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Synthesis and characterization of cobalt–molybdenum bimetallic carbides catalysts

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Abstract

Co_3Mo_3C, Co_6Mo_6C and MCM41-supported Co_3Mo_3C catalyst are prepared by a simple one-step thermal decomposition method without the conventional temperature-programmed carburization. The resultant carbides are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscope (HRTEM) and BET surface area measurements. The as-prepared Co_3Mo_3C/MCM41 catalyst exhibits good performance in both probe reactions of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), which proves the one-step decomposition method to be an effective route for the preparation of bimetallic carbide catalyst.

Keywords: Bimetallic carbide; HMT; Catalyst; HDS; HDN

1. Introduction

In recent years, because the allowable amount of emissions, such as SO_x, NO_x and aromatics from the combustion of fuels has been greatly decreased, petroleum refining industry is facing real challenges. Co(Ni)Mo(W)/Al_2O_3 catalysts have been commercially used for more than half a century in petroleum refining industry due to their reliable activity and thermal resistance. In order to meet the new regulation, it is essential for the refiners to develop novel catalytic materials for the production of high-purity and clean fuels.

Since the last decade, metal carbides have been expected to be one of the potential substitutes to conventional refining catalysts. In this regard, interstitial molybdenum-based carbides have attracted much attention of catalysis researchers in hydrogen-involved reactions, such as hydrogenolysis, hydrogenation, dehydrogenation, isomerization, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), ammonia synthesis, etc. [1–16]. However, most research findings focused on the outstanding functions and new preparation methods of monometallic molybdenum carbides, rather than those of bimetallic molybdenum-based carbides, despite the potential advantages of attaining multi-functional catalysts from bimetallic ones. To the best of our knowledge, it could be ascribed to inexperience in the preparation of bimetallic carbides, which generally included the temperature-programmed nitridation of corresponding oxides and the subsequent carburization of the nitrides.

The prime study concerning the preparation and characterization of cobalt-molybdenum bimetallic carbides was reported by Newsam et al. [17]. They successfully synthesized $Co_6Mo_6C_2$ (Co_3Mo_3C) as well as Co_6Mo_6C with $Co(en)_2MoO_4$ as precursor by a two-stage reaction method, and the structures of these carbides were firstly confirmed by Rietveld analyses of powder neutron diffraction data. In recent years, Bussell's group synthesized the bulk and alumina supported Co_3Mo_3C through a temperature-programmed nitridation and subsequent topotactic carburization route [18]. The thiophene HDS property of as-prepared catalysts was investigated and compared with those of the corresponding nitride and oxide [8]. Although such a multi-staged method based on the temperature-programmed procedure was proved to be effective for the synthesis of bulk and supported Co_3Mo_3C [18,19], Co_6Mo_6C could not be synthesized by this method and no other synthesis route has been proposed since 1988 [17]. Besides, another carburization approach for the preparation of Co-Mo carbides was presented by Xiao et al., who used oxidic precursor instead of nitride and operated the carburization under the flow of C_2H_6/H_2 mixture [20]. This method resulted

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in a series of carbides, namely $Co_{0.2}Mo_{0.8}C_x$, $Co_{0.33}Mo_{0.67}C_x$, $Co_{0.4}Mo_{0.6}C_x$ and $Co_{0.5}Mo_{0.5}C_x$. The authors also tested their activities toward HDN of pyridine and concluded that all the bimetallic catalysts were more stable and active than pure molybdenum carbide and corresponding bimetallic nitride, oxide and sulfide ($CoMoN_x$, $CoMoO_x$ and $CoMoS_x$) [21,22]. On the other hand, Liang et al. developed a carbothermal hydrogen reduction method for the preparation of Co–Mo carbide [23] as well as nanostructured β-Mo_2C [24] and W_2C [25]. In this novel synthesis route, activated carbon material was used as carbon source and support. However, it was difficult to prepare bimetallic Co–Mo carbide loading on other supports for catalytic applications through this method. So the aim of this study is to propose a novel and simple method to prepare bulk and supported Co–Mo carbides and to evaluate the catalytic activity of as-prepared catalysts.

