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Enhanced catalytic performance and promotional effect of molybdenum sulfide cluster-derived catalysts for higher alcohols synthesis from syngas

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ABSTRACT

A series of catalysts were prepared using molybdenum sulfide clusters as precursors and their catalytic performance for higher alcohols synthesis was evaluated. It was found that the cluster precursors could provide well-dispersed MoS₂ particles and a number of coordinated unsaturated Mo sites with all the catalysts in varying degrees, which were favorable for the formation of intermediate active phases thereby enhancing catalytic performance. In particular, K-NiMo₃S_x catalyst obtained by using heterobimetallic cluster NiMo₃S₁₃ as precursor exhibited the highest activity with the space-time-yield (STY) of total alcohols (497 mg/g/h) and the selectivity of higher alcohols (59.71%), which could be attributed to the interaction effect of the Ni promoter and Mo species and the resultant formation of active phase NiMo₃S_x. Thus, the most key factor for obtaining highly efficient molybdenum sulfide catalysts was to produce a number of coordinated unsaturated sites, on which abundant NiMoS active phase can be formed and the formation of bulk inactive phase should be avoided.

1. Introduction

The rapid growing energy demand with serious environment issue has attracted enormous attention to look for alternative and sustainable resources [1–3]. Higher alcohols have received extensive attention because they can improve the octane number of gasoline and the heat of vaporization, taking advantage of lower vapor pressure and negligible emission of pollution [4–7]. In the past years, various catalysts for the conversion of syngas to higher alcohols have been researched. As a result, several catalytic systems were developed for hydrogenating CO to higher alcohols [8–12]. Among them, alkali-modified molybdenum sulfide catalysts have been extensively investigated since they have high activity for the synthesis of higher alcohols and sulfur-resistant property [13–15]. However, it seems that the reported activity of catalysts is far from the requirement for practical application. Thus, it is necessary to further enhance the activity and selectivity to higher alcohols synthesis. Previous studies showed that the 3d transition metals (such as Ni) were able to enhance the alcohol yield and C₂₊OH selectivity over K modified MoS₂ catalysts [16–18]. Typical conventional alkali-modified MoS₂ catalysts were prepared by impregnating an aqueous solution of an oxidic Mo and transition metals salts on support, subsequently calcining and sulfiding [19,20]. For such traditional method, it is very difficult to control the surface composition or define the nature of the active site. Besides, it is easy to form inactive bulk

particles, leading to few exposed active sites [21,22]. In fact, small crystallites have advantages to produce alcohols while larger crystallites to hydrocarbons [16]. Furthermore, it has been recognized that the promotion effects are closely related to the structure and morphology of promoter, and the highly-dispersed promoter species always lead to the high performance of the higher alcohol synthesis [20,23]. On this basis, it is interesting to search for new Mo-based catalysts with a number of exposed active sites and highly dispersive MoS₂ species.

The numerous computational and experimental studies have shown that the edge sites of MoS₂ planes have excellent catalytic activity for higher alcohols synthesis [23–25]. A promising approach is to directly design molybdenum sulfide catalyst using organometallic clusters, because their structures are well defined and offer an opportunity to form the nature of the active site, which can vividly simulate the MoS₂ edge sites in catalytic reactions. In particular, heterobimetallic cluster catalysts can be used to further understand the correlation of the structural characteristics and the activity of these catalysts.

Herein, we investigated the catalytic performance of Mo sulfide catalysts prepared from the cluster compound (NH₄)₂Mo₃S₁₃·H₂O and NiMo₃S₁₃·2H₂O for higher alcohols synthesis. The cluster [Mo₃S₁₃]²⁻ is a trimer analogue. In addition, these materials have excellent thermal stability and abundant exposed active sites. In particular, NiMo₃S₁₃·2H₂O bimetallic sulfide cluster is a great promising precursor for the higher alcohols synthesis because it can form molecularly-

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dispersed Ni on the surface of catalyst. Therefore, they can be used to elucidate the fundamental reaction mechanisms. It was found that the catalytic activity remarkably increased over K-NiMo₃S_x catalyst derived from NiMo₃S₁₃·2H₂O bimetallic sulfide cluster, and it exhibited the highest higher alcohols selectivity (59.71%) and STY of total alcohols (497 mg/g/h) among the three samples. On the basis of the characterizations of catalysts, the high catalytic performance of K-NiMo₃S_x was related to the interaction between Ni and Mo in the NiMo₃S₁₃·2H₂O molecular structure, which facilitated the formation of active phase NiMo₃S_x.

