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The Influence of the Chelating Agent Nitrilotriacetic Acid on Promotion of Hydrodesulfurization Activity by Co in CoMo Catalysts Prepared on Al_2O_3, C, and ZrO_2 Supports

Luděk Kaluža*, Miroslav Zdražil, Daniela Gulková, Zdeněk Vít

Institute of Chemical Process Fundamentals of the ASCR, v. v. i.; Rozvojová 135; 165 02 Prague 6 – Suchdol; Czech Republic
kaluza@icpf.cas.cz

Increasingly stringent regulations on sulfur level in liquid fuels have been recently driving the research on highly active hydrodesulfurization (HDS) catalysts. The conventional CoMo catalysts are supported onto gamma-Al_2O_3 and they are mostly prepared by consecutive deposition of ammonium heptamolybdate and cobalt nitrate followed by calcination and sulfidation. Alternatively, chelating agent such as nitrilotriacetic acid (NTA) is employed during the preparation to increase the HDS activity. In the present paper, a new method based on impregnation of unconventional supports (i.e. activated carbon and ZrO_2) by the NTA assisted spreading of molybdenum trioxide with cobalt carbonate, or ammonium heaptamolybdate with cobalt carbonate was investigated. The selected prepared catalysts were characterized by X-ray diffraction, N_2 physisorption, O_2 chemisorption and activity in thiophene (TH) at 1.0 MPa and 400 °C or 1-benzothiophene (BT) at 1.6 MPa and 360 °C HDS reaction in the gas phase. It was found that NTA dissolved the low soluble precursors (MoO_3 with $CoCO_3$ or the mixture of ammonium heptamolybdate with $CoCO_3$) at NTA/(Co+Mo) molar ratio of 0.3-1.0/1.0, which allowed the deposition of the compounds onto the supports by impregnation. The NTA systematically increased the promotion effect of Co in the sulfided catalysts in comparison to samples prepared without NTA from ammonium heptamolybdate and cobalt nitrate. The promotion effect of Co was expressed as ratio of activity of CoMo catalyst and its Mo counterpart and NTA increased it by the factor 1.13-1.58 for the studied supports.

1. Introduction

The research into highly active catalysts for hydrodesulfurization (HDS) reaction is of actual importance due to increasingly stringent regulations on sulfur level in liquid fuels, processing of crude oil of progressively deteriorating quality, and increasing demand on the hydrogen management of refineries (Smith et al., 2012) . The conventional HDS catalysts are CoMo, NiMo or NiW sulfides supported on gamma-Al_2O_3 (Topsøe et al., 1996). The catalysts have been recently also studied for hydrotreating of crude oil alternatives such as bio oils (Baladincz et al., 2012). The preparation of these catalysts is mostly based on impregnation of the support with aqueous solutions of well soluble salts ammonium heptamolybdate and cobalt nitrate followed by calcination and sulfidation. New concepts of improving HDS activity of CoMo sulfide phase are searched among employing alternative supports (Breysse et al., 2003) or methods of CoMo deposition. For example, we have previously reported on high capacity of activated carbons to adsorb about 30 wt.% MoO_3 from the slurry MoO_3/H_2O in the form active in HDS reaction and accessible for activity promotion by Co (Kaluža et al., 2001). Over the zirconium dioxide support, the effect of employing nitrilotriacetic acid (NTA) for the deposition of ammonium heptamolybdate with cobalt nitrate or molybdenum trioxide with cobalt carbonate was manifested by the increase in HDS activity by the factor 1.2-1.7 (Kaluža et al., 2012). Similar improvement has been reported for the conventional support Al_2O_3 (e.g. Hensen et al., 2002). The purpose of the present work was to investigate the effect of NTA on promotion of hydrodesulfurization activity in CoMo catalyst supported onto gamma-alumina, activated carbon (C), and zirconium dioxide.

