Sonochemical Preparation of Supported Hydrodesulfurization Catalysts

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Abstract: Sonochemical preparation of Co and Ni promoted MoS 2 supported on alumina was achieved by high-intensity ultrasonic irradiation of isodurene solutions containing molybdenum carbonyl, dicobalt octacarbonyl, elemental sulfur, and Al 2 O 3 or Ni−Al 2 O 3 under Ar flow. The sonochemically prepared catalysts were characterized by elemental analysis, XPS, SEM, TEM, and XEDS, and hydrodesulfurization (HDS) activity evaluated for thiophene and dibenzothiophene substrates. The TEM studies on the sonochemically prepared catalysts indicate the formation of layered hexagonal MoS 2 (lattice fringes ~6.2 Å) on the alumina support. The sonochemically prepared Co−Mo−S/Al 2 O 3, Ni−Mo−S/Al 2 O 3, and Co−Ni−Mo−S/Al 2 O 3 are extremely active catalysts for the HDS of thiophene and dibenzothiophene, with activities severalfold those of comparable commercial catalysts under identical conditions. The layered structure of MoS 2 remained intact after 120 h of HDS, and the catalyst is reusable.

Introduction

Removing heteroatoms, especially sulfur, from petroleum constituents has always been an integral part of petroleum processing. 1 In a recent EPA regulatory change, 2 a 10-fold reduction in fuel sulfur emission makes the need for improved hydrodesulfurization (HDS) catalysts urgent. Alumina-supported molybdenum sulfide promoted with cobalt or nickel has been for several decades the catalyst of choice for hydrodesulfurization of fossil fuels due to its remarkable activity. 1,3 Formation of this so-called “Co−Mo−S” structure is known to dominate the catalytic activity of the system. 6 At higher Co loading (Co/Mo > 0.4), however, CoS 2 domains are formed that do not contribute significantly to the HDS activity. Ni can interact with MoS 2 in similar fashion, and there is evidence for a Ni−Mo−S phase. 12

Chianelli et al. 4 proposed that Co or Ni adatoms increase the electron density at the Mo sites and that this results in stronger Mo−S bonds (and thus weaker C−S bonds), which leads to a higher HDS activity. Smit and Johnson, 5 however, have proposed that although Co and Ni do indeed contribute electron density to Mo, this transfer of electron density somewhat reduces the activity of Mo while greatly increasing the activity of the Co or Ni; in essence, MoS 2 can be viewed as a complex support with less sulfide activity than Mo, because of its lower electron density. The traditional synthesis of promoted MoS 2/Al 2 O 3 catalyst by simultaneous or successive impregnation of molybdenum and promoter salts onto alumina, followed by calcination (producing oxides), and sulfidation under the flow of H 2 prior to use, 1,3−7 The HDS activity could be modified by using different molybdenum/promoter precursors, and also by changing the sequence of impregnation of molybdenum and promoter ions on alumina.


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was used to internally calibrate the binding energies. To avoid exposing the catalysts to air, a special transfer vessel was used to load the sample inside the inert atmosphere box and transfer it to the XPS specimen exchange chamber.

Synthesis of Sonocatalytic Co—Mo—S/Al2O3 Catalyst. The synthetic methodology is similar to our previous sonochemical synthesis of nanostructured MoS2.18 The Co promoter ions were also incorporated in the MoS2 lattice sonochemically. In a typical preparation, sulfur (150 mg) is first dispersed in isodurene (35 mL) by short pulses of ultrasound followed by addition of 275 mg of Mo(CO)6, 75 mg of Co2(CO)8, and 750 mg of γ-Al2O3. The vessel was sealed, transferred out of the inert atmosphere box, and sonicated under a flow of Ar for 1.5 h at 80 °C (60 °C bath temperature). The black slurry was then filtered inside the inert atmosphere box using a fine frit and washed several times with pentane. The washed powder was then heat treated to 80 °C under vacuum to remove any unreacted precursors and adsorbed solvent. The powder was annealed by heat treatment at 450 °C under a flow of 10% H2 in He at 30 mL/min for 10 h using a single pass quartz microreactor, which also removes the excess sulfur. The elemental analysis gives a 5.5% Mo and ~4.0% Co loading on alumina support. Similarly, sonochemical preparations were made of unsupported MoS2/Al2O3 and unsupported Co—Mo—S for comparison.

