



Effect of Mg addition on the structure and performance of sulfide Mo/Al₂O₃ in HDS and HDN reaction



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ABSTRACT

The effect of Mg addition on alumina on the properties of sulfided Mo/Al₂O₃Mg(x) (x = 0–3.2 wt.% Mg) catalysts has been investigated using various characterization techniques (transmission electron microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy) and catalytic tests (hydrodesulfurization of 4,6-dimethyldibenzothiophene and hydrodenitrogenation of 2,6-dimethylaniline). It is observed that Mg addition decreases the weak Brønsted acidity and increases the basicity of the alumina support. Mg addition also increases the electronic density of the MoS₂ slabs, as revealed by the shift of the frequency of CO adsorbed on the sulfide Mo phase. A parallel between the increase of the electronic density of the sulfide slabs and the decrease of the Brønsted acidity of the support is evidenced. The addition of Mg does not lead to significant changes of dispersion of the MoS₂ phase but tends to decrease its stacking. The addition of a small amount of Mg increases the hydrogenation activity of the Mo catalysts for hydrodesulfurization and hydrodenitrogenation. This beneficial effect is more marked in case of co-addition of Mg and B. These data show that the addition of Mg, through the modification of the electronic properties of the sulfide sites and by the presence of Mg, leads to improvement of the intrinsic hydrogenation activity of Mo catalyst supported on alumina.

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1. Introduction

Hydrotreating catalysts have received worldwide attention for several decades, since they play a key role in the removal of impurities (sulfur, nitrogen, metals) from crude oil feedstock [1–13]. Due to increasingly stringent environmental regulations, the catalytic properties of hydrotreating catalysts require improvement to increase the fuel quality [14–22]. The traditional catalysts consist of small slabs of molybdenum or tungsten sulfide with cobalt or nickel as promoters, supported on alumina. To obtain catalysts with enhanced performances, special attention has been paid on the support effect, since it is evident that the support not only is used to disperse the active components finely but also has an influence on the properties of the active phase [23–28]. The strategy for changing the effect of the support is to modify the characteristics of the alumina-type support by adding dopants or to explore novel supports as alternatives to alumina, such as TiO₂, ZrO₂, amorphous silica alumina (ASA), zeolites, or their mixtures [29–38]. A large number of positive results have been achieved and may be

attributed to the influences of the properties of the support on the dispersion and morphology of the active phase, the metal-support interaction, and the electronic properties of the sulfide phase [23,24]. Among the various properties of the supports, acidity and basicity are the main aspects and have been paid much attention [39–42].

In the literature, the support acidity has been suggested to have a relationship with the electronic deficiency of the sulfide phase, as observed from the parallel variation of the frequency of CO interacting with the sulfides with the acid–base properties of various supports, including β-zeolite, ASA, Nb₂O₅–Al₂O₃, and K–Al₂O₃ [43–47]. As a result, the variation of the electronic properties of the sulfides can lead to enhanced activity in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. However, the relation of the electronic properties to the catalytic performance of the sulfide phase could not be completely singled out from other factors such as the pore effect of the zeolite and the change of morphology and dispersion of the sulfide phase. In order to specify the direct influence of the acidity on the catalytic properties, the previous work reported that the addition of a small amount of boron into alumina finely increases the Brønsted acidity (BAS) and tunes the electronic properties of the Mo and CoMo phases without substantially modifying their dispersion and morphology. Thus, a

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direct relationship has been established between BAS and the electronic properties as well as the hydrogenation function of the sulfide phase [48]. The electronic properties are indicated by the infrared (IR) frequency of CO adsorbed on the sulfide Mo phase [43–46,48]. With the change of support acidity, the CO frequencies on the MoS₂ sites are varied from 2158 to 2108 cm⁻¹, indicating a decrease of the electron deficiency of MoS₂ phase. One question is if the electronic deficiency of MoS₂ can be further decreased and how low it can reach? Therefore, it is fundamentally important to further investigate the variation of electron deficiency in another direction. As is known, alumina is an amphoteric oxide that possesses various kinds of acidic and basic Brønsted sites as well as Lewis acid sites (LAS) on its surface [49,50]. Therefore, the effect of decreasing the acidity and increasing the basicity of alumina on the properties of the sulfide phase deserves study.

Mg is one of the elements frequently used to decrease the acidity and increase the basicity of alumina [4,23,51,52]. In the literature, the influence of Mg addition to alumina on the properties of the hydrotreating catalysts is rather complex. Jiratova and Kraus observed that the addition of 1.0 wt.% Mg slightly increases the thiophene HDS activity and substantially suppresses the isomerization of cyclohexene on NiMo catalysts [53]. Caloch et al. observed maximum activity for thiophene HDS on Co(Ni)Mo catalysts supported on Al₂O₃ containing 5 wt.% MgO [54]. The catalyst also increased stability and hydrogenolysis (C-S, C-M) functions in the real feedstock. The authors demonstrated that MgO played a structural promoting role in the support and altered the nature of active phase interaction with the support surface. It was reported by Kumar et al. that the incorporation of basic MgO introduced moderate acidity, neutralizing the strong acid sites of alumina [55]. The catalytic activity results indicated that the HDS of thiophene was related to the dispersion of Mo, whereas the hydrogenation of cyclohexene was related to the acidity of the catalysts. In addition, the authors revealed by temperature-programmed reduction that the dispersion of Mo and the metal–support interaction were increased when Mo was supported on MgO as compared with Al₂O₃ and MgO–Al₂O₃. Furthermore, Trejo et al. reported that the optimum magnesia content in CoMo/MgO–Al₂O₃ catalysts for thiophene HDS at 10 wt.% MgO was likely due to better dispersion and morphology of the active components [56]. The Raman spectra results indicated that the Mo ions could easily react with subsurface layers of MgO to form MgMoO₄ species, which could easily be converted to MoS₂ during the sulfidation.

