Unsupported MoS₂ and CoMoS₂ catalysts for hydrodeoxygenation of phenol

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HIGHLIGHTS

► Activity and selectivity of MoS₂ catalysts for phenol HDO strongly depends on structure and promoter.
► Molybdenum–sulfur bond strength of MoS-A is weaker than that of MoS-C.
► HYD pathway was favored over crystalline catalysts with high stacking of MoS₂ slabs.
► Co addition decreased the Mo–S–Co bond strength causing the increasing activity.
► High activity observed with CoMoS-A was due to the increase in DDO rate.

ARTICLE INFO

ABSTRACT

The structural properties and catalytic functionality of two different morphologies of unsupported MoS₂ catalysts were investigated systematically. Hydrodeoxygenation (HDO) of phenol was used as the model reaction to examine the effect of the catalyst structure on the hydrogenolysis and hydrogenation activity and selectivity. The unsupported MoS₂, with amorphous and highly bent multi-layer structures, was much more active than the highly crystalline structured MoS₂ and resulted in direct oxygen elimination. Co promoter showed a strong effect on the activity and selectivity of Mo sulfides. Temperature programmed reduction (TPR) exhibited the close interaction between Co and Mo in the bimetallic sulfide catalysts resulting in shift of TPR peaks to lower temperatures. The addition of promoter also affected the textural properties of amorphous Mo sulfide by decreasing the surface area, changing the pore characteristics and shifting the pore-size distribution towards smaller sizes. The growth of MoS₂ crystallized particles was inhibited when Co was incorporated. The enhanced catalytic activity observed with the promoter addition was essentially due to the enhancement of the rate of direct-deoxygenation route. The present study indicated that the activity and selectivity for phenol HDO can be controlled by tailoring the morphology and the promoter of the unsupported MoS₂ catalysts.

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1. Introduction

During the 20th century, fuel consumption has increased rapidly and much of this is derived from non-renewable fossil fuels. Thus, many countries are increasingly looking to other renewable sources of fuel for their energy needs. In this regard, bio-oil, which can be obtained from various biomasses, including waste biomass, by liquefaction or pyrolysis, is an interesting alternative to liquid fuel. However, bio-oil typically contains a relatively high amount of phenolic compounds, aldehydes and esters (Chumpoo and Prasassarakich, 2010; Xu and Etcheverry, 2008), and this high oxygen content leads to detrimental properties. To overcome these problems, bio-oil can be upgraded by catalytic hydrodeoxygenation (HDO), using procedures which have been adapted from petroleum hydrotreatment, to remove the oxygen and increase the hydrogen content to form the required hydrocarbon product (Laurent and Delmon, 1993; Li et al., 2008). Conventional catalysts used in the hydrotreating process are mainly molybdenum sulphide (MoS₂) based catalysts, most often supported on γ-Al₂O₃ and promoted by Ni or Co (Girgis and Gates, 1991; Speight and Ozum, 2002). In 2001, a new family of highly loaded or bulk sulfide catalysts emerged in the market (NEBULA-type catalysts) (Eijsbouts et al., 2007). Such systems, bearing a very high amount of active sites per unit

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volume, provide a higher activity than conventional catalysts. Thus, the preparation of new bulk or highly loaded sulfide catalysts seems to be a promising research direction.

Understanding the relationship between the active sites and the structure of MoS_2 catalysts is important when trying to improve the catalyst's performance. A number of studies have reported on the structure–activity relationships for MoS_2 catalysts, but these have mainly focused upon the hydrodesulfurization (HDS) process (Hensen et al., 2001; Schweiger et al., 2002). These studies have indicated that the catalytic activity is closely associated with the edges of the planes of the MoS_2 layers, and in particular with the sulfur vacancies that are formed on the edge sites. A good correlation between the HDS conversion and the number of Mo atoms at the corners and edges of the MoS_2 crystallites was reported by Eijsbouts et al. (1993). Considerable effort has been directed towards atomistic theory models of the catalytically active phases (Cristol et al., 2002; Paul et al., 2008). Current models consider the difference between the crystallographically distinct MoS_2 slab terminations, (namely metal M (1 0 1 0) and sulfur S (1 0 1 0) edges) as a key point for the understanding of catalytic activity and promotion trend (Byskov et al., 1999).

It is well established that Mo-based catalysts are promoted by the addition of cobalt (Co) or nickel (Ni) in much more than trace amounts. The synergetic effects of promoter on the catalytic activity of the Mo sulfides have been reported by many researchers in the literatures (Alvarez et al., 2004; Pedraza and Fuentes, 2000). The effect of promoter in Mo sulfide catalysts has been attributed to the number of promoter atoms that can be accommodated on the edges of MoS_2 layers and also to the electronic transfer that the promoter atom induces on Mo atoms located at these sites (Harris and Chianelli, 1986).

