



Synthesis, characterization, and application of hydrotalcites in hydrodesulfurization of FCC gasoline

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Abstract

Magnesium–aluminum, copper–aluminum, zinc–aluminum hydrotalcite(HT) compounds were synthesized using co-precipitation method. The effects of stirring rate, feeding rate of reactants, pH, calcination temperature on the properties of Mg–Al mixed oxides were investigated by using XRD, TG-DTA and BET techniques. The catalytic activity and selectivity of CoMo/ γ -Al₂O₃, CoMo/ γ -Al₂O₃+HT catalysts for hydrodesulfurization of FCC gasoline were examined in a high pressure microreactor. The results showed that the catalysts with mixed oxide obtained from hydrotalcite as support give lower levels of olefin hydrogenation than the catalyst with γ -Al₂O₃ as support, and lower octane number reduction and hydrodesulfurization yield, too. The hydrodesulfurization activity order was as follows: CoMo/ γ -Al₂O₃>CoMo/ γ -Al₂O₃+Mg–Al(HT)>CoMo/ γ -Al₂O₃+Cu–Al(HT)>CoMo/ γ -Al₂O₃+Zn–Al(HT), and the olefin hydrogenation activity and octane number reduction order were as follows: CoMo/ γ -Al₂O₃+Zn–Al(HT)<CoMo/ γ -Al₂O₃+Cu–Al(HT)<CoMo/ γ -Al₂O₃+Mg–Al(HT)<CoMo/ γ -Al₂O₃.

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1. Introduction

It is well known that a major source of air pollution is the exhausts from fuel combusted in hundreds of millions of motor vehicles. Regulations have been enacted to reduce harmful motor vehicle emissions through more stringent fuel standards. Fuels containing

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sulfur give sulfur oxide, which is the largest contributor to NO_x emissions from fuel combustion [1]. On the other hand, sulfur compounds in the fuel are poisonous to catalytic converter fixed in the automobile. To reduce or resolve these environmental problems, the sulfur content in the fuel has been, and will continue to be reduced to a lower and lower level.

All cuts go to the gasoline pool, nearly all of the sulfur (85–95%), in a typical refining factory, comes from FCC gasoline containing a high olefin content and thus a high octane number [2,3]. As a result, FCC gasoline is the focus for sulfur reduction. Elimination of the sulfur from cracked naphtha is easy, but during the HDS processing using traditional HDS catalysts, saturation of the olefins occurs significantly, resulting in the great reduction of the octane number. Therefore, the key technical problem for HDS of FCC gasoline is to do deep sulfur removal, at same time, to reduce the loss of octane number occurring in the HDS process. One feasible method for the aim is to design a catalyst with favorable activity that can finish needed HDS but with lower loss of octane number.

In order to reach the target, some researches have been carried out. Yu and Myers [4] and Sudhakar [5] disclose selective desulfurization of cracked naphtha by using special catalysts with hydrotalcite as support. Kukes et al. [6] reported the use of novel catalysts comprising a hydrogenation component and a support component which comprises a magnesium component and an alkali metal component. Hydrotalcite compounds have been used in recent years as precursors of oxide catalysts and catalyst support [7–9]. It is the key for HDS of FCC gasoline to prepare an efficient catalyst for removing sulfur from olefin containing feedstocks with minimum loss of octane number. Now, it has been found that the selectivity for hydrodesulfurization was improved significantly by using a catalyst support comprising essentially a Mg–Al hydrotalcite composition, but HDS activity was reduced unavoidably [10].

In this paper, Mg–Al, Cu–Al, Zn–Al hydrotalcite compounds were synthesized using co-precipitation method. The activity and selectivity of CoMo sulfide catalysts supported on Mg–Al, Cu–Al, Zn–Al mixed oxide supports obtained from hydrotalcite compounds were evaluated by hydrodesulfurization of FCC gasoline. TG-DTA, XRD, BET techniques were used to characterize the structure and properties of supports. The relationship between the hydrodesulfurization activity and catalysts properties were discussed. The discussion is focus on the affection of support on the HDS, hydrogenation (HYD) activity and research octane number (RON) loss of FCC gasoline.

