

SYNERGIC PROMOTION OF CATALYST BY GROUP VIII B ELEMENTS

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Abstract

Group VIII B metal oxides supported on gamma-alumina were investigated as catalysts and promoters of MoO₃ hydrodesulfurization catalysis. Superior promotion was observed in PbO promoted catalyst compared to that of CoO, the typically accepted promoter. Other metal oxides, SnO and Ho₂O₃ exhibited reasonable hydrodesulfurization catalysis promotion but lower than for CoO promoted catalyst.

Keywords: Synergic promoter; Gamma-alumina; Catalyst; Hydrodesulfurization

Introduction

Over the past four decades, several opinions have been offered for the promotion of MoO₃ by group VIII metal oxides. The hydrodesulfurization (HDS) activity of cobalt oxide promoted MoO₃ on gamma-alumina catalyst is at least twice (and may be as much as ten times) that of the unpromoted catalyst [1]. There are four major opinions explaining the promotion of MoO₃ catalyst, these are:

Bulk Compound (Phase) Formation Theory

According to this theory, HDS activity enhancement is due to the formation of Co-Mo-S phase in the catalyst. Co-MoS phase is believed to be the active phase, and is formed by the intercalation of Co at the edges of MoS₂ slabs [2].

Below the optimum concentration of Co and Ni in supported CoMo and NiMo, a second promoter element such as Fe, Pt, Pd, Ru, Ni, or Co can be used to co-

promote the HDS activity of MoO₃ on gamma-alumina [3]. In the absence of Co and Ni, some of these elements, notably Ru, Os, and Pd, have been shown to be as good or better promoter elements in supported molybdenum oxide catalysts [4]. For these other promoter elements except Ni, equivalent intercalation of the promoter elements at the edges of MoS₂ slabs may take place but no study has identified such phases.

Surface Modification of MoO₃ (Dispersion) Theory

According to this theory, the promoter elements help better disperse MoO₃ catalyst on the gamma-alumina support. This model suggests that MoO₃ remained in the presence of CoO as the active phase, but MoO₃ was better dispersed.

The active phase is obtained when the two terminal oxygen atoms are sulfided and the catalyst forms MoS₂ crystallites. This theory applies to both the supported and unsupported catalysts and is supported by Gates *et al.* [5].

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Contact Synergism Theory

According to this theory, proposed by Delmon [6], two active and stable phases, *i.e.*, MoS₂ and Co₉S₈, are formed as a result of sulfidation of CoO promoted MoO₃ catalyst. MoO₃ promotion is a result of close contact between the two phases formed and was shown to be independent of the support. The synergic action can be achieved if either chemical or physical mixture of MoS₂ and Co₉S₈ was used for HDS catalysis. The effectiveness of the promotion is dependent on the level of intimacy provided by the mixing.

Electronic Modification Theory

According to this theory, the observed HDS activity strongly depends on the energy and number of “d” electrons in the highest occupied orbitals. It also depends on a strong covalent contribution to the metal-sulfur bonding. A promoted catalyst with high values for both of these factors usually possesses high HDS activity (these two factors are influenced by the presence of promoter ions). The good promoter elements formally reduce the oxidation state of the Mo atom relative to the Mo in MoS₂ by donating electrons to Mo atoms thereby increasing the number of 4d electrons. Likewise non-promoter elements neither donate nor receive electrons from Mo atoms while a poison element like Cu actually accepts electrons from Mo atoms and thus decreases the number of 4d electrons. Electron donation by a promoter element was considered more important than its metal-sulfur bonding contribution [2]. The complexity associated with supported CoMo as an HDS catalyst is the reason why Wachs and Hu [7] investigated the catalytical properties of MoO₃ on different supports for HDS catalysis and one of the driving forces behind the investigation of PbO, Ho₂O₃, and SnO promoted MoS₂, for HDS catalysis.

Materials and Methods

The chemicals used were Pb(NO₃)₂ (Fischer, 99.8+%), (NH₄)₆Mo₇O₂₄·4H₂O (Mallinckrodt, 99.7+%), CoCl₂·6H₂O (Merck, 99.9+%), Ho(NO₃)₃·5H₂O (Aldrich, 99%), SnCl₂·2H₂O (MC & B, 99.3+%), and gamma-alumina (United Catalysts Inc., #L-2252, 215 m²/g). The gamma-alumina was received as 1/16 inch pellets. It was then crushed and sieved to 30-40 mesh.

The supported PbMo Oxide was prepared by the incipient wetness impregnation of ammonium heptamolybdate aqueous solution into gamma alumina. The powder obtained was then dried at 120°C for 6 h

and calcined at 500°C for another 6 h. The resulting solid was impregnated with lead nitrate aqueous solution, and dried and calcined as before, to yield typical loadings of 20 wt% MoO₃ and 5 wt% PbO.