Synthesis of Sonocatalytic Ni—Mo—S/Al2O3 Catalyst. We have designed a different route to incorporate Ni in MoS2/Al2O3 because volatile Ni precursors (e.g., Ni(CO)4) are exceptionally toxic and dangerous to use.19 Nickel coated on Al2O3 (Ni—Al2O3) has been used both as the Al2O3 support and as the source for Ni in the sonochemical preparation of Ni—Mo—S/Al2O3. To prepare Ni—Al2O3, γ-Al2O3 is first soaked in an aqueous solution of Ni(NH3)2(NH2COO)·H2O complex for 1 h, dried in air, and heat treated under 10% H2 in He at 300 °C for 2 h. Ni(NH3)2(NH2COO)·H2O was synthesized and characterized according to methods outlined in the literature.20 The sonochemical Ni—Mo—S/Al2O3 catalyst is then made by the same method as Co—Mo—S/Al2O3 by using Ni—Al2O3 (750 mg), Mo(CO)6 (275 mg), and sulfur (150 mg). The initial sonochemical Ni—Mo—S/Al2O3 was annealed by heat treatment at 450 °C under a flow of 10% H2 in He (30 mL/min) for 10 h using a single pass quartz microreactor. The sonochemically prepared catalyst typically has a 5.5% Mo and ~2.8% Ni loading.

Synthesis of Sonocatalytic CoNi—Mo—S/Al2O3 Catalyst. For the preparation of CoNi—Mo—S/Al2O3, we use 3.5% Ni—Al2O3, Mo(CO)6, Co2(CO)8, and sulfur. The sonochemical CoNi—Mo—S/Al2O3 catalyst is then made by the same method as Co—Mo—S/Al2O3 by using Ni—Al2O3 (750 mg), Mo(CO)6 (275 mg), Co2(CO)8 (40 mg), and sulfur (150 mg). The initial sonochemical Ni—Mo—S/Al2O3 was annealed by heat treatment at 450 °C for 10 h under 10% H2 in He flow (30 mL/min). The catalyst has a 5.5% Mo, 1.5% Co, and ~2.5% Ni loading.

HDS of Thiophene. Catalytic studies of HDS of thiophene were performed at atmospheric pressure in a single-pass microreactor. The thiophene vapors were carried at a constant partial pressure of 75 mbar by a flow of hydrogen [flow rate = 23 cm3(STP)/min]. The reaction products were analyzed with an on-line HP GC-MS and a 5730A HP GC fitted with a 9-R-octane/Porasil C column and a flame ionization detector.

HDS of Dibenzothiophene. DBT HDS was accomplished using a home-built stainless steel pressure vessel and sample withdrawal system. Catalyst (30–50 mg) was dispersed in 50 mL of decane containing 1% w/w dibenzothiophene (40 mL, 370 mg). The vessel was flushed with H2 and pressurized to 3.4 MPa (500 psig) and heated to 375 °C during 1 h. For consistency, t0 was denoted as the time when the target temperature was reached (at the end of ramping). In all cases, reactions reached equilibrium within 15 min after t0. Samples were withdrawn in duplicate at 30, 45, 60, 75, and 90 min after t0. The sampling system was equipped with a 2 μm stainless steel filter to prevent the removal of catalyst from the system. Aliquot size was about 0.25 mL. The samples were then centrifuged to remove any solid particulate, diluted 1:10 in pentane, and analyzed with GC-MS.


