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Role of Citric Acid Modification on Hydrodesulfurization of DBT and 4,6 DMDBT in the Presence of Pyridine Over CoMo/Al_2O_3

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In this study, the effect of pyridine as a basic nitrogen compound on HDS activity of DBT and 4,6 DMDBT in treated diesel over modified CoMo/Al_2O_3 by citric acid has been investigated. It has been obviously found that the modification of CoMo/Al_2O_3 catalyst by citric acid can inhibit the influence of pyridine on HDS activity of DBT and 4,6 DMDBT. This can be explained that when citric acid was applied in the catalyst preparation, the increasing of total amount of acid sites and the enhancement of HDN activity play an important role in the tolerance of pyridine.

Keywords : Hydrodesulfurization; CoMo/Al_2O_3; Citric acid; DBT; 4,6 DMDBT; Pyridine

INTRODUCTION

The Co(Ni)-Mo-S phases which the Co(Ni) atoms are decorated on the edges of MoS_2 crystallites proposed by Tosoe et al. have been renowned as the active sites of HDS catalysts (Topsøe 1996). The greater number of these active sites is significantly necessary for the removal of the refractory sulfur compounds such as dibenzothiophene (DBT), 4-methyldibenzothiophene (4 MDBT) and 4,6-dimethyldibenzothiophehe (4,6 DMDBT) (Topsøe 1996, Yumoto 1997, Takatsuka 1997, Robinson 1999, Segawa 2000, Song 2003). It has been found that the use of chelating agents in HDS catalyst preparation has been a very effective approach in increasing the number of Co(Ni)-Mo-S (Mazoyer 2008, Lélias 2009, 2010, Rinaldi 2009, 2010, Castillo-Villalón 2012, Badoga 2012, Leonova 2014, Wu 2014). Citric acid (CA) is found to be an effective chelating agent (Rinaldi 2009, Rinaldi 2010, Li 2011, Valencia 2012, Valencia 2013, Nikulshin 2014, Castillo-Villalón 2014). Rinadi et al. (2009, 2010) have investigated that the Co-CA complex is more selectively formed on CoMo/Al_2O_3 than on CoMo/B/Al_2O_3, in agreement with a greater promoting effect of citric acid at a lower CA/Mo mole ratio for CoMo/Al_2O_3 than for CoMo/B/Al_2O_3. Nikulshin et al. (2014) have studied the composition and morphology of active phase of CoMo/Al_2O_3 prepared using Co_2Mo_{10}-heteropolyacid and chelating agents, e.g, NTA, EDTA, CA, and tartaric acid (TA). They have found that the HDS activity of thiophene and 4,6 DMDBT over CoMo/Al_2O_3 catalyst without a basic nitrogen compound evidently enhances when citric acid was used. However, the HDS activity of DBT over modified CoMo/Al_2O_3 catalyst is a bit higher than that of unmodified one. Castillo-Villalón et al. (2014) have found that citric acid induces the better sulfidation, the increased surface reducibility, and the greater number of Co–Mo–S sites which contribute to the improvement in rate constant for hydrodesulfurization of DBT and 4,6 DMDBT over CoMo/Al_2O_3 catalyst.

Furthermore, as mentioned in our previous work and the others (Kwak 2001, Laredo 2001, 2003, Murti 2003, Yang 2004, Mizutani 2005, Turaga 2003, Zhang 2010, Vit 2014, Sintarako 2015), the nitrogen compounds generally occurred in petroleum significantly inhibit the HDS activity. The adding of ZrO_2 a secondary support can suppresses the influence of pyridine (basic nitrogen compound) on DBT hydrodesulfurization over CoMo/Al_2O_3 based catalyst (Sintarako 2015). U.T. Turaga et al. (2003) have studied the effect of nitrogen compounds on HDS activity of 4,6 DMDBT over CoMo/Al_2O_3 and CoMo/MCM-41 catalyst. They have found that the basic nitrogen (quinoline) inhibits the HDS activity of both Al_2O_3 and MCM-41 supported CoMo catalysts by the reduction of hydrogenation and hydrogenolysis activities. However, the effect of nitrogen compound on hydrodesulfurization of modified CoMo/Al_2O_3 by citric acid has not been studied yet.