Corresponding precursor salts were utilized to prepare CoMo, HoMo and SnMo oxides following the procedure used above for PbMo oxide. Single cation oxide catalysts of PbO, SnO, Ho₂O₃, CoO and MoO₃ were also prepared using the first step of the impregnation method described above for the dual cation oxide catalysts.

Specific surface areas were obtained with the standard N₂ BET technique in a volumetric apparatus equipped with a Barocell. Oxygen chemisorption was performed in the same apparatus, with the typical low temperature static technique for HDS catalysts (LTOC) at -78°C and 20 Torr, as reported by Reddy *et al.* [8]. Pretreatment of catalysts before physisorption or chemisorption included careful drying at 120°C under vacuum, before oxygen chemisorption. Used sulfided catalysts were subsequently reduced with hydrogen at 120°C for 1 h and at 400°C for another 1 h, and then degassed at the same temperature again for 1 h. The oxygen chemisorption values reported later were not corrected for the minor physisorption occurring at this temperature.

Activity Determination

Reaction of thiophene was performed in an integral reactor made with a ¼ in OD quartz tube. The reactor was maintained at 400°C and atmospheric pressure, and fed 30 ml/min of 1 vol% thiophene/H₂. The all-glass apparatus included a gas selection valve, a gas saturator to introduce thiophene in the H₂ stream, bypass lines for saturator and reactor, and direct connection to high vacuum. The product stream was sampled periodically with an on-line chromatographic valve and analysed with an HP5710 gas chromatograph connected to an HP3393 integrator. The packed column contained n-octane on porasil C and its outlet was directed to a FID chromatograph. Pretreatment of the catalysts included drying at 120°C in He and reducing in 30 ml/min of pure H₂ at 400°C for 4 h. Reaction was carried out in 24 h; the activities reported later correspond to the maximum activities observed during that lapse.

Results

The operating conditions used, were similar for all tested catalysts (catalyst loading, temperature, pressure, flow rate, and mesh sizing), so that comparison of rates is possible. The reported rates are the averaged rates

over the reaction period. The HDS activity is expressed as the generation rate of all products except coke. Tables 1 and 2 show the results obtained for the single and dual cation oxides HDS catalysis respectively. Figures 1 and 2 below show the progressive HDS rates over the reaction period for the single and dual cation oxide catalysts respectively.

Table 1. Selectivity and activity of single-cation oxides on gamma-Al₂O₃*

Catalyst Reduction	PbO	SnO	Ho ₂ O ₃	CoO	MoO ₃
Wt% CH ₄	-	-	-	-	-
Wt% C ₂ H _x	31.00	28.00	46.00	19.00	7.00
Wt% C ₃ H ₈	-	-	-	-	9.00
Wt% C ₃ H ₆	-	-	-	-	-
Wt% C ₄ H ₁₀	-	-	-	-	-
Wt% C ₄ H ₈	69.00	72.00	54.00	81.00	84.00
% Conversion	0.93	0.66	0.53	1.84	7.43
HDS Rate					
i (mol/s/g)×10 ⁸	67	53	28	325	160
ii (mol/s/m ²)×10 ¹⁰	33	28	15	137	75
Surface area (m ² /g)	205	192	191	213	213

* Data for thiophene HDS at 400°C after 4 h H₂ reduction at the same temperature. C₂H_x is for mixed C₂H₆ and C₂H₄.

Table 2. Selectivity and activity of dual-cation oxide on gamma-Al₂O₃*

Catalyst Reduction	SnMo	HoMo	CoMo	PbMo
Wt% CH ₄	-	-	-	-
Wt% C ₂ H _x	26.00	30.00	-	1.00
Wt% C ₃ H ₈	-	-	-	-
Wt% C ₃ H ₆	-	-	18.00	-
Wt% C ₄ H ₁₀	-	-	14.00	35.00
Wt% C ₄ H ₈	74.00	70.00	67.00	64.00
% Conversion	39.27	51.84	78.61	84.81
HDS Rate				
i (mol/s/g)×10 ⁸	441	475	900	1060
ii (mol/s/m ²)×10 ¹⁰	238	290	638	803
Surface area (m ² /g)	185	164	141	132
O ₂ -Chemisorption (μmol/m ²)	-	-	0.26	0.55

* Data for thiophene HDS at 400°C after 4 h H₂ reduction at the same temperature. C₂H_x is for mixed C₂H₆ and C₂H₄.