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2. Experimental

2.1 Supports and reference catalysts

The supports and reference catalysts were crushed and sieved to a particle size fraction of 0.16-0.32 mm. Carbon support was the commercial active carbon GA-05 (Slovenské lučobné závody, Slovak Republic) produced from wood. It was refluxed several times with distilled water to remove alkali and dried in a rotary vacuum evaporator. Alumina support was the commercial product AKZO HDS-000-1.5 (AKZO Chemicals, The Netherlands), which is intended for hydrotreating catalysts. It contained 1.3 wt.% of SO_4^{2-}. The ZrO_2 was purchased from Alfa Aesar (product no. 043815, Germany). The following industrial gamma-Al_2O_3 supported catalysts were used for comparison: Mo(BASF) containing 15.0 wt.% MoO_3 (Mo/Al_2O_3, M8-30, BASF, Germany) and CoMo(KF756) containing 3.2 wt% CoO and 15.5 wt.% MoO_3 (CoMo/Al_2O_3, KF 756, Albemarle, the Netherlands).

2.2 Catalysts preparation

Co and Mo were deposited onto the supports to achieve the molar ratio Co/(Co+Mo) equal to 0.3. The Mo content in carbon and gamma-alumina supported catalysts was chosen to correspond to 13.0 wt.% of MoO_3, which was slightly below the saturated adsorption loadings. The full capacity of ZrO_2 to disperse Mo (saturated adsorption monolayer density 3.5 at. Mo nm^{-2}) was used because this support exhibited low surface area (see Table 1). That capacity corresponds to the loading 8.3 wt. % MoO_3. The relation among support surface area, saturated adsorption loading and HDS activity was discussed in our previous papers about carbon supported catalysts (Kaluža et al., 2001) and gamma- Al_2O_3 supported catalysts (Kaluža et al., 2005). The surface areas of the supports studied are summarized in Table 1.

The catalysts were prepared by two methods: i) conventional consecutive impregnation and ii) the impregnation with the use of nitrilotriacetic acid (NTA).

i) The support (5 g) was mixed with aqueous solution of ammonium heptamolybdate (20 ml) and it was shaken for 1 h. It was dried in a rotary vacuum evaporator at 95 °C for 1 h and calcined in air flow at 400 °C for 1 h with a temperature ramp of 6 °C min^{-1}. Part of the Mo sample (2.5 g) was impregnated with the solution of $Co(NO_3)_2$ (10 ml), and it was dried and calcined in the same way.

(ii) The support (2.5 g) was immersed into 20 ml of the aqueous solution containing the ammonium heptamolybdate and NTA, or ammonium heptamolybdate, cobalt nitrate and NTA for 1 h. The sample was dried in a vacuum evaporator at 95 °C for 1 h and it was not calcined. The Mo samples and CoMo samples supported on carbon and Al_2O_3 were prepared with NTA/Mo = 1 and NTA/Co = 1, respectively. The solution for impregnation of the ZrO_2 were prepared from MoO_3 and NTA, or MoO_3, $CoCO_3$, and NTA with molar ratio NTA/Mo = 1, or NTA/(Co+Mo) = 1, respectively. The support (2.5 g) was immersed into this solution and the slurry was mixed for 1 h. The sample was dried in vacuum evaporator at 95 °C for 1 h and it was not calcined.

2.3 Catalysts characterizations

N_2 adsorption isotherms were measured using a Micromeritics ASAP 2010M instrument. Before the measurements, the samples were evacuated at 110 °C for 12 h. Specific surface area, S(BET), specific surface area of the mesopores, S(M), and the volume of the micropores, V(Micro), were determined by the Brunauer–Emmett–Teller (BET) procedure and t-plot method (Table 1). The volume of pores V(Total) was calculated from the amount of N_2 adsorbed at $p/p_0 = 0.98$. All textural parameters were normalized per gram of the sample.