In this study, the effect of pyridine (basic nitrogen compound) over HDS activity of DBT and 4,6 DMDBT in treated diesel on Al_2O_3 supported CoMo catalysts modified by citric acid have been investigated.

EXPERIMENTAL

Catalyst Preparation

The Al_2O_3 support with surface area 120 m^2/g used in this study was the product of Merck. The unmodified CoMo/Al_2O_3 catalyst, consisted of MoO_3 15wt.% and CoO 3wt.%, was prepared by co-incipient wetness impregnation method (Sintarako 2015), followed by the modification of citric acid solution and dried at 120°C for 15 h. The 20wt.% of critic acid was used in this study. The symbols of unmodified and modified CoMo supported on Al_2O_3 were CoMo and

Citric-CoMo, respectively.

Catalyst Characterization

The XRD, N_2 physisorption, NH_3 TPD and H_2 TPR techniques, as previously described in details (Sintarako 2015), have been applied to investigate the crystal structure, BET surface area, the total amount of acid sites, and the reduction behavior of the prepared catalysts, respectively. The X-rays diffraction (XRD) patterns were determined by Siemens D5000 using CuKα radiation. The specific surface area was measured by using BELSORP-max. The total amount of acid sites on the catalyst was analyzed by NH_3 TPD technique using BELCAT-A. The H_2 TPR results were also investigated by BELCAT-A.

Catalytic Activity Measurement

The HDS activity of DBT and 4,6 DMDBT and HDN activity of pyridine over prepared catalysts were evaluated at 350°C and 8 MPa in a fixed-bed reactor made of stainless steel (Sintarako 2015). The treated diesels with 2000 ppm S (from DBT) and 100 ppm S (from 4,6 DMDBT) were prepared as the feedstocks. The nitrogen contents with 500 ppm N and 25 ppm N (from pyridine) were used to study the effect of a basic nitrogen compound on DBT and 4,6 DMDBT hydrodesulfurizations, respectively.

RESULTS AND DISCUSSION

XRD Patterns

The XRD patterns of CoMo and Citric-CoMo catalyst are show in **Figure 1**. For CoMo catalyst, the characteristics of gamma-Al_2O_3 were observed as detested the peaks at 46° and 67° (Zhang 2010, Sintarako 2015). The peaks at around 23°, 26°, and 27° which represented the crystal MoO_3 were found (Rinaldi 2010, Sintarako

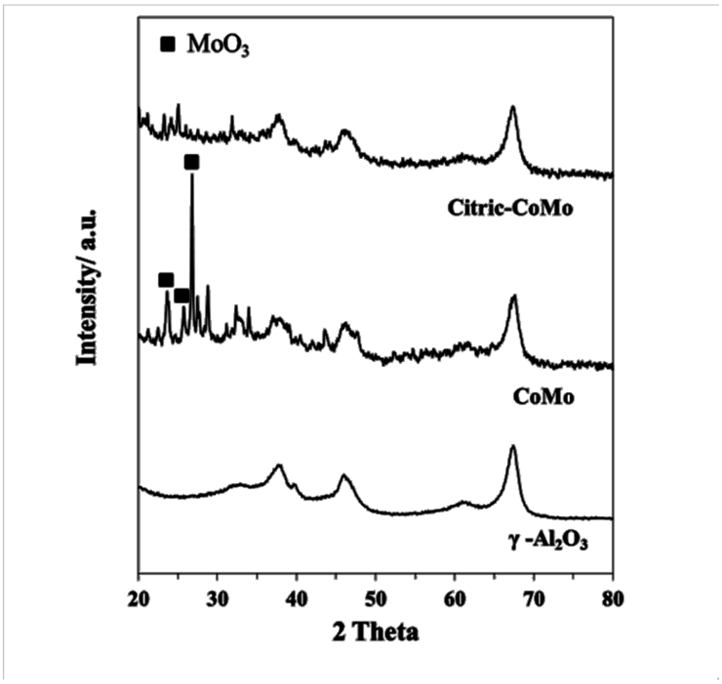

Fig. 1 : The XRD patterns of Al_2O_3 support, CoMo and Citric-CoMo catalysts

Table 1. The BET surface area, pore volume and average pore diameter of CoMo and Citric-CoMo catalysts