2. Experimental

2.1. Preparation of hydrotalcite

Hydrotalcite samples were prepared by co-precipitating an aqueous solution of magnesium and aluminum salts with a highly basic carbonate solution [11]. The first solution (A solution) containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively, dissolved in deionized water at Mg/Al, Cu/Al, Zn/Al molar ratio of 3:1. The second solution (B solution) containing appropriate amounts of sodium hydroxide–sodium carbonate was

added on a certain ratio so that the final $\text{Al}/\text{CO}_3^{2-}$ molar ratio equals to 2 and the pH of the final solution was kept at 8.5 ± 0.3 . Two solutions were added dropwise at different rate to keep the pH of the slurry in the range of 8.5 ± 0.3 . Then the mother liquid was poured into a closed vessel with inner liner of teflon (polytetrafluoroethylene) and aged at 110 °C for 12 h. The precipitate was separated by filtering and washed with deionized water, and then the precipitate was dried at 393 K overnight.

2.2. Preparation of catalysts

The $\gamma\text{-Al}_2\text{O}_3$ was mixed with Mg–Al, Zn–Al, Cu–Al hydrotalcites in mass ratio of 1:3, respectively, to obtain the intermixtures. The $\gamma\text{-Al}_2\text{O}_3$ and the intermixtures were mixed with 1% nitric acid, then extruded into extrude bar of 1.6 mm diameter. The extrudes were dried at 383 K overnight, then calcined at 773 K for 4 h to obtain supports. CoMo/ $\gamma\text{-Al}_2\text{O}_3$ +Mg–Al, CoMo/ $\gamma\text{-Al}_2\text{O}_3$ +Zn–Al, CoMo/ $\gamma\text{-Al}_2\text{O}_3$ +Cu–Al and CoMo/ $\gamma\text{-Al}_2\text{O}_3$ were prepared by a standard incipient wetness technique. The calcined supports were impregnated with an aqueous solution of ammonium heptamolybdate and cobalt nitrate according to the required Mo and Co loading. After each impregnation, the supports were dried at 383 K overnight, then calcined at 723 K for 4 h.

2.3. Characterization of the catalysts

The specific surface area and average pore size of supports were determined by nitrogen adsorption using an ASAP 2010 micrometer instrument.

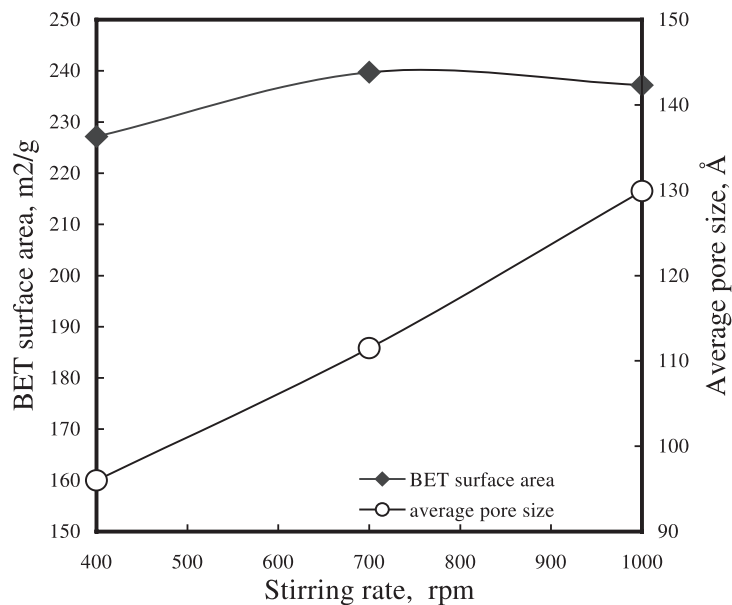


Fig. 1. Effect of stirring rate on the physical properties of Mg–Al hydrotalcite.