The X-ray diffraction data were measured using a Philips X'Pert MPD system in Bragg–Brentano reflecting geometry using Co Ka radiation (40 kV, 30 mA) with wavelength 0.178897 nm and a secondary graphite monochromator. The data were collected in the range of 10–80 ° 2 theta, at the rate of 0.02 ° per 1.6 s.

2.4 Hydrodesulfurization reactions

The model reactions were HDS of thiophene (TH) at 1.0 MPa and 1-benzothiophene (BT) at 1.6 MPa in the gas phase in a fixed bed flow reactors. The feed rates of TH, F(TH), and hydrogen, F(H_2), were 0.43 mmol h^{-1} and 1.1 mol h^{-1}, respectively. The catalyst charge, W, was 0.01 g and it was diluted with an inert corundum. The catalyst was presulfided in-situ by a H_2S/H_2 mixture (1:10) at atmospheric pressure with the following temperature program: ramp 6 °C min^{-1} to 400 °C and dwell 1 h at 400 °C. The feed TH/H_2 was introduced at the temperature of 400 °C and the pressure of 1 MPa. The conversion x(TH) was determined at 400 °C using a gas chromatograph (Hewlett-Packard, 4890D, Germany); it was defined as $x(TH) = (n_0(TH) – n(TH))/n_0(TH)$, where n_0 and n are the initial and final number of moles.

The HDS of 1-benzothiophene (BT) was performed at 360 °C. Before the measurements, the catalysts were sulfided as described above. The composition of the feed was 16 kPa of BT, 200 kPa of decane and 1384 kPa of hydrogen. The catalyst charge, W, was 0.02-0.2 g depending on the catalyst activity and it was diluted with an inert corundum. The reaction was run at three feed rates of BT, F(BT): 7.7 mmol h^{-1}, 10.3 mmol h^{-1} and 15.5 mmol h^{-1}. Steady state was reached in 30 min after each change in the feed rate. The reaction mixture was analyzed on a gas chromatograph (Hewlett-Packard, 6890 series, Germany) equipped with a capillary column (HP-5, 30 m, 0.53 mm, 1.5 μm). Dihydrobenzothiophene (DH) and ethylbenzene (EB) were identified in the reaction products. The relative compositions a(BT), a(EB) and a(DH) and conversions x(BT), x(EB), and x(DH) were defined as a(BT) = (1-x(BT) = n(BT)/n_0(BT), a(EB) = x(EB) = n(EB)/n_0 (BT), a(DH) = x(DH) = n(DH)/n_0(BT), where n_0(BT), n(BT), n(EB), and n(DH) are the initial and final number of moles.

The empirical pseudo-first-order rate constants of thiophene HDS k(TH) and ethylbenzene formation k(EB) were calculated from the dependence of the conversion x(TH) and relative composition a(EB) within the range 0.05-0.95 on space time W/F and it was normalized per unit weight of sulfided catalyst. The relative activity A(Rel) was expressed as a ratio of the rate constants of the prepared catalysts and the rate constant of the reference industrial Mo catalyst BASF M8-30 (15 wt.% MoO_3, gamma-Al_2O_3 support). The promotion effect of Co was defined as a ratio of the activity of CoMo catalyst and its Mo counterpart.

3. Results and discussion

The concept of conventional impregnation form aqueous solutions is based on consecutive deposition of the metals (Mo first, Co second) because cobalt molybdates precipitate is normally formed by the reaction of ammonium heptamolybdate and cobalt nitrate. Calcination at temperature above 350 °C is applied to decompose the Mo salt prior to Co deposition. The presence of NTA, however, prevents the precipitation reaction by formation of well soluble metal complexes. The impregnation method with the use of NTA was found to be convenient to deposit the metals onto the supports in one impregnation step. Furthermore, the chelating power of NTA is so strong that it allowed the dissolution of MoO_3 and, surprisingly, also the dissolution of the mixture of MoO_3 and $CoCO_3$ (Kaluža et al., 2012). Another advantage of this method was that addition of NH_4OH was not needed to keep the precursors dissolved. Ammonia forms ammonium sulfide during in situ sulfidation, which leads to plugging of the reaction apparatus if the reactor exit is not sufficiently heated. This advantage is particularly important for preparation of activated carbon supported catalysts because the surplus of ammonia can not be removed from the surface by calcination due to the support oxidation in air.