Results and Discussion

Sonochemistry introduces a fundamentally different way of making materials by taking advantage of the intense energy within a collapsing bubble in a sound field\(^\text{16,21}\). A bubble expands and contracts in response to the negative and positive pressure induced by a sound field. The bubble grows larger during each cycle due to rectified diffusion and inertial growth. Once the bubble reaches a critical size, the next compression wave can create a violent collapse, the last stage of which is a near-adiabatic process. The temperatures during this stage reach upward of 5000 K with pressures above 300 atm\(^\text{22}\). In our experimental conditions, Mo(CO)\(_6\) vapor in the bubble decomposes to give Mo atoms due to the local hot spots formed after bubble collapse. The hot Mo atoms coming out of the bubble react with the sulfur in the medium to form nanostructured MoS\(_2\) (size \(\sim\) 3 nm)\(^\text{17}\) and deposit on the alumina support as small clusters. The added Co\(_2\)(CO)\(_8\) decomposes in a fashion similar to give Co atoms along with Mo atoms during the bubble collapse.

Nickel hydrazine carboxylate complex, Ni(N\(_2\)H\(_4\))(N\(_2\)H\(_3\)-COO)\(_3\)\(\cdot\)H\(_2\)O, has been used as precursor for Ni for the preparation of sonochemical Ni–Mo–S/Al\(_2\)O\(_3\). We were attracted by the low-temperature autocatalytic decomposition of the complex to yield pure nanocrystalline Ni (\(\sim\)3 nm) particles. A large amount of work has been carried out on decomposition of metal hydrazine carboxylate complexes under aerobic conditions for the synthesis of ultrafine particles of pervoskites and spinel metal oxides\(^\text{20}\). The fine particle nature of the oxide residue is due to the evolution of a large amount of gases during the decomposition of hydrazine carboxylate complexes. We have exploited this feature to prepare metallic clusters by decomposing the hydrazine carboxylate complex under a 1:10 H\(_2\)/He flow.

Characterization. The powder XRD of the sonochemical sample primarily showed the reflections of \(\gamma\)-Al\(_2\)O\(_3\) with small broad peaks correspond to MoS\(_2\). The nanostructured nature of the sonochemical MoS\(_2\) particles causes the XRD line broadening and does not yield any information about the crystal structures of active components. SEM micrographs of sonochemically prepared catalysts show the MoS\(_2\) particles made up of small spherical clusters as observed earlier for bulk sonochemical MoS\(_2\). Each spherical cluster is made up of finer particles of \(\sim\) 3 nm diameter, and the cluster rests atop a porous platelet of the alumina support. Representative micrographs of the sonochemical and commercial Ni–Mo–S/Al\(_2\)O\(_3\) are shown in Figure 1. The SEM-XEDS analysis on the small spherical clusters showed increased signal intensity of the Mo compared to Al and O. This confirms our conclusion that in the sonochemically prepared catalysts, the small spherical clusters on the alumina support are indeed mostly MoS\(_2\). The SEM morphologies of sonochemically prepared Co–Mo–S/Al\(_2\)O\(_3\) and Co–Ni–Mo–S/Al\(_2\)O\(_3\) are identical to the Ni–Mo–S/Al\(_2\)O\(_3\). The elemental analysis and composition have also been examined using XEDS analysis coupled to SEM. The SEM-XEDS analysis profiles of sonochemically prepared catalyst are shown in Figure 2. The presence of Co and Ni has been confirmed by the characteristic signals of K lines at \(\sim\)7 and

\(~7.5\) keV, respectively. The L lines of Co and Ni can also be seen at \(~1\) keV. Unambiguous determination of sulfur and molybdenum were not possible on the SEM due to the overlap of the S K and Mo L lines at \(~2.5\) keV. The Mo K lines,
however, could be resolved at around 17.5 keV using high-resolution STEM-XEDS analysis (discussed below). The XEDS peak intensities were calibrated using a Cu grid for the calculation of elemental composition. The percentage of Mo is enhanced by 3-fold compared with the bulk elemental analysis values which indicate the surface enhancement of Mo (penetration depth under these conditions for XEDS ~4.5 μm).

Therefore, the SEM-XEDS studies on sonochemically prepared catalysts confirm that the active component is indeed mostly on the exterior surface of the support.