The HDO of phenolic compounds using unsupported MoS_2 catalysts with different morphologies was compared based on rate constants, evaluated from a kinetic study, and stacking degree morphology, evaluated from transmission electron microscopy (TEM; Yang et al., 2008b). The ammonium heptamolybdate (AHM) derived MoS_2 catalyst exhibited the highest activity for HDO of phenolic compounds, and the effect of the reaction temperature on the HDO conversion efficiency was explained in terms of equilibrium effects and reversible reaction kinetics (Yang et al., 2008a). In the present study the activity and substrate specificity of unsupported amorphous MoS_2 (MoS-A) prepared by the hydrothermal method (Song et al., 2002; Yoneyama and Song, 1999; Yoosuk et al., 2010) is compared with a commercial crystalline MoS_2 preparation (MoS-C) for HDO reaction using phenol as the model reactant. This allows the study of the catalyst selectivity for hydrogenolysis (via the direct deoxygenation (DDO) pathway) and hydrogenation (via the combined hydrogenation and dehydration (HYD) pathway) reactions in the HDO system. The effect of promoter (Co) on activity and morphology of MoS-A catalyst is also studied. Our aim is to evaluate and discuss the structure and promoter effect of unsupported MoS_2 and to determine their influence on the two main HDO pathways (DDO and HYD) of phenolic compounds.

2. Experimental

2.1. Preparation of catalysts

High-purity ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$, ATTM, Sigma-Aldrich), phenol (Fisher Scientific), decahydronaphthalene (decalin, Fluka), and n-decane (Fluka) were used without further purification. It was noted that during the long-time storage of ATTM in closed vials exposure to air may led to degradation of the reagent and resulted in deviation in the observed activity of the in-situ generated MoS_2 catalysts from different bottles of the ATTM reagent. In this work, a bottle of newly purchased ATTM was used in synthesis, and the ATTM reagent was stored in a refrigerator in order to minimize oxidative degradation.

The amorphous Co–Mo sulfide catalysts (CoMoS-A) were synthesized using a step hydrothermal method. The catalyst synthesis was carried out in a 250 mL Parr reactor. ATTM (0.15 g) was dissolved in 25 g of deionized water and 2.5 g of organic solvent (decalin) was then added to this solution. Co $(NO_3)_2 \cdot 6H_2O$ was dissolved in the minimum amount of water and the desired amount of cobalt was added so as to give the atomic ratio of Co/(Mo+Co) as 0.2, 0.3, 0.4, and 0.6. The reactor was purged, then pressurized with hydrogen gas to an initial pressure of 2.8 MPa and then heated to 350 °C. After 1 h, the resulting catalysts were separated and immersed in an organic solvent. Each amorphous Co–Mo sulfide catalyst was designated as 'CoMoS-A-X, where X represents the molar ratio Co/(Mo+Co).

The amorphous Mo sulfide catalyst (MoS-A) was prepared by the same procedure as for the Co–Mo sulfide catalysts, but without the Co precursor. Crystalline MoS_2 (MoS-C) powder purchased from Sigma-Aldrich was used as received.

2.2. Characterization of catalysts

The crystalline Mo sulfide (MoS-C), amorphous Mo sulfide (MoS-A) and amorphous Co–Mo sulfide (CoMoS-A-0.2; Co/(Mo+Co) ratio=0.2) catalysts were characterized. The N_2 adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 instrument. Pore-size distributions of the samples were determined from the isotherms by the Barrett–Joyner–Hallenda (BJH) method. Fresh samples were vacuum dried before the adsorption measurement. The X-ray diffraction (XRD) patterns were obtained on a Scintag Powder diffractometer with Cu Kα emission and 0.02° per step. The diffractograms were analyzed using the standard JCPDS files. The transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 transmission electron microscope. A small amount of the sample was ground with a mortar and a pestle. The sample was then suspended in ethanol and sonicated. A drop of the suspension was put on a layer carbon film supported by a Cu grid.

Temperature-programmed reduction (TPR) was conducted with a Micromeritics AutoChem 2910 instrument in Materials Research Laboratory. About 0.1 g of sample was charged in the reactor and heated up to 500 °C at a rate of 10 °C/min, held at 500 °C for 30 min and then cooled to room temperature under an Ar flow to remove the adsorbed materials. A mixture of 4.8 vol% H_2/Ar was introduced at 50 mL/min into the sample loop. The heat treated sample was again heated at a rate of 10 °C/min to 650 °C and the effluent gas was passed through a cold viscous solution of isopropanol (cooled by liquid N_2) to remove the water produced during the reduction reaction and analyzed using a thermal conductivity detector.

2.3. Hydrodeoxygenation (HDO) reaction

The HDO of phenol was carried out in a 250 mL Parr reactor. The reactor was charged with phenol (0.3 g), n-decane (19.7 g) and catalyst (0.075 g). The reactor was purged with hydrogen and then pressurized up to an initial pressure of 2.8 MPa. The reactor was heated to the temperature of 350 °C and maintained at that temperature for the reaction time of 60 min with constant stirring at 150 rpm. Then, the reactor was cooled down to room temperature, the gas inside was vented, and the liquid products were rinsed from the reactor. The resulting suspension was filtered