The textural and structural parameters of the selected CoMo catalysts were studied by N_2 physisorption and X-ray diffraction. The X-ray diffraction did not detect presence of crystalline phase of NTA, Mo or Co species in the catalysts after drying or sulfidation. Only the monoclinic phase of ZrO_2 (baddeleyite) and low intensity diffuse peaks of cubic gamma-Al_2O_3 supports were found in the catalysts. The N_2 adsorption isotherms and textural parameters of the selected samples are shown in Table 1 and Figure 1. It was

Table 1: Textural parameters of the supports, reference catalysts and selected sulfided catalysts

Sample	S(BET) $m^2 g^{-1}$	V(Total) $cm^3 g^{-1}$	S(M) $m^2 g^{-1}$	V(Micro) $cm^3 g^{-1}$
Al_2O_3	262	0.60	157	0.07
CoMo(NTA)/Al_2O_3	193	0.45	125	0.04
C	1053	0.64	271	0.38
CoMo(NTA)/C	950	0.54	340	0.29
ZrO_2	108	0.26	66	0.03
CoMo(NTA)/ZrO_2	94	0.20	61	0.02
Reference catalysts:				
Mo/Al_2O_3	198	0.48	165	0.02
CoMo/Al_2O_3	264	0.48	167	0.06

found that the activated carbon and activated carbon supported sample exhibited high volume of micropores, which was manifested by more than 4 fold higher values V(Micro) and more extensive knee of the isotherms at low partial pressures (isotherms of type I) in comparison to the samples containing the oxidic supports (isotherms of type IV). In contrast, total pore volume V(Total) of the carbon and Al_2O_3 containing samples were similar. The surface areas S(BET) of the carbon containing samples were thus unrealistically large. To avoid the influence of the microporosity of activated carbon, the mesoporous surface areas S(M) were calculated by t-plot method. It is seen from Table 1 that deposition of the active phase with the assistance of NTA and sulfidation of the sample did not decrease the S(M) values of the original supports. The values remained in the range typical for the HDS catalysts with exception of the relatively new type of support the monoclinic ZrO_2.

The rate constants of thiophene HDS, k(TH), and benzothiophene HDS, k(EB), over the studied catalysts are summarized in Table 2. The activities of the catalysts normalized to the reference Mo/Al_2O_3 catalysts BASF are shown in Figure 2 along with the promotion effect of Co. First, it was found that activated carbon supported Mo and CoMo catalysts exhibited more than 2-fold activities in comparison to the counterparts supported on oxidic supports. Secondly the studied catalysts resulted in the same activity ranking in both model reactions i.e. HDS of thiophene and benzothiophene at 400 and 360 °C, respectively, despite the fact that HDS of benzothiophene was slightly more sensitive to the NTA use than HDS of thiophene. Third, the use of NTA during the Co and Mo deposition systematically increased the promotion effect of Co. For the reaction of thiophene and benzothiophene, the promotion increased by the factor 1.25 and 1.23 for gamma-Al_2O_3 supported catalysts, 1.13 and 1.28 for C supported catalysts and 1.25 and 1.58 for ZrO_2 supported catalysts, respectively.