Sample	BET (m^2/g)	Pore volume (cm^3/g)	Avg. Pore diameter (nm)
CoMo	97	0.17	4.82
Citric-CoMo	140	0.12	3.76

Table 2. The amount of acid sites on CoMo and Citric-CoMo catalysts

Sample	Amount of acid sites (mmol/g)		
	Weak	Strong	Total
CoMo	0.266	0.020	0.286
Citric-CoMo	0.174	0.283	0.457

2015). When citric acid was added during the preparation step, the peaks which presented the gamma phase of Al_2O_3 were still detected. However, the peaks of the MoO_3 phase were hardly observable. It might be indicated that more Mo species were suitably dispersed on Al_2O_3 support. Additionally, the characteristic peak of CoO or any cobalt oxide was not detectable form, thus it could be concluded that the Co species were properly dispersed on all prepared catalysts.

N_2 Physisorption

The BET surface area, pore volume and average pore diameter of CoMo and Citric-CoMo catalysts are summarized in **Table 1**. When citric acid was added during the catalyst preparation step, the BET surface area of Citric-CoMo catalyst significantly increased compared to that of CoMo catalyst. However, the pore volume and average pore diameter of the Citric-CoMo catalyst were certainly decreased, especially for the average pore diameter.

NH_3 TPD

Table 2 summarizes the total amount of acid sites on the prepared catalysts by using NH_3 TPD technique. The detected peaks at around 100-300°C and 500-600°C were classified to be the weak acid sites and the strong acid sites, respectively. It was found that when citric acid was introduced in the step of catalyst preparation, the Citric-CoMo catalyst certainly increased in the total amount of acid sites. The amount of strong acid sites was highly promoted which provided the increase of the total amount of acid sites. According to their amounts of weak acid sites, it dramatically decreased comparing to that of CoMo catalyst.

H_2 TPR

The H_2 TPR result of the prepared catalysts which is used to evaluate the interaction of support and active metals is

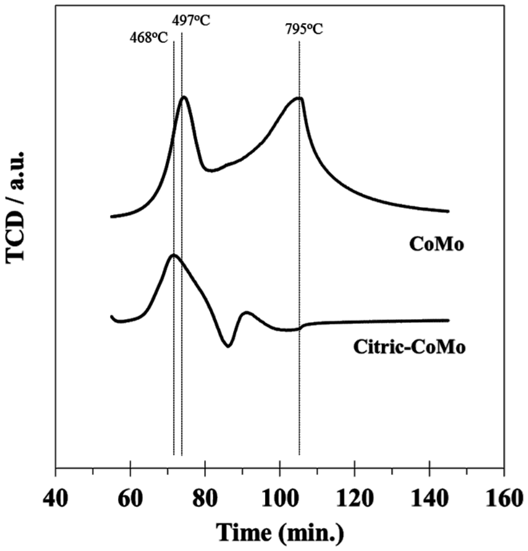

Fig.2 : The H_2 TPR results of CoMo and Citric-CoMo catalysts

shown in **Figure 2**. The reduction of Mo^{6+} to Mo^{4+} (MoO_3 to MoO_2) (Montesinos-Castellanos 2008) and Mo^{4+} (MoO_2) to Mo^0 (Cordero 2000, Zhang 2010) were found as determined the reduction peaks around 450 to 550°C and 770 to 800°C, respectively. It was also found that the first reduction peak of Citric-CoMo catalyst was shifted to the lower temperature than that of CoMo catalyst. For the second peak, the peak height of Citric-CoMo catalyst was totally disappeared. This can be indicated that when citric acid is introduced in the preparation step, the interaction of support and active metals has been reduced as determined the reduction peaks at lower temperature for Citric-CoMo catalyst.

Catalytic Activity

The HDS activities of DBT and 4,6 DMDBT in treated diesel on CoMo and Citric-CoMo catalysts are show in **Figure 3** and **Figure 4**, respectively. In the absence of pyridine, both CoMo and Citric-CoMo catalysts exhibits the same HDS activity of DBT. In the presence of pyridine, the CoMo catalyst dramatically decreases in HDS activity whereas the Citric-CoMo catalyst can significantly obtain its own activity. It has been obviously indicated that the modification of CoMo catalyst by citric acid potentially inhibit the influence of a basic nitrogen compound (pyridine) on the HDS activity of DBT. Furthermore, the HDN activity of pyridine has also been studied. In **Figure 3**, it has been found that the HDN activity of CoMo and Citric-CoMo catalysts is almost the same.