Table 1
Effect of feeding rate of reactants on the physical properties of Mg–Al hydrotalcite

Feeding rate ^a , ml/min	BET surface area, m ² /g	Average pore size, Å
4.0	237.9	129.9
8.0	259.2	121.9
12.0	242.0	116.0

^a Volume flow rate of A solution.

X-ray powder diffraction analysis was carried out with a Rigaku D/max-II diffractometer using a graphite-filter CuK α radiation at a scan rate of 2°/min.

TG-DTA analysis was carried out with WCT-2 computer controlled TG-DTA meter using temperature program of 5 °C/min.

Catalytic activity measurements were carried out in a high pressure microreactor. The catalyst was ground to 20–40 mesh and 8 ml catalyst was loaded into the reactor. Presulfiding of catalysts was carried out at 260 °C for 3 h, and 280 °C for 3 h with a liquid stream containing 3 wt.% CS₂ in cyclohexane. FCC gasoline was then pumped at test temperature. Reaction conditions are temperature 280 °C, pressure 2.1 MPa, H₂/oil volume ratio 150, space velocity 3.53 h⁻¹. The average hydrodesulfurization activity was calculated as the percentage conversion of sulfur compounds and in units of HDS%. The average hydrogenation activity was calculated as the conversion of olefin and in units of HYD%. The PIONA (paraffin, isoalkane, olefin, naphthene, and aromatics) components and RON (research octane number) of feedstock and effluents were analyzed by GC with FID detector.

3. Results and discussion

3.1. Effects of preparation conditions on the physical properties of hydrotalcites

The relationship between the stirring rate and the BET surface area and average pore size of Mg–Al mixed oxide is showed in Fig. 1. The experimental results in the Fig. 1

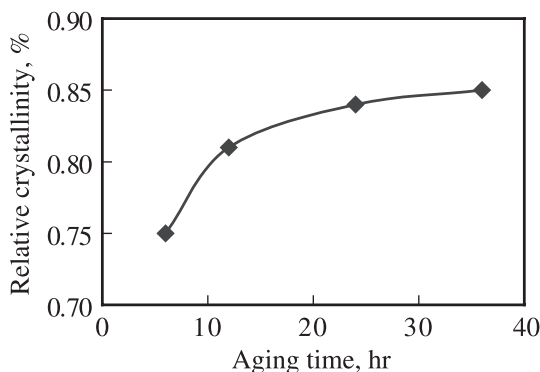


Fig. 2. The effects of aging time on relative crystallinity of Mg–Al hydrotalcite at 65 °C.

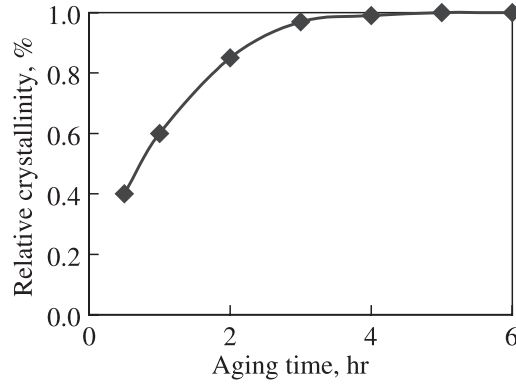


Fig. 3. The effects of aging time on relative crystallinity of Mg–Al hydrotalcite at 110 °C.

reveal that the BET surface area varies slightly with the increase of stirring rate, but the average pore size increases rapidly with the rising of stirring rate.

The effects of reactant feeding rate on the properties of Mg–Al hydrotalcite are listed in the Table 1. The experimental results showed that the feeding rate of reactants affects the physical properties of Mg–Al oxides. The samples have lower BET surface area at both lower and faster feed rate and bigger BET surface area when the feed rate of A solution is 8 ml/min. However, the average pore size was reduced gradually with increase of the feed rate of A solution.