The effect of NTA over the studied supports (Table 2, Figure 2) is undoubtedly combination of several factors. The references to the numerous previous literature explanations can be found in the recent paper (Lélias et al., 2009). NTA improves the dispersion of metals on the support. Without NTA, the coarse-grained crystalline phase is deposited during drying. In the presence of NTA, gel-like phase is deposited which transforms to fine-grained solid during sulfidation. Before sulfidation, NTA ligands separate metal ions from the support and from each other; dissolution of Co in Al_2O_3 and formation of hard to sulfide Co_3O_4 is suppressed. The complexing of Co delays its sulfidation until MoS_2 structures are formed and ready for decoration with Co atoms. NTA promotes the formation of the Type-II Co(Ni)-Mo-S phase (weaker interaction with support), which is more active than the Type-I Co(Ni)-Mo-S phase (stronger interaction with support). The present work contributed with the additional activity data (for instance, NTA effect in TH HDS and have been evaluated only at atmospheric pressure in the literature) and provided novel view of data and their analysis (activities of conventional and NTA catalysts of the same composition were compared and the NTA effect on promotion has not been evaluated over Al_2O_3, C, and ZrO_2 previously).

Table 2: Catalytic activities k(TH) and k(EB) in thiophene and 1-benzothiophene HDS at 1.0 MPa and 400 °C and 1.6 MPa and 360 °C, respectively

Active phase	Support	k(TH), mmol $g^{-1}h^{-1}$	k(EB), mmol $g^{-1}h^{-1}$
Mo	Al_2O_3	33	40
Mo(NTA)	Al_2O_3	41	49
CoMo	Al_2O_3	106	330
CoMo(NTA)	Al_2O_3	163	500
Mo	C	73	69
Mo(NTA)	C	87	88
CoMo	C	489	747
CoMo(NTA)	C	664	1215
Mo	ZrO_2	11	27
Mo(NTA)	ZrO_2	13	31
CoMo	ZrO_2	31	96
CoMo(NTA)	ZrO_2	45	177
Mo-BASF	Al_2O_3	28	29
CoMo-KF	Al_2O_3	115	421