In comparison of 4,6 DMDBT hydrodesulfurization on CoMo and Citric-CoMo catalysts , as shown in **Figure 4**, the Citric-CoMo catalyst performs the higher HDS activity in both absence and presence of pyridine than that of CoMo catalyst. It has also been found that the Citric-CoMo catalyst provides the higher HDN activity of pyridine than that of CoMo catalyst.

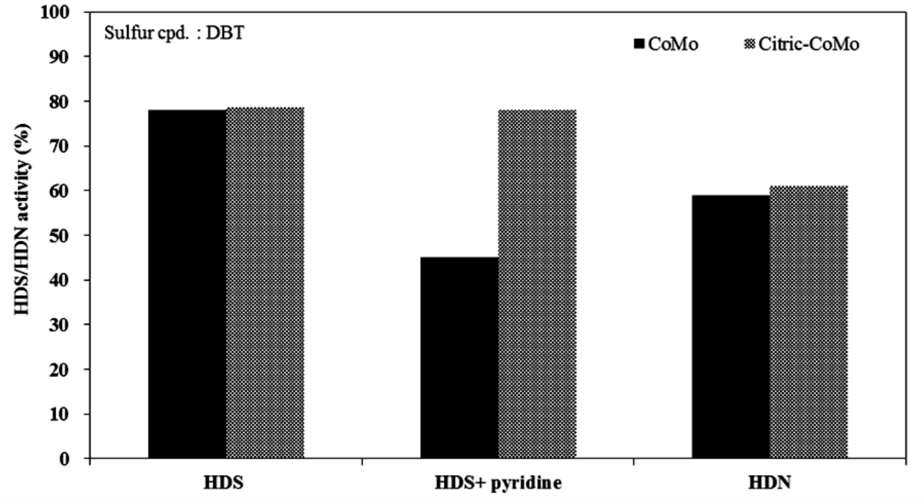

Fig. 3 : The HDS activity of DBT and HDN activity of pyridine over CoMo/Al_2O_3 and citric acid-CoMo/Al_2O_3 catalysts

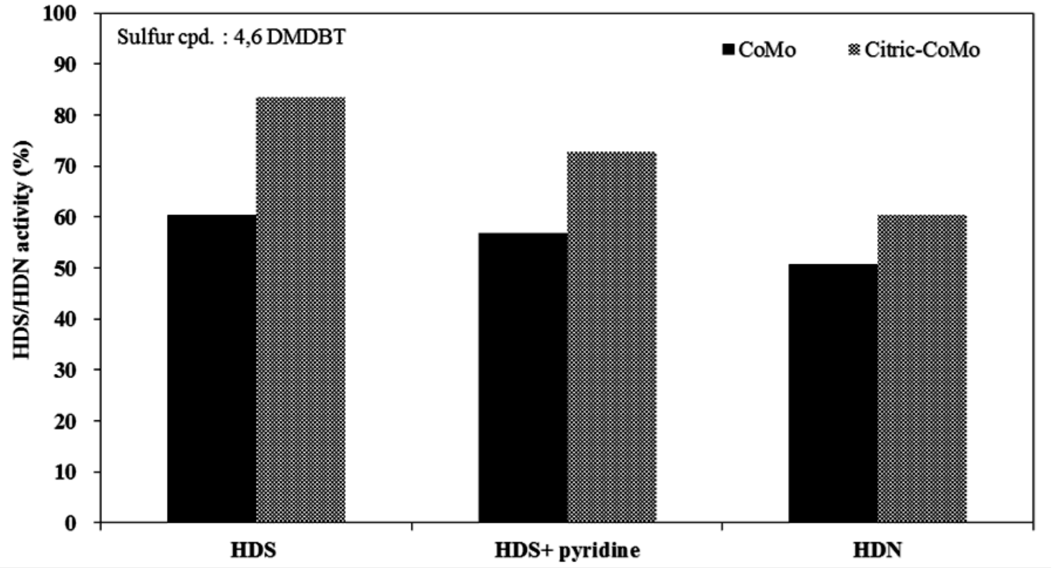

Fig.4 : The HDS activity of 4,6 DMDBT and HDN activity of pyridine over CoMo/Al_2O_3 and citric acid- CoMo/Al_2O_3 catalysts