The effects of aging temperature and time on relative degree of crystallinity are showed in Figs. 2 and 3. The experiment results in Figs. 2 and 3 show that the relative crystallinity increases with rising of aging temperature and prolonging of crystallization time, however, the crystallization time decreases with rising of aging temperature. When aging at 110 °C, the relative crystallinity reaches about 100% after 4 h, whereas aging at 65 °C the relative crystallinity just reaches about 85% after 36 h. The results in Fig. 4 reveal that the crystal size of Mg–Al hydrotalcite increases with the aging time at 110 °C, so the sample

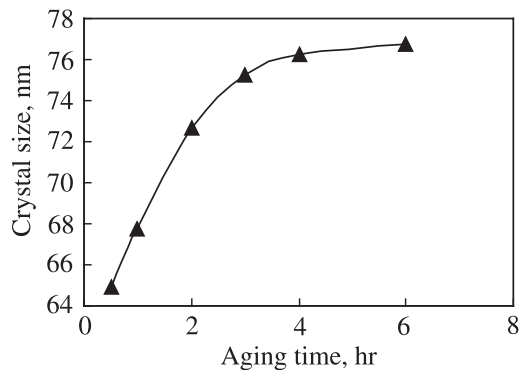


Fig. 4. The effects of aging time on crystal size of Mg–Al hydrotalcite at 110 °C.

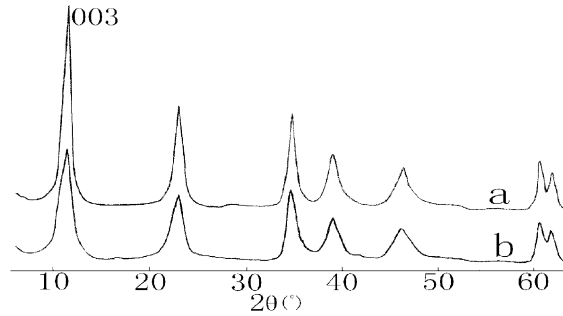


Fig. 5. XRD patterns of hydrotalcite samples obtained at different aging temperature; (a) hydrothermal aging at 110 °C, (b) aging at 65 °C.

obtained from aging at 110 °C has bigger crystal size. In a word, aging at 110 °C can give bigger crystal size and need shorter time to finish crystallization.

The XRD patterns of sample obtained by hydrothermal aging at 110 and 65 °C were illustrated in Fig. 5. The XRD peaks of the samples obtained from hydrothermal aging at 110 °C are narrower in width and higher in intensity, compared with the sample obtained from aging at 65 °C. It is well known that the crystal size is inverse proportional to the half band width according to Scherrer's equation. Therefore, above results indicate that the hydrotalcite aged at 110 °C has more uniform crystal and bigger crystal size.

The X-ray diffraction patterns of Zn–Al, Mg–Al, Cu–Al hydrotalcites prepared in our laboratory were showed in Fig. 6. The patterns reveal that all of the hydrotalcites samples of Zn–Al, Mg–Al, Cu–Al have similar XRD pattern and typical hydrotalcite's structure. It is also found that the XRD peaks, particularly 003 peak, of the Zn–Al hydrotalcite are narrower in width and higher in intensity, compared with the Mg–Al hydrotalcite, while the Cu–Al hydrotalcite has widest band and lowest intensity. These indicate that the Zn–

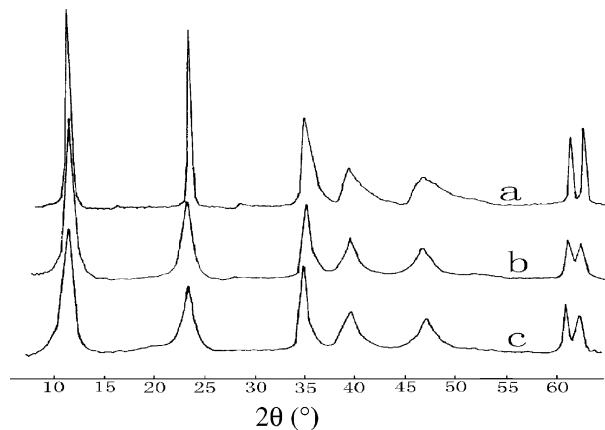


Fig. 6. The X-ray diffraction patterns of hydrotalcites; (a) Zn–Al HT, (b) Mg–Al HT, (c) Cu–Al HT.