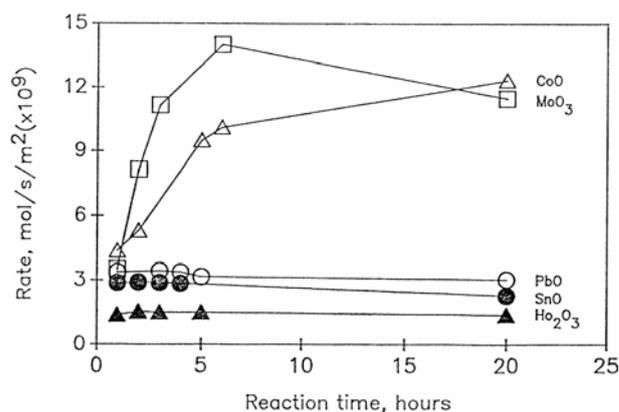


Figure 1. HDS activity of single cation oxide catalysts.

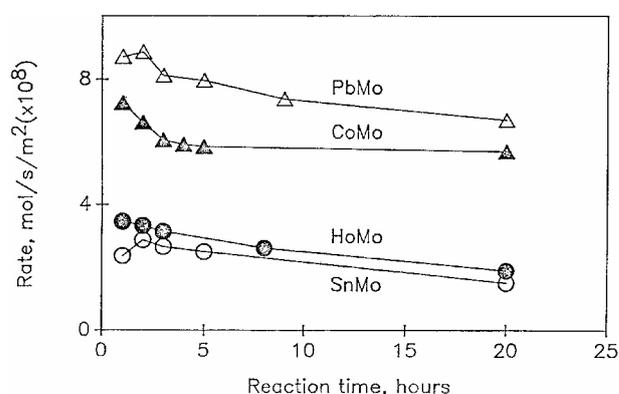


Figure 2. HDS activity of dual cation oxide catalysts.

Discussion

Overall, four cations were investigated as promoter elements of MoO₃. Table 2 and Figure 2 show the results obtained for supported PbMo, CoMo, SnMo and HoMo catalysts prepared with a 1:6 metal: Mo ratio. All the HDS results are comparable to those of supported CoMo. All the catalysts except PbMo showed significant cracking activity. The HDS activity increased in the following order: SnMo, HoMo, CoMo, PbMo. Table 1 and Figure 1 show the results obtained when gamma-alumina-supported single cation oxides were investigated for their HDS activities.

Ho₂O₃ showed the lowest HDS activity and the highest cracking activity. CoO and MoO₃ catalysts showed significantly higher HDS rates than the other three single cation oxide catalysts. Apparently, the supported PbMo catalyst, with a large degree of unsaturation, provides a synergic combination of

Pb:Mo, or a promotion of Mo by Pb, that places its HDS activity per m^2 above that of the best known HDS catalysts (CoMo).

Table 1 and Figure 1 show the results obtained when gamma-alumina-supported single cation oxides were investigated for their HDS activities. Even in the investigation, Pb was a better HDS catalyst element compared to Sn and Ho. Unlike the gamma-alumina-supported binary oxide catalysts, none of the single cation oxide catalysts showed hydrogenation activity.

Conclusion

For the first time ever, this study has shown that Pb, Ho, and Sn oxides are good promoter elements for gamma-alumina-supported MoO_3 as HDS catalyst. The order of promotion is $Pb > Ho > Sn$. Single-cation oxides of Pb, Sn, Ho, Co, and Mo supported on gamma-alumina are also shown to be good HDS catalysts. The order of their HDS activity is $Co \gg Mo \gg Pb \gg Sn \gg Ho$. The gamma-alumina-supported 1:6 Pb:Mo catalyst provides a synergic combination of Pb:Mo, or an optimum promotion of Mo by Pb, that makes this catalyst comparable to the commercially available HDS catalyst (CoMo). Saturated hydrocarbons are not produced when single cation oxides are used for HDS catalysis, suggesting that a second promoter element (dual-cation oxide) is a necessary condition for the olefinic conversion to paraffin during HDS. The mechanism of reaction must therefore be different when switching from single cation oxide HDS catalysis to dual cation oxide. The HDS activity of the dual cation oxide catalyst is at least ten times that of the corresponding single cation oxide catalysts, suggesting that for enhanced HDS catalysis, dual cation oxide is preferable. It can also be inferred from this study that single cation oxide catalysis promotes hydrocracking. The rates observed in the five single cation oxides investigated

suggest further that the mechanism of HDS catalysis may be fairly uniform and that the rate of hydrocracking also appears uniform in the single cation oxide catalysts. The level of hydrocracking was reduced minimally in the PbO-promoted dual cation oxide catalyst. However, in the other promoted dual cation oxides used, the level of hydrocracking varied but not as much as observed in the corresponding single cation oxides.

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