Lathlike mesostructured γ-alumina as a hydrodesulfurization catalyst support

Randall W. Hicks a, Norma B. Castagnola b, Zhaorong Zhang a, Thomas J. Pinnavaia a,∗, Christopher L. Marshall b

a Department of Chemistry, Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824, USA
b Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, IL 60439-4831, USA

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Abstract

A mesostructured γ-alumina with a lathlike framework morphology, denoted MSU-γ, has been prepared according to previously described methods through the reassembly and crystallization of a mesostructured alumina precursor with initially amorphous framework walls and used as a support for the catalytic hydrodesulfurization (HDS) of dibenzothiophene (DBT). The alumina support was loaded with molybdenum and cobalt ions via incipient wetness impregnation methods and then converted to the active sulfide form by reaction with H2S. HDS reactions of DBT were carried out at 400 °C and 400 psi to achieve a DBT conversion of 69–77% and a biphenyl (BP) product selectivity of 60–64% after a reaction time of 3 h, indicating that most of the DBT could undergo desulfurization while limiting excessive hydrogen consumption through aromatic hydrogenation. Although the dispersion of the active MoCo sulfide phase supported on lathlike MSU-γ alumina remained very high after several hours on stream, the conversions most likely were limited by a loss of surface area and porosity under HDS conditions.

Keywords: γ-Alumina; Mesostructured; Hydrodesulfurization; Catalyst support

1. Introduction

Catalytic hydrodesulfurization (HDS) is used extensively in petroleum refining in order to reduce the sulfur content of fuels and to minimize the poison-}

ing effect of sulfur on downstream catalysts. Providing motivation for the removal of more sulfur from petroleum products, the EPA has recently set guidelines to restrict the amounts of sulfur allowed in diesel fuels to 1.3 × 10−2 g/dl by the year 2010, which corresponds to a 97% reduction in current levels [1].

Promoted transition metal sulfides (TMS) have proven to be effective HDS catalysts [2–8]. In the case of cobalt- or nickel-promoted MoS2 catalysts, the active metal centers occur at coordinatively unsaturated metal ions at the edges of the MoS2 lamellae. Dispersion of the MoS2 on a support matrix, such as carbon [9–11], mesoporous clays [12,13], aluminosilicates [14–16], and zeolites [17] can expose more of the active edge sites for reaction with sulfur-containing molecules. However, alumina is the most commonly used support matrix for HDS catalysts, owing primarily to its desirable combination of surface and textural properties.

Mesostructured forms of γ-Al2O3, denoted MSU-γ aluminas, have been reported [18] recently that have...
higher surface areas and pore volumes than conventional forms of α-Al₂O₃. Amorphous aluminas can exhibit surface areas up to 800 m²/g depending in part on the calcination temperature. γ-Aluminas typically have surface areas below 250 m²/g and pore volumes less than 0.50 cm³/g, when calcined at 500–550 °C [19]. In comparison, MSU-γ aluminas generally have surface areas above 300 m²/g over this calcination temperature range. The improved textural properties of these materials may allow for greater dispersion of MoS₂ nanolayers, along with increased access to active edge sites. Additionally, the mesopores associated with these new forms of γ-Al₂O₃ should accommodate larger sulfur containing substrate molecules, such as dibenzothiophene (DBT)-based molecules, which mimic more closely the sulfur-bearing contaminants in oil stocks. Toward this end, we have initiated a study of mesostructured MSU-γ aluminas as HDS catalyst supports. The present work reports the properties of a lathlike mesostructured MSU-γ alumina as a support for the HDS of dibenzothiophene.

2. Experimental

2.1. Lathlike MSU-γ alumina

A surfactant-boehmite mesostructure with a lathlike framework morphology, denoted MSU-S/B, was prepared by aging an aqueous mixture of [Al₁₃O₄(OH)₂₄(H₂O)₁₂]Cl₇ and P84 surfactant at 80 °C for 10 h, hydrolyzing the mixture through the addition of concentrated NH₄OH at 80 °C, then aging the hydrolysis product first at 80 °C for 6 h and then at 100 °C for 24 h. The resulting air-dried mixture of the as-made MSU-S/B mesostructure and the NH₄Cl by-product was calcined at 325 °C for 3 h to sublime the ammonium salt, and then at 550 °C for 4 h to remove the surfactant and convert the boehmite phase to mesostructured MSU-γ alumina with retention of a lathlike framework structure.