The TEM of sonochemically prepared catalyst shows the lattice fringes of MoS₂ layers with interlayer spacing of ~6.2 Å, the same as those for bulk MoS₂. The TEM shown in Figure 3 shows the microstructure of sonochemically prepared Co–Mo–S/Al₂O₃ and commercial Co–Mo–S/Al₂O₃ catalysts. The lattice fringes of MoS₂ are clearly seen on the surface of the support. Comparing TEM of the industrial and sonochemically prepared catalysts reveals an important difference: the industrial catalyst is mostly composed of multi-stacked and ordered layers with few wrinkled fringes, while the sonochemical Co–Mo–S catalyst shows short lengths of wrinkled layers that are highly disordered, and have only minimal layer stacking. The disordered, fractured, and defective nature of sonochemically prepared MoS₂ layers is inherent in having clusters made up of nanometer sized, highly dispersed MoS₂ particles. The sonochemically prepared MoS₂ has increased edge density and higher dispersion, both of which are desirable for HDS activity. Similarly layered MoS₂ structures are also observed for the sonochemically prepared Ni–Mo–S/Al₂O₃ and Co–Ni–Mo–S/Al₂O₃.

The electronic states of metals and sulfur in the catalyst were probed by X-ray photoelectron spectroscopy (XPS). XPS of the sonochemically prepared catalyst showed that the Mo is concentrated at the surface (X-ray penetration depth ~50 Å). The XPS signal intensities were corrected with sensitivity factors for the calculations of atomic concentration. The atomic concentration calculations indicated that there is a 5-fold enhancement of surface Mo versus the bulk material for the sonochemically prepared catalyst. On the other hand, the commercial catalyst did not show Mo surface enhancement in XPS.

Table 1 summarizes the XPS binding energies (BE) of Mo, Co, Ni, and S of sonochemical Co–Mo–S/Al₂O₃, Ni–Mo–S/Al₂O₃, and Co–Ni–Mo–S/Al₂O₃ as well as binding energy differences ΔE₁ and ΔE₂ (which are obtained by subtracting the BE of M(2p₃/₂) (M = Co, Ni) and Mo(3d₅/₂) from the S(2p₃/₂), respectively). The XPS BE, ΔE₁, and ΔE₂ values of unsupported sonochemical Co–Mo–S and commercial supported samples are also included in Table 1 for comparison.

It is known that Co interacts with the Al₂O₃ support due to the facile formation of spinel CoAl₂O₄ oxide phase; the spinel phase actually decreases HDS activity. The BE of sonochemical unsupported Co–Mo–S and supported Co–Mo–S/Al₂O₃ is identical, indicating a negligible interaction between the support and cobalt under the sonochemical samples. This is further supported by BE values of a commercial carbon supported catalyst (Co–Mo–S/C), which are identical to those of supported and unsupported sonochemically prepared catalysts. The peak positions of M, Mo, and S in the sonochemically prepared catalyst are in good agreement with the conventional samples.

We also performed STEM-XEDS spot analysis on the sonochemical samples to determine if the promoter-metal and Mo atoms coexist spatially or if they phase segregate. Figure 4a shows a STEM micrograph of sonochemical Ni–Mo–S/Al₂O₃ catalyst. The circles represent the locations and the areas of analysis. Analysis was done both on and off MoS₂ fringes (“on-fringe” and “off-fringe”, respectively), and the intensities


Table 1. XPS Binding Energy Values for Sonochemically Prepared Catalysts

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<tr>
<td>M (Co, Ni) 2p₉₂</td>
<td>778.6</td>
<td>778.6 (778.6)</td>
<td>853.6 (852.8)</td>
<td>778.6, 853.5</td>
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<td>S 2p₉₂</td>
<td>162.4</td>
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<td>ΛΔ E₁ (M 2p₉₂ − S 2p₉₂)</td>
<td>616.2</td>
<td>616.1 (617.4)</td>
<td>691.0 (690.7)</td>
<td>661.6, 691.0</td>
<td>661.6</td>
</tr>
<tr>
<td>Mo 3d₃/₂</td>
<td>229.1</td>
<td>229.0 (228.1)</td>
<td>229.2 (228.8)</td>
<td>229.2</td>
<td>229.1</td>
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<tr>
<td>ΛΔ E₂ (Mo 3d₃/₂ − S 2p₉₂)</td>
<td>66.7</td>
<td>66.5 (66.9)</td>
<td>66.6 (66.7)</td>
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a Values determined for the equivalent conventional catalyst (ref 25) are given in parentheses. b Reference 25.