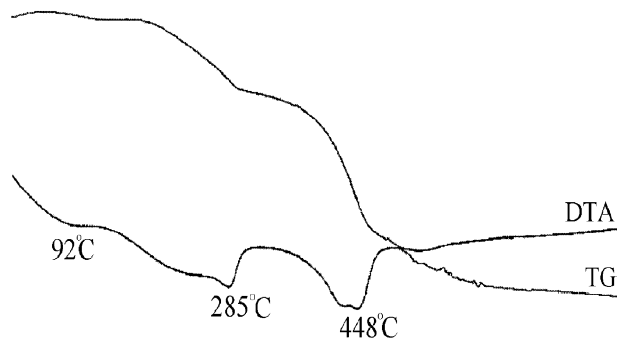


Fig. 7. TG-DTA profiles of Mg–Al hydrotalcites.

Al hydrotalcite has more uniform crystal and bigger crystal size than the Mg–Al and Cu–Al hydrotalcites.

Figs. 7–9 provides the TG-DTA profiles of Mg–Al, Cu–Al and Zn–Al hydrotalcites. The results of TG-DTA analysis of hydrotalcites revealed that Mg–Al hydrotalcite has two obvious weight loss processes. The Mg–Al hydrotalcite loses interbedded water at about 285 °C, while loses OH^{-1} and anion in the layer and between the layers, respectively, at about 448 °C, and completed decomposition over about 550 °C. As to Cu–Al hydrotalcite, it loses interbedded water at about 218 °C, and loses OH^{-1} and anion in the layer and between the layers, respectively, at about 440 °C, and completed decomposition over about 520 °C. As to Zn–Al hydrotalcite, it loses interbedded water at 322 °C, and loses OH^{-1} and anion in the layer and between the layers at about 483 °C. These indicate that 500–550 °C is the appropriate temperature for calcination of supports containing hydrotalcites.

3.2. Catalytic activities of Co–Mo catalysts supported on hydrotalcites

The experimental results of various catalyst evaluated for the hydrodesulfurization of FCC gasoline are listed in Fig. 10 (RONR: octane number retention percentage of effluents).

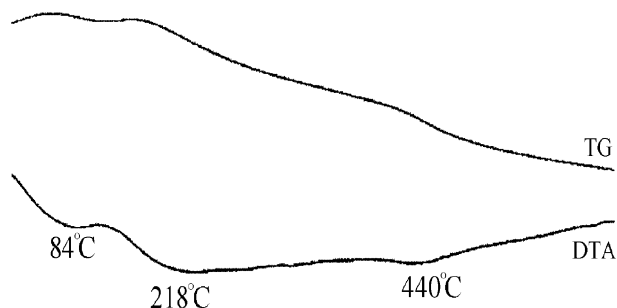


Fig. 8. TG-DTA profiles of Cu–Al hydrotalcites.

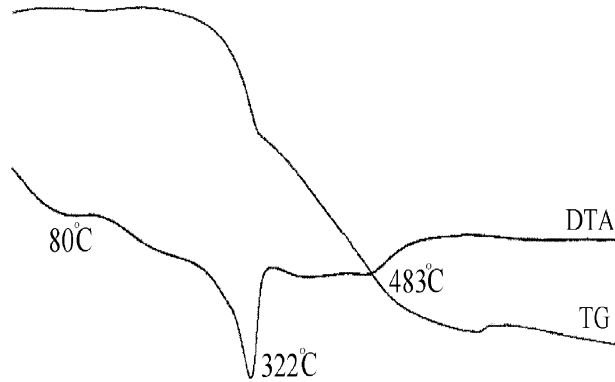


Fig. 9. TG-DTA profiles of Zn-Al hydrotalcites.