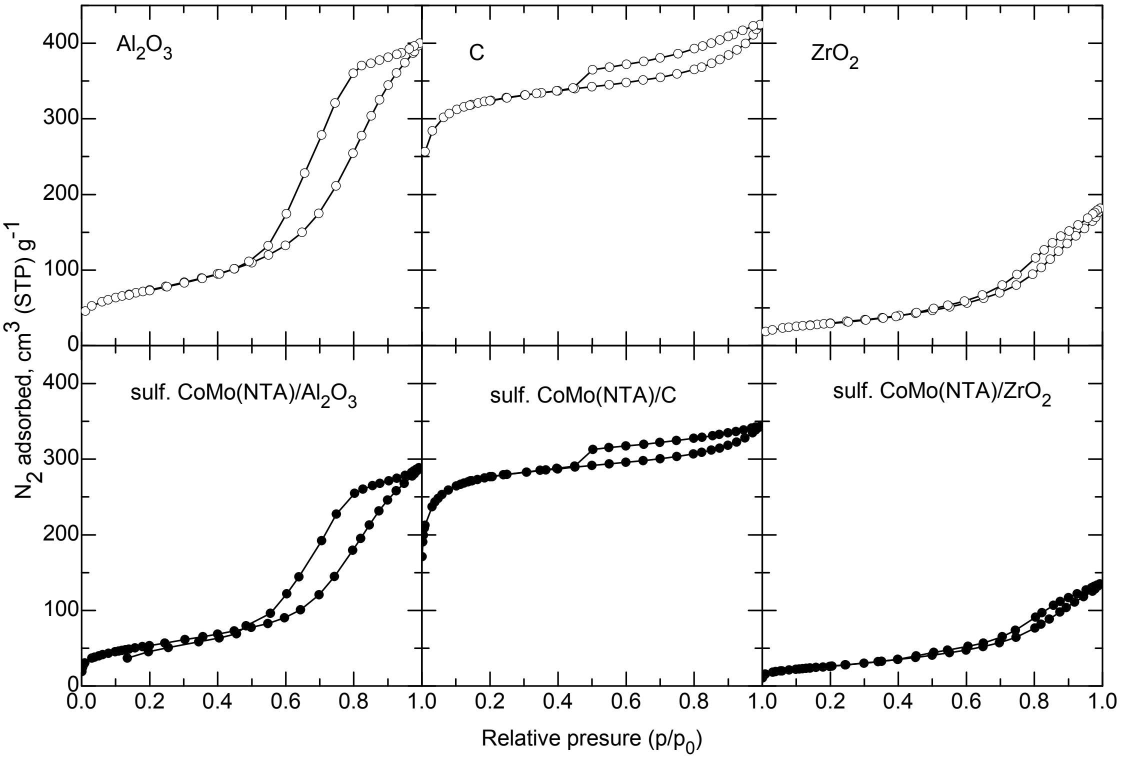

Figure 1: Adsorption isotherms of N_2 at -196 °C over the supports and sulfided CoMo catalysts prepared with the assistance of NTA.

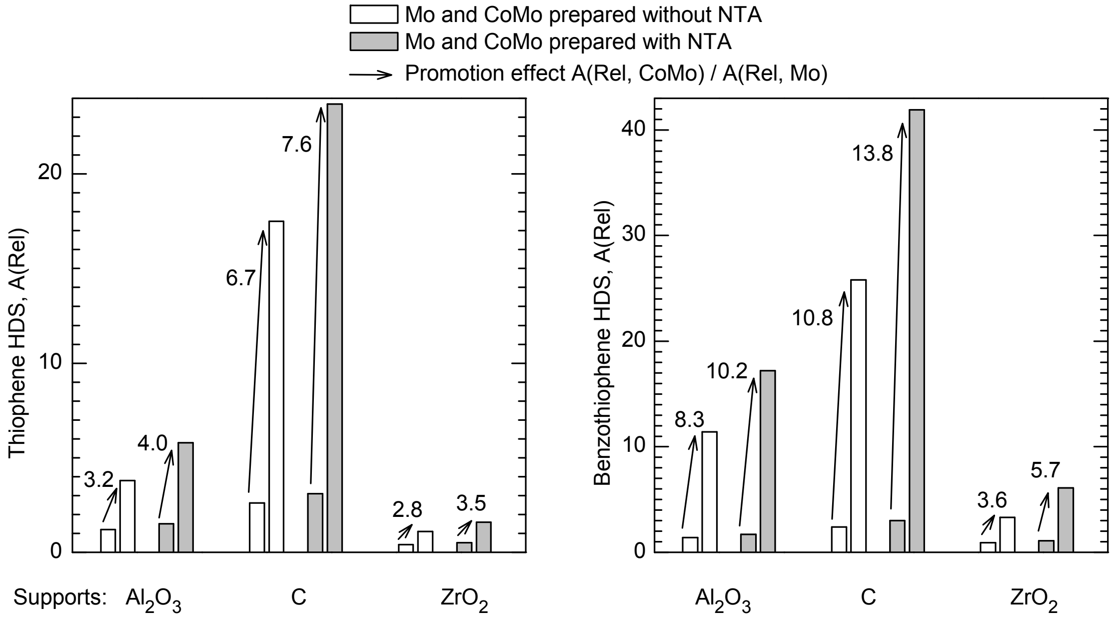

Figure 2: Increase in promotion effect of Co by NTA in thiophene and benzothiophene HDS.

4. Conclusion

The support effect is the main factor governing the activity of Mo and CoMo catalysts. The carbon supported Mo and CoMo catalysts exhibited more than 2 times higher HDS activities than their Al_2O_3 and ZrO_2 supported counterparts. The employing of the chelating agent nitrilotriacetic acid in the preparation of the CoMo catalysts supported on gamma-Al_2O_3, activated carbon, and monoclinic-ZrO_2 systematically increased the promotion effect of Co in hydrodesulfurization reaction of thiophene and benzothiophene at high pressure by the factor 1.13-1.58.

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