Figure 4. (A) STEM of sonochemically prepared Ni–Mo–S/Al₂O₃ showing MoS₂ lattice fringes and displaying the areas of analysis. (B) Spot XEDS analysis on and off fringes for Ni–Mo–S/Al₂O₃ scaled to Mo K intensity. The inset shows an enlarged view of Ni K/Cu K and Mo K regions.

Figure 5. Longevity of catalytic activity for hydrodesulfurization of thiophene at 400 °C. From left to right at each time: sonochemically prepared CoNi–Mo–S/Al₂O₃; sonochemically prepared Co–Mo–S/Al₂O₃; Ni–Mo–S/Al₂O₃, treated thermally with H₂ in He; commercial (Crosfield) Co–Mo–S/Al₂O₃; and commercial (Crosfield) Co–Mo–S/Al₂O₃.

HDS of Thiophene. The specific surface areas of the pretreated sonochemical and commercial catalysts were ~170 and ~220 m²/g, respectively, but this simply reflects the total surface area of the support. Given the different degree of dispersion for sonochemical and industrial catalysts and the fact that the active sites are located at the edges of MoS₂ layers, activity is normalized to the mass of metal, rather than to the surface area. The stability of the sonochemical and commercial catalysts was measured over the course of 5 days by continuous HDS of thiophene using a single-pass microreactor at 400 °C. Figure 5 displays the turnover frequencies as a function of catalytic use over time. The stabilities of the promoted sonochemically prepared catalysts were calculated using a first-order exponential fit after reaching a steady state conversion (60 h). The half-lives for the sonochemically prepared catalysts are around 25 days, comparable to the commercial catalyst. In addition, the sonochemically prepared catalysts can be easily regenerated at 450 °C for 10 h under 10% H₂ in He flow and return to nearly their initial activity.

As is seen in Figure 5 (and discussed below), the sonochemical Co–Ni–Mo–S/Al₂O₃ catalyst shows higher activity for HDS of thiophene than the Co or Ni promoted sonochemical and commercial catalysts. The variation of catalytic activity as a function of Co wt % in Co–Ni–Mo–S/Al₂O₃ is shown in Figure 6. The activity values plotted here were measured after 60 h of use. As the concentration of Co promoter increases in Co–Ni–MoS/Al₂O₃, the catalytic activity increases to an optimum composition of 2% Co and 2.8% Ni.

It is worth mentioning that the HDS activity of Ni and Co promoted sonochemically prepared catalyst is higher after thermal treatment with 10% H₂ in He than if treated only with He. This is most likely because H₂ removes sulfur atoms from the edges of the Co–Mo–S or Ni–Mo–S structures, resulting in coordinatively unsaturated Mo and promoter atoms that are more active catalytic sites for HDS.
The principal products detected by GC-MS were the C₄ hydrocarbons: butane, 1-butene, trans-2-butene, and cis-2-butene (Figure 7). We do not see butadiene due to the high reactivity of the catalyst (40% conversion); the amount of tetrahydrothiophene in the product is <0.2%. The promoted catalysts show high selectivity for butenes compared with the unpromoted MoS₂, which gives more butane. In the absence of promoters the butadiene or thiophene strongly adsorbs on MoS₂ and undergoes extensive hydrogenation. On the basis of the observed products, a plausible mechanism for thiophene HDS would involve initial homolytic cleavage of the thiophene C=S bond and hydrogenolysis to give H₂S and butadiene. Butadiene undergoes rapid hydrogenation to 1-butene, which is subsequently hydrogenated slowly to butane or isomerized to a thermodynamic mixture of cis- and trans-2-butenes (Scheme 1). Tetrahydrothiophene can also undergo HDS to give butane.