2. Experimental

2.1. Chemicals

All chemicals were obtained from commercial sources and used without further purification. Ammonium heptamolybdate ((NH₄)₂Mo₇O₂₄·4H₂O, Sinopharm Chemical Reagent Co., Ltd, > 99%), ammonium sulphide ((NH₄)₂S, Alfa Aesar, 20% aq. soln.), potassium carbonate (K₂CO₃, Alfa Aesar, > 99%) and nickel (II) chloride hexahydrate (NiCl₂·6H₂O, Sinopharm Chemical Reagent Co., Ltd, > 99%) were used in the experiments.

2.2. Catalyst preparation

(NH₄)₂Mo₃S₁₃·H₂O was obtained through the reaction of (NH₄)₂S, (NH₄)₂Mo₇O₂₄·4H₂O and S [26]. (NH₄)₆Mo₇O₂₄·4H₂O (3.02 g) was dissolved in 40 mL of a (NH₄)₂S aqueous solution (20%) until the precipitation of (NH₄)₂MoS₄ as an abundant crystalline red solid formed. Elemental sulfur (1.23 g) was added to the solution, which was heated under reflux at about 90 °C for 12 h. Then, the hot solution was filtered, and the resultant solid was washed with water (25 mL) and dried with ethanol and diethylether. NiMo₃S₁₃·2H₂O was obtained through the reaction of Na₂Mo₃S₁₃·H₂O and NiCl₂·6H₂O.

Molybdenum sulfide catalysts were prepared using molybdenum sulfide cluster as precursor by in situ thermal decomposition method, which were labelled as K-NiMo₃S_x and K-Mo₃S_x. The molar ratio of K/Mo in the two catalysts was 0.7:1. K-NiMo₃S_x was synthesized by grinding K₂CO₃ with NiMo₃S₁₃·2H₂O (K/Mo = 0.7) in a mortar and pestle in ether for 1h, and the resulting mixture was dried. Before reaction, the catalysts were decomposed in situ by syngas at 10MPa with WHSV of 3000 h⁻¹ and 330 °C for 12 h K-Mo₃S_x (K/Mo = 0.7) was prepared by mixing (NH₄)₂Mo₃S₁₃·H₂O with K₂CO₃ in a mortar and pestle and the procedure was similar to that of K-NiMo₃S_x.

In order to demonstrate that K-NiMo₃S_x catalyst derived from heterobimetallic cluster could significantly improve the formation of higher alcohols, the Ni promoter was introduced to K-Mo₃S_x catalyst by mechanical mixing method to give K-Mo₃S_x-NiAc with a K/Ni/Mo molar ratio of 2.1/1/3. The preparation procedure of K-Mo₃S_x-NiAc was the same as the K-Mo₃S_x except the introduction of Ni(CH₃COO)₂·4H₂O. The actual molar ratios K/Mo, K/Mo/Ni and K/Mo/Ni in the three catalysts K-Mo₃S_x, K-Mo₃S_x-NiAc and K-NiMo₃S_x calculated by the ICP-AES results were 0.696: 1, 0.720:1:0.338 and 0.703:1:0.331, respectively (Table S1). The molar ratios K/Mo/S, K/Mo/Ni/S and K/Mo/Ni/S in K-Mo₃S_x, K-Mo₃S_x-NiAc and K-NiMo₃S_x measured by XPS were 0.728:1:2.32, 0.668:1:0.385:2.59 and 0.742:1:0.367:2.74 respectively (Table S2).

