PH-HT (0.25)	NPB (3.40)	400	23.8	Benzene (0.13) Toluene (0.5)

PH-HT = Molybdenum-exchanged terephthalate-pillared hydrotalcite
DPS = Diphenyl sulfide
BB = Bibenzyl
NPB = Neopentylbenzene

CONCLUSIONS

Thiomolybdate-exchanged terephthalate-pillared hydrotalcite is converted to active hydrogenation catalyst during heating with the substrates. Effective hydrodesulfurization activity resides with the hydrotalcite portion of the catalyst. At higher temperatures, hydrocracking activity is also observed.

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