Hexamethylenetetramine (HMT), an organic compound containing both C, N elements, has been utilized as molybdate ion ligand and reducing agent to prepare Mo_2N as well as bimetallic Ni_2Mo_3N and Co_3Mo_3N by a one-step decomposition method [26,27]. Recently, bulk and alumina supported β-Mo_2C has also been successfully synthesized by the HMT-based method in our previous work [28]. In the current study, two phases of cobalt–molybdenum bimetallic carbides, Co_3Mo_3C and Co_6Mo_6C, were both prepared by the HMT-based one-step thermal decomposition method. The microstructures and properties of the bulk carbides were investigated and compared by XRD, BET, SEM and HRTEM characterizations. With respect to extend the simple synthesis route to catalysis research, the MCM41 zeolite was employed as a steady support, due to its good thermal stability, high surface area, and large adsorption capacity for organic molecules. To testify the catalytic performance of the resultant Co_3Mo_3C/MCM41 catalyst, the HDS of dibenzothiphene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) and HDN of 3-methylpyridine were used as two probe reactions. In general, this method is proved to be successful and has the potential to be a general and convenient route to prepare Co-Mo bimetallic carbide on various supports.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of Co_3Mo_3C

Commercially available solvents and reagents were used in the whole procedure. A precursor to pure phase Co_3Mo_3C was prepared by dissolving $Co(CH_3COO)_2·4H_2O$, $(NH_4)_6Mo_7O_{24}·4H_2O$ and HMT with a mole ratio of 7:1:37 in 15% $NH_3·H_2O$ solution under stirring. The molar ratio of the above compounds was confirmed by trial and error with the fixed atomic ratio of Co/Mo = 1. The magenta solution was evaporated at room temperature to dryness to obtain the magenta slurry. The resulting material was dried under vacuum at 353 K for 6 h and then crushed to get a fine powder. Co_3Mo_3C was synthesized by thermal decomposition of the as-prepared powder precursor in a stainless steel reactor under a flow of argon (99.99%). In the thermal treatment process, the system was heated to 1023 K at a rate of 10 K min^{-1} and held at this temperature for 2 h. After the heat treatment, the samples were cooled to room temperature naturally under argon and passivated in a flow of 1% (v/v) O_2/N_2 for 2 h.

2.1.2. Synthesis of Co_6Mo_6C

A mixed-salt precursor to bulk Co_6Mo_6C was prepared by dissolving $Co(NO_3)_2·6H_2O$, $(NH_4)_6Mo_7O_{24}·4H_2O$ and HMT with a mole ratio of 7:1:23 in 15% $NH_3·H_2O$ solution under stirring, then evaporating to dryness. The subsequent steps were carried out as described above for the synthesis of Co_3Mo_3C.

2.1.3. Synthesis of Co_3Mo_3C/MCM41

The Co_3Mo_3C/MCM41 catalyst with the theoretical loading of 16.7 wt.% Co_3Mo_3C was prepared by incipient wetness impregnation of finely ground MCM41 with the above described homogenous solution. The subsequent procedure followed that of the bulk sample through the thermal decomposition method.

For comparison purpose, 17 wt.% Co_3Mo_3C/MCM41 was also synthesized from the supported bimetallic nitride precursor by the conventional temperature-programmed carburization method under flowing 20 mol.% CH_4/H_2 mixture at a VHSV (volume hourly space velocity) of 6000 h^{-1}. The Co_3Mo_3N/MCM41 precursor was prepared by ammonolysis of supported metal oxides, which obtained by incipient wetness impregnation of MCM41 using aqueous solutions of $(NH_4)_6Mo_7O_{24}·4H_2O$ and $Co(CH_3COO)_2·4H_2O$ followed by drying and calcination in air. The temperature of nitridation process was increased in two steps: rapidly from room temperature to 623 K (at 6 K min^{-1}), and then slowly from 623 to 973 K (at 1 K min^{-1}). The temperature was then held at 973 K for 2 h. The sample was cooled in flowing NH_3 and passivated for 2 h. Before carburization, the nitride intermediate was reduced under H_2 flow at 673 K for 3 h to remove the passivation layer. Subsequently, the system was heated to 923 K at the ramping rate of 5 K min^{-1} under carburizing agent CH_4/H_2, and then cooled and passivated in 1% (v/v) O_2/N_2 for 2 h to avoid strong bulk oxidation.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were acquired on a Rigaku D/max-2500 powder diffractometer employing Cu-Kα source (λ = 1.5418 Å, 40 kV, 40 mA). The powder samples were mounted on a silicon plate for XRD characterization. The carbon analysis of the samples was carried out with an Elementar Vario EL elemental analyzer. The particle size and morphology of the samples were characterized using a LEO 1530VP scanning electron microscopy (SEM). The samples were covered by a thin film of gold for better image definition. A JEM-2010FEF high-resolution transmission electron microscope (HRTEM) equipped with an EDX system (EDAX) operating at 200 kV was conducted to observe the morphology and microstructure of the bulk samples. BET surface areas of the samples were determined from N_2 BET