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were measured on a Panalytical X-Pert PRO diffractometer. Thermogravimetric analysis of the molybdenum sulfide clusters was carried out in a TG-DTG Instruments Exstar 7300 apparatus, with a heating rate of 5 K/min, in the 298–1173 K range under a 50 ml/min nitrogen flow. Temperature programmed reduction (TPR) experiments were carried

out on a Micromeritics AutoChem II 2920 automatic analyzer equipped with a TCD and the reactor effluent composition was continuously monitored as a function of sample temperature by a mass spectrometer (Hiden, QIC-20). Prior to the experiments, the catalysts (0.08 g) were activated for 1 h in Ar at 330 °C, and then cooled to room temperature under the same gas flow. The reduction step was performed in 10% H₂ in Ar, with a heating rate of 5 °C/min up to 900 °C. The transmission electron microscopy (TEM, FEI Tecnai F20) equipped with an energy dispersive X-ray (EDX) spectroscopy was applied for the morphology and composition analyses of the as-synthesized samples. X-ray photoelectron spectroscopy (XPS) was performed using an XSAM800 XPS spectrometer. Detailed analyses for catalytic products were performed on gas chromatography (GC) (Shimadzu GC-2014).

2.4. Catalytic tests

The catalytic test for higher alcohols synthesis was conducted at 10.0 MPa, 330 °C and 3000 h⁻¹ in a fixed-bed stainless-steel reactor with id 10 mm. The analyses for catalytic products were described in detail in our previous work [23].

3. Results and discussion

3.1. TG-DTG-MS characterization

The decomposition of Mo sulfide clusters was studied by TG-DTG coupled mass spectrometry to understand the decomposition processes. TG-DTG results obtained for (NH₄)₂Mo₃S₁₃·H₂O were shown in Fig. 1, which demonstrated the stability of the triangle of quadrivalent molybdenum. The TG and DTG curves showed three steps of decomposition. The weight loss for the first step corresponded to the removal of water. The second decomposition step started at about 209 °C and ended at 271 °C with a weight loss of 4.45% (the calculated value 4.48%). The analysis of MS data demonstrated that both NH₃ and H₂S were emitted in the second step. According to the TG-MS results, we could conclude that the loss of the half mole of sulfur occurred as H₂S from the removal of the μ₃-S atom. Since there was only one μ₃-S atom per cluster formula, the rearrangement took place in the remaining cluster and formed an intermediate (NH₄)₂Mo₆S₂₅ with only one central sulfur during the decomposition process. For this decomposition step, the positions of three molybdenum atoms remain almost unchanged. To further confirm the intermediate, SEM-EDS was applied to the intermediate phase obtained by the decomposition of (NH₄)₂Mo₃S₁₃·H₂O in Ar at 270 °C. From the EDS analysis, it is observed that the Mo/S atomic

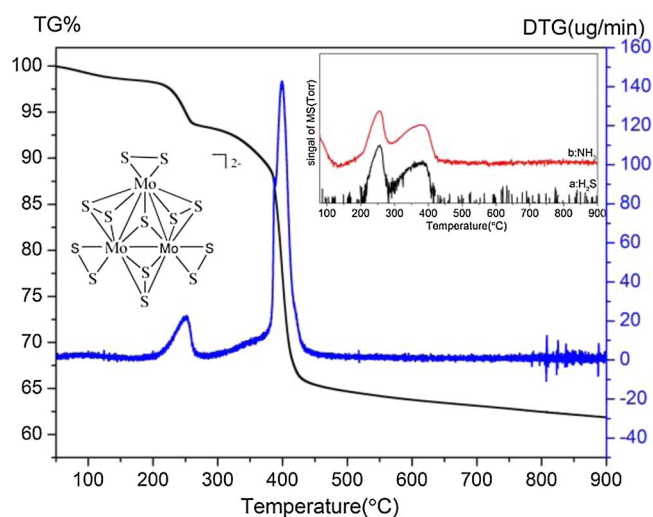


Fig. 1. TG and DTG curves for (NH₄)₂Mo₃S₁₃. Inset: Mass spectrometer signal followed during the temperature-programmed decomposition of (NH₄)₂Mo₃S₁₃·H₂O.

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