This discovery conforms to the study of Nikulshin et al. (2014), they have studied the CoMo/Al_2O_3 catalysts prepared using Co_2Mo_{10}-heteropolyacid and chelating agents on their catalytic properties of thiophene, DBT and 4,6 DMDBT in the absence of nitrogen compound. They have observed that the modified CoMo/Al_2O_3 catalyst by citric acid evidently enhances the HDS activity of 4,6 DMDBT whereas its HDS activity of DBT is a bit higher than that of unmodified one. According to the catalyst characterization, the characteristics of MoO3 and CoO on Citric-CoMo catalyst were hardly detected by XRD analysis. This indicates that the modification of CoMo catalyst by citric acid significantly enhances the dispersion of Mo and Co components. The interaction of support and active metals has also been reduced as determined the reduction peaks at lower temperature for Citric-CoMo catalyst. These benefits of citric acid promote the higher CoMoS slabs and Co atom on the edges of MoS_2 which enhance the higher HDS activity of CoMo/Al_2O_3 catalyst, especially for 4,6 DMDBT hydrodesulfurization (Rinaldi 2009, Rinaldi 2010, Li 2011, Valencia 2012, Valencia 2013, Nikulshin 2014, Castillo-Villalón 2014).

Furthermore, the Citric-CoMo catalyst significantly increases in the total amount of acid sites. It has been observed that the amount of strong acid sites is highly promoted which results in the increase of the total amount of acid sites. According to the amount of weak acid sites over Citric-CoMo catalyst, it dramatically decreases comparing to that of CoMo catalyst. In the previous research (Ding 2007, Pawelec 2008, Chen 2013), the modification of support acidity has a beneficial effect on the catalytic properties of catalyst. Pawelecet et al. (2008) have found that CoMo/P/Ti-HMS, which has a greater amount of total acid sites, exhibits the higher HDS activity of 4,6 DMDBT than that of CoMo/P/Al_2O_3. The modification of the alumina acidity by boron addition changes on the properties of sulfide Mo and CoMo catalysts (2013). This acidity change has a direct influence on the electronic properties of MoS_2 and CoMoS sites which provide the positive effect on the hydrogenation activity of the catalysts. Vit et al. (2014) have studied the nitrogen tolerance of PdMo/Al_2O_3 and CoMo/Al_2O_3 in thiophene hydrodesulfurization and have found that PdMo/Al_2O_3 catalyst possesses the higher C-N bond hydrogenolytic activity of the adsorbed intermediate piperidine than that of CoMo/Al_2O_3 catalyst which leads to the recovery of active sites and provides the higher HDS activity. Therefore, this might be concluded that the modification of CoMo catalyst by citric acid play an important role in adjusting the suitable amount of acid sites and enhance HDN activity which can suppress the influence of pyridine. Additionally, since the hydrogenation route is believably known as the predominant reaction pathway for 4,6 DMDBT (2004) and the hydrogenolysis route is selectively occurred for DBT over CoMo/Al_2O_3 in the presence of a basic nitrogen compound (2003). Thus, this would be helpful for DBT hydrodesulfurization of Citric-CoMo catalyst.

CONCLUSION

It has been found that, in the absence of pyridine, both CoMo and Citric-CoMo catalysts can perform the same HDS activities of DBT in the reaction without pyridine. In the presence of pyridine, the CoMo catalyst dramatically decreases in HDS activity of DBT whereas the Citric-CoMo catalyst can significantly obtain its own activity. For 4,6 DMDBT, in both atmosphere with or without pyridine, the Citric-CoMo catalyst performs the higher HDS activity than that of CoMo catalyst. It can be concluded that the modification of CoMo catalyst by citric acid can inhibit the influence of pyridine. This can be explained that when citric acid was applied in the catalyst preparation, the increasing of total amount of acid sites and the enhancement of HDN activity play an important role in the tolerance of pyridine.

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