**Scheme 1**

![Scheme 1](image)

HDS of Dibenzothiophene. Analysis of the aliquots withdrawn from the pressure vessel during the reaction shows a linear decrease in the concentration of dibenzothiophene (DBT) over time. This indicates zero order kinetics, observed when the substrate concentration is high and turnover is determined by the availability of active sites on the catalyst. Figure 8 shows specific activity of each catalyst measured as molecules of DBT consumed per gram of metal per minute.

Comparing sonochemically prepared catalysts to industrial ones, it is clear that sonochemically prepared catalysts are superior for HDS of DBT. The sonochemical Co-Mo-S/Al₂O₃ is more active than the sonochemical Ni-Mo-S/Al₂O₃, and they are about two and four times more active than their commercial counterparts, respectively. The enhancements in activity of the sonochemically prepared catalyst could be due to improved mass transport since the active species are predominantly on the outside surface of the alumina support. The beneficial effect on the HDS performance of Co-Mo-S/Al₂O₃ is probably due to the different stages and nature of incorporation of Co and Ni to MoS₂.

Product distribution afforded by an HDS catalyst is also of importance. Numerous studies have been carried out on coordination of DBT and other thiophenic species on model catalysts. Dibenzothiophene adsorbed on the catalyst can undergo either hydrodesulfurization or hydrogenation. Scheme 2 shows the general pathways for DBT reactions. The two major products of hydrodesulfurization of DBT are biphenyl (BP) and cyclohexylbenzene (CHB). BP is the direct HDS product and is desired due to its commercial application and smaller hydrogen consumption, while CHB is a product of HDS of tetrahydrodibenzothiophene (TH-DBT), which itself is an incomplete hydrogenation product of DBT. Classic experimental and theoretical work by Chianelli, Daage, and Murray have shown that HDS can happen on the rim and edge sites of a multilayer MoS₂ catalyst, while hydrogenation probably only happens on the rim sites. Furthermore, selectivity [CHB]/[BP] is greatly dependent on partial pressure of H₂ and temperature. High temperatures and H₂ pressures yield more CHB. The product distribution of sonochemically prepared catalysts is shown in Figure 8.


was nearly identical or slightly better than that of the industrial catalyst (Figure 9). All of the product distribution measurements were obtained at 74% DBT conversion. For all catalysts studied, BP was the major product, although the Co-promoted catalysts were more selective than the Ni-promoted ones. The amount of TH-DBT also reflected catalyst selectivity. In the case of Co catalysts, TH-DBT only constituted 1.0–1.3% of the total product, while for the Ni catalyst, the amount was ~1.9%. In all cases, complete hydrogenation products such as bicyclohexane accounted for less than 0.3% of products.

**Conclusion**

Co, Ni, and Co–Ni promoted molybdenum sulfide on alumina catalysts have been generated ultrasonically using molybdenum carbonyl, elemental sulfur, dicobalt octacarbonyl, and Al₂O₃ (or nickel on Al₂O₃). TEM studies demonstrated that the sonochemical technique enhances the dispersion of MoS₂ layers on the alumina support compared to the conventional, commercial catalyst (Crosfield). SEM-XEDS and XPS studies have shown that the Mo is mostly concentrated on the surface of alumina in the case of the sonochemically prepared catalysts, but not for conventionally prepared catalysts. STEM-XEDS spot analysis showed that Mo is not phase segregated from the promoter metals (Co, Ni, and Co–Ni) on the scale of ~3 nm, indicating the formation of binary metal sulfide M–Mo–S structures. The HDS activity of sonochemical Co promoted MoS₂/Al₂O₃ is slightly higher than that of the Ni counterpart, and they are 2-fold times and 3-fold times more active than their respective commercial counterparts. The bimetallic Co–Ni promoted MoS₂/Al₂O₃ has HDS activity 3-fold and 7-fold times better than the commercial Co–Mo–S/Al₂O₃ and Ni–Mo–S/Al₂O₃ catalysts, respectively. The superior HDS activity of sonochemical MoS₂ catalysts is likely to arise from the higher dispersion of the MoS₂ on the support and the consequent higher concentration of the catalytically active edge sites.

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