However, there is no general agreement on the beneficial role of Mg addition, since a negative effect of Mg on the catalytic behavior of hydrotreating catalysts has also been reported. Saini et al. found lower activity on Mg-containing catalysts in thiophene HDS, likely due to the relatively large slab sizes of the Mo phase as a consequence of the modification of the metal–support interaction [57]. A study of introducing magnesium ions into NiMo catalysts by Lewandowski showed that magnesium decreased the acidity of the catalysts and markedly decreased the HDN activity, but insignificantly decreased the HDS activity of the catalysts in the hydrorefining of coal liquid [58]. It was mentioned that the decrease of activity of the catalyst should not only be attributed to the decreased acidity of the catalysts, but also to the structural changes brought about by the introduction of magnesium. The authors proposed that the decrease of HDS activity might be induced by a weaker promoting effect of Ni²⁺ brought about by modification with magnesium. Klimova et al. investigated Mo and NiMo catalysts supported on Mg–Al mixed oxides prepared by a sol–gel method and reported that the hydrogenation function of the catalysts is substantially reduced even with the incorporation of a small amounts of magnesia into the alumina support

[59]. The formation of magnesium molybdate and a NiO–MgO solid solution that reduced the promoting effect of Ni seemed to account for the changes in the HDS and hydrogenation functions of the catalysts.

To investigate the effect of Mg addition, it is worthwhile to have insight into the characteristics of the catalysts supported on pure MgO. A series of Mo/MgO catalysts with different Mo loadings were investigated by Chary et al. [60]. The results showed that the specific HDS activity of Mo/MgO was comparable to the case of Mo/Al₂O₃, ascribed to an increase of the dispersion of Mo on MgO. Magnesia itself was claimed to be selective for HDS with minimum hydrogenation of alkenes, to have a low propensity to coking and metalation, and to have very low hydrocracking activity [60]. Klicpera and Zdražil [61] found that the activity of Mo catalysts in dibenzothiophene (DBT) HDS was at the same level and the ratio of hydrogenation/C–S bond hydrogenolysis activity was slightly higher for the MgO-supported catalysts than for the Al₂O₃-supported catalyst. Later, the same authors reported a strong synergetic effect of Co(Ni) on Mo when supported on MgO, likely related to the basicity on the support, which promoted the dispersion of MoS₂ and inhibited the growth of MoS₂ crystals in the direction of the basal plane, leading to an increase in the sites available for promotion [62].

The influence of the MgO support on HDN activity is less pronounced than that on HDS activity. Hillerova et al. pointed out that the NiMo/MgO catalyst showed a lower selectivity to HDN in the simultaneous HDN of pyridine and HDS of thiophene [63]. The main reason for the decrease in HDN activity was the decreased acidity of the catalyst surface, since the process of C–N bond hydrogenolysis proceeds on acid centers of the support [64]. Cini-bulk et al. reported that the performance of the Mo catalyst supported on MgO was similar to that of the catalyst on Al₂O₃ in the HDN reaction, whereas the Co(Ni)/MgO catalysts were less active than the Co(Ni)Mo/Al₂O₃ catalysts [65].

From the above descriptions, the effect of Mg on the properties of hydrotreating catalysts is rather controversial. The variations of activity are generally explained by considering the changes in dispersion, morphology, and support acidity. Few works have considered the effect of Mg on the electronic properties of the sulfide phase as accounting for the catalytic changes. The electronic properties represents one of the important factors of HDS catalysts. The effect of Mg is supposed to be explained by this aspect. In previous work, we found that increasing the acidity of alumina by boron addition has an influence on the electronic properties of the sulfide phases [48]. One of the aims of the present work is to determine the effect of decreasing the alumina acidity by adding Mg on the electronic properties of the sulfide Mo phase. Is it opposite to that observed on the catalysts with acidity increased by boron addition [48]? Do other modifications of the sulfide phase occur? For this purpose, a deep characterization of the catalysts was performed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy of CO adsorption, and catalytic tests of the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) and HDN of 2,6-dimethylaniline (DMA) reactions. A support with co-addition of B and Mg was studied to verify the change of electronic properties and intrinsic activity of the sulfide phase. Since alumina has weak Brønsted acidity, the addition of Mg would further decrease its acidity, which would make it more difficult to characterize. IR spectroscopy of 2,6-dimethylpyridine (2,6-DMP) was used to determine the variation of Brønsted acid properties. This makes the weak Brønsted acidity change with Mg addition identifiable. Furthermore, the basicity of the support was also characterized by IR spectroscopy of CO₂ adsorption.

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