The results of Fig. 10 display that the catalyst with γ - Al_2O_3 as support and Co-Mo as active components has higher HDS and hydrogenation (HYD) activity, but lower octane number retention percentage (RONR). As to the catalysts with hydrotalcites as support, the results show that they have lower HDS and HYD activity, but have higher RONR compared with Co-Mo/ γ - Al_2O_3 catalyst. This indicated that hydrotalcites increase the selectivity of catalysts for hydrodesulfurization of sulfur-containing compounds over hydrogenation of olefins. Of the hydrotalcite-containing catalysts, Zn-Al catalyst shows lowest HDS and HYD activity, and highest RONR, while Cu-Al and Mg-Al catalyst show lower HDS and HYD activity, and higher RONR than CoMo/ γ - Al_2O_3 catalyst. The reason for CoMo/ γ - Al_2O_3 +Mg-Al catalyst having the lower HDS and HYD, as well as higher RONR, can attribute in part to that the Mg-Al mixed oxide has greater number of basic sites per unit of surface area compared with γ - Al_2O_3 . As to Cu-Al and Zn-Al hydrotalcite catalysts, there are still mechanism problems need to make clear.

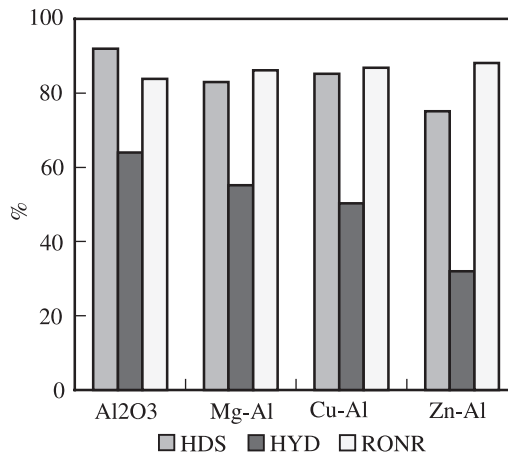


Fig. 10. Activity and selectivity of Co-Mo catalysts for hydrodesulfurization of FCC gasoline (conditions: pressure 2.0 MPa, temperature 280 °C, H_2 /oil ratio 150, LHSV 3.5 h^{-1}).

4. Conclusions

The properties of Mg–Al mixed oxides obtained from hydrotalcite were affected by the preparation conditions of hydrotalcites. BET surface areas increase with the raise of stirring rate. The hydrotalcite has bigger surface area and the greater average pore size when the feeding rate of reactants was 4 ml/min of Mg–Al salt solution. The Mg–Al mixed oxides show the biggest surface area when the hydrotalcite was calcined at 550 °C, while it has the greater average pore size at 500 °C. It can also be concluded from the results of desulfurization test of FCC gasoline that the Co–Mo catalysts supported on hydrotalcite are superior to the Co–Mo catalyst supported on alumina for the octane number retention. The hydrodesulfurization activity order was as follows: CoMo/ γ -Al₂O₃>CoMo/ γ -Al₂O₃+Mg–Al(HT)>CoMo/ γ -Al₂O₃+Cu–Al(HT)>CoMo/ γ -Al₂O₃+Zn–Al(HT), and the olefin hydrogenation activity and octane number reduction orders were as follows: CoMo/ γ -Al₂O₃+Zn–Al(HT)<CoMo/ γ -Al₂O₃+Cu–Al(HT)<CoMo/ γ -Al₂O₃+Mg–Al(HT)<CoMo/ γ -Al₂O₃.

Acknowledgements

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