2.2. Catalyst preparation

The lathlike MSU-γ alumina support described above was loaded with catalyst precursors through separate, sequential incipient wetness impregnations of ammonium heptamolybdate tetrahydrate and cobalt(II) nitrate hexahydrate, followed by the thermal degradation (400 °C) of these supported salts to the oxides. The initial molybdenum loadings were 6.0, 9.0, and 12% by mass and the cobalt loading was sufficient to provide a 3:1 molar ratio of Mo:Co. Each impregnation was followed by calcination at 400 °C for 2 h to decompose the salt to the oxide, yielding the pre-catalyst in its non-active oxidic form.

The conversion of the alumina-supported oxides to the catalytically active sulfided form was achieved by heating the mixtures to 400 °C in a tube furnace while a stream of 8.0% H₂S in hydrogen was passed over the material for 1 h. This resulted in the formation of a black powder that was readied for use by pressing into a pellet.

2.3. Catalytic studies

The HDS pilot plant used in this study is housed in the Chemical Technology Division of Argonne National Laboratory, Argonne, IL. The liquid feed was 0.8 wt.% S as dibenzothiophene in hexadecane, and the gas feed was a hydrogen (500 cm³/min) and nitrogen (200 cm³/min) mixture. The two feeds were mixed and allowed to exit the preheater into the reactor. The catalyst bed contained approximately 1.0 g of catalyst diluted with 2.0 g SiC, resting between plugs of glass wool. The space velocity was approximately 41 h⁻¹. Liquid products were condensed and collected while gas products, mainly H₂S, were passed through a NaOH scrubber solution before being vented. The preheater furnace was set to 350 °C and the reactor furnace to set to 400 °C. The system pressure (400 psi) was controlled by a back pressure regulator. Liquid products were collected at desired intervals.

2.4. Characterization

The catalysts were characterized by powder X-ray diffraction (XRD), nitrogen adsorption, and
transmission electron microscopy (TEM). XRD patterns were obtained on a Rigaku Rotoflex diffractometer with Cu Kα radiation of 1.54 Å. Nitrogen adsorption-desorption isotherms were collected on a Micromeritics TriStar 3000 sorptometer at 77 K. Samples were degassed at least 12 h at 150 °C under a vacuum of $1.3 \times 10^{-4}$ Pa prior to analysis. Surface areas and pore sizes were determined by the BET and BHJ methods, respectively. TEM images were collected on a JEOL 100CX microscope with a CeB₆ filament at an accelerating voltage of 120 kV. Liquid collections from the HDS reactor were diluted in hexane for GC–MS analysis. The products were separated on a DB5-MS column and analyzed using an HP 5890 GC–MS Series II Plus. The conversion was determined as the percentage of DBT converted to products. The selectivity was defined as the percentage of product formed as biphenyl (BP).

3. Results and discussion

3.1. Catalytic conversions of dibenzothiophene

Regardless of the initial molybdenum loading on the lathlike MSU-γ alumina support (6.0–12.0 wt.%), the products resulting from the HDS of dibenzothiophene contained primarily biphenyl, cyclohexylbenzene (CHB), the ring-hydrogenated form of DBT, namely 4H-DBT. The structures of these products are provided in Fig. 1.

From the conversion and selectivity data presented in Table 1, it can be seen that DBT conversions tended to increase with increasing metal loading, though the sample loaded with 9% Mo showed a small decrease in conversion from that of the 6% loaded sample. As expected, the conversion was the highest for the sample loaded with 12.0% (w/w) Mo. After a reaction time on stream of 3.0 h, the 12% catalyst gave a DBT conversion of 77% and biphenyl selectivity of 64%, for an overall biphenyl yield of 49%.

### Table 1

<table>
<thead>
<tr>
<th>Supported Mo (wt.%)</th>
<th>Time-on-stream (h)</th>
<th>DBT conversion (%)</th>
<th>Biphenyl selectivity (%)</th>
<th>Biphenyl yield (%)</th>
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*Percentage of DBT converted to products.

*Percentage of product as biphenyl.
high selectivity toward BP indicates that most of the sulfur can be removed from the DBT molecule prior to the hydrogenation reaction of the aromatic rings. Nevertheless, the lack of a linear relationship between the metal loading and DBT conversion suggests that the optimal dispersion of the sulfided Mo/Co phase occurs at a much lower metal loading.

Because the MSU-γ alumina sample containing 12% Mo (w/w) showed the highest conversion and was the most selective, this catalyst was characterized in greater detail.

3.2. Structural and textural properties

The structural and textural properties of lathlike MSU-γ alumina containing 12% Mo (w/w) were measured at different stages throughout the catalyst preparation and testing processes. Powder XRD patterns and nitrogen adsorption–desorption isotherms were obtained after each of the following four stages: (i) after calcining the pristine MSU-γ alumina support, (ii) following impregnation of the support with Mo and Co precursors, (iii) after sulfiding the metal-loaded support with H2S, and (iv) after DBT catalytic testing. The aluminas at each of these stages are referred to as “pristine”, “loaded”, “sulfided”, and “spent”, respectively.

The wide angle powder XRD patterns for the 12% (w/w) Mo on lathlike MSU-γ system are provided in Fig. 2. The structural integrity of the MSU-γ support remained intact over the duration of the processing and HDS reaction, as evident by the well expressed γ-Al2O3 phase in each pattern. Little or no change in the intensities of the diffraction lines was observed over the entire sequence starting with the pristine alumina and ending with the spent catalyst. Also, no diffraction lines assignable to MoS2 were observed, indicating that the active catalyst is present in small domains and well dispersed on the support.

The nitrogen adsorption–desorption isotherms shown in Fig. 3 make it clear that the process of loading the pre-catalyst onto the support, followed by sulfiding and catalytic testing, compromises the pore structure and textual properties of the lathlike MSU-γ alumina. The data in Table 2 verify the substantial
loss in pore volume and surface area, regardless of the Mo loading over the range 6.0–12% (w/w). A further loss in pore volume and surface area was observed for the spent catalysts. In addition, the pore size distributions became so broad after the initial loading with Mo/Co that it was not possible to determine the mean pore size for the sulfided and spent catalysts (see inset, Fig. 4).

The TEM images shown in Fig. 4 illustrate the morphologies of the lathlike MSU-γ catalyst before and after use under HDS conditions. The pores in the lathlike alumina are slit-like and run in the direction of the fundamental lathlike particles comprising the framework. This lathlike morphology is retained following use under HDS reaction conditions, suggesting that the loss in surface area and pore volume observed by nitrogen adsorption measurements are a consequence of pore filling, perhaps through a thickening of the framework walls. Support for this interpretation is provided by the fact that the low angle diffraction line indicative of a regular pore–pore correlation length is lost following HDS catalysis.
4. Conclusions

As evidenced by XRD results, HDS catalysts supported on lathlike MSU-γ alumina maintained good Mo/Co sulfide phase dispersion under reaction conditions, which is desirable for achieving high activity [20–22]. In addition to differences in the dispersion of the sulfided Mo/Co phase with increasing metal loading, the performance properties of the supported catalyst are almost certainly limited by a loss in surface area and pore volume of the mesostructured support under sulfiding and HDS reaction conditions. The decrease in surface area and porosity occurred with retention of the lathlike framework morphology, suggesting that pore narrowing, rather than structural rearrangement, controls reactivity under HDS conditions.

We note that mesostructured aluminas with amorphous framework walls also have been examined recently as support matrices for the catalytic HDS reaction of thiophene [23]. Although differences in the substrate, catalyst composition, and reaction conditions do not allow a direct evaluation of catalytic efficiency, selectivity, and longevity in comparison with the lathlike MSU-γ aluminas of the present work, we expect the crystalline walls of MSU-γ to provide a measure of improved structural stability relative to amorphous alumina mesostructures. This expected improvement in structural stability should be manifested in improved catalytic performance.

It is important to emphasize that the lathlike framework structure investigated in the present work was obtained by first assembling an atomically disordered alumina–surfactant composite through the hydrolysis of Al13 oligocations in the presence of a polyethylene oxide block copolymer and then transforming the mesostructured composite to mesostructured boehmite and ultimately to mesostructured MSU-γ alumina. An alternative mesostructured form of MSU-γ alumina with a scaffoldlike framework morphology can be obtained using an aluminum alkoxide as a precursor in place of Al13 oligocations [18a]. In the scaffold like mesostructures, the pore network is formed through the intersection of fibrous γ-alumina nanoparticles. As reported by the recent work of Zhu et al. [24], fibrous nanoparticles of γ-alumina can also be prepared through the hydrolysis of sodium aluminate in the presence of a block co-polymer, though in this latter case the resulting product apparently is not mesostructured. Mesostructured scaffoldlike γ-aluminas and related fibrous γ-aluminas may exhibit different changes in textural properties under HDS reaction conditions in comparison to lathlike aluminas. A comparison of the HDS properties of lathlike and scaffoldlike MSU-γ aluminas, along with a comparison with a conventional γ-alumina, will be the subject of future investigations.

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References


