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Editor's choice paper

The effect of alkali metals on the synthesis of methanethiol from $CO/H_2/H_2S$ mixtures on the SBA-15 supported Mo-based catalysts

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ABSTRACT

The effects of alkali promoters on catalytic behaviors for synthesizing CH_3SH over Mo-based catalysts were investigated. The selectivity of CH_3SH for Na, K, Cs and non-alkali promoted catalysts are following in the order of Cs-Mo/SBA–15> K-Mo/SBA–15> Na-Mo/SBA–15> Mo/SBA-15. The addition of alkali metals dramatically improved the CH_3SH selectivity and CO conversion. The highest selectivity of CH_3SH was 66% obtained by incorporating Cs into Mo/SBA-15 which was superior to those reported in the current literature. Based on N_2 adsorption-desorption, XRD, Raman, XPS and NO-TPD characterizations, active MoS_2 species on oxidized Mo O-S species, obtained from the sulfidation temperature as low as 553 K, was considered as active sites for synthesizing CH_3SH. And it deemed that the different alkali metals (Na, K, Cs) could give rise to the difference in the sulfidation degree of Mo oxidized species and modify the chemical and electronic environment of the active sites, which resulted in the generation of distinguished concentration of Mo containing coordinatively unsaturated sites (Mo-CUS). Those concentrations of Mo-CUS were detected by NO-TPD to be 161, 210 and 222μmol/g, respectively, which had a positive relationship with the selectivity of CH_3SH.

1. Introduction

Methanethiol is a significant chemical intermediate extensively applied for the production of pharmaceuticals, pesticides, petrochemicals, especially, methionine, an amino acid used as an animal feed supplement. The demand for CH_3SH has been growing extensively with the rapid increase in the requirement for methionine over the past decades. Therefore, the synthesis of methanethiol has been the subject of several studies, and the production of high-performance catalysts and knowledge of alternative routes have been explored.

At present, the methods for the production of methanethiol mainly include the thiolation reaction of methanol and hydrogen sulfide [1], the gas-phase synthesis from H_2S-containing syngas [2], the demethiolation of sulfur-containing amino acids by bacteria [3], the reaction of thiourea or sodium hydrosulfide with dimethyl sulfate [4] and so on. Among these, the thiolation of methanol and hydrogen sulfide is a conventional and relative commercial process because of the high rate of production [5]. However, methanol needs to be firstly produced by carbon monoxide and hydrogen (i.e. synthesis gas) over molybdenum-based catalysts [6], causing enormous resources and energy wasting. The gas-phase reaction, recently, employing H_2S-containing syngas (CO/H_2) as raw material for synthesizing methanethiol has received considerable attention due to the low-cost and wide-range sources of synthesis gas (CO/H_2) and acid gas (H_2S) [7–10].

For this synthetic reaction, alkali-promoted Mo-based materials were widely used as effective active catalysts [11–13]. Silicon based and aluminium based oxides, in general, were selected as supports for loading and dispersing molybdenum-containing active phase components. However, the low catalytic activity obtained from alkali-promoted Mo-based catalyst supported on SiO_2 suggests that the acidity and basicity of support would not be the main factor to determine catalytic performance. And its intrinsic low surface area together with irregular pore structure probably restrains the improvement in catalytic performance. Therefore, the ordered mesoporous molecular sieves materials with large surface area and regular channel framework might be considered as an option to improve the dispersion of active phases so as to produce more active sites. SBA-15, in the present paper, was selected as

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the support of catalyst, and the corresponding catalyst exhibited the relative higher catalytic performance in comparison with the catalyst supported on SiO_2.

Although the support SBA-15 could influence indirectly the catalytic performance of Mo-based catalyst, the active phases and promoters on the support seem to play more important role in the catalytic performance for synthesis of methanethiol. Alkali metals are, among them, frequently selected to introduce into catalysts as additives mainly due to their significant improvement of catalytic activity, selectivity and durability via the modification of surface electron density of alkali-promoted metal or electrostatic interactions associated with alkali-metal ions to change the chemisorptive characteristics of catalyst surface [14,15]. Currently, a few fundamental studies focusing on the area of the alkane oxidation [16,17], CO_2 hydrogenation [18], water-gas shift reaction [19], higher-alcohol synthesis [20] have investigated the effect of alkali promoters on catalytic performance. Nevertheless, the investigation of the influence of alkali metals on catalytic performance for this reaction of methanethiol synthesis is less reported [21].

In order to further investigate the cause of high catalytic performance of methanethiol synthesis, we analyzed the catalytic synthesis of methanethiol over Mo-containing catalysts with no alkali addition and three different alkali metal additives (K, Na, Cs) by combining physicochemical characterizations of corresponding catalysts, which involve N_2 adsorption-desorption, X-Ray Diffraction (XRD), Raman spectroscopy, Transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and NO- temperature programmed desorption (NO-TPD) with detailed activity evaluation measurements.

2. Experimental

2.1. Catalysts preparation

SBA-15 was prepared by using nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) and tetraethyl silicate TEOS as the structure-directing agent and silicon source, respectively, in according with our previous literatures [22,23]. All the catalysts were prepared by SBA-15, $(NH_4)_6Mo_7O_{24}{\cdot}6H_2O$ and alkali metal salts via the incipient-wetness impregnation method, and the loading of Mo (based on MoO_3) and molar ratios of alkali/Mo were 25 wt% and 2/1, respectively. After impregnation, all the samples were dried at 120 °C for 24 h and subsequently calcined at 400 °C for 3 h in the air. The samples promoted with K_2CO_3, Na_2CO_3, Cs_2CO_3 are denoted as K-Mo/SBA-15, Na-Mo/SBA-15 and Cs-Mo/SBA-15.

2.2. Catalysts characterization

The textural properties were conducted on a Beckman Coulter's SA3100 automatic analyzer at −196 °C. BET surface area of the samples was performed by using BET method according to the data of adsorption branch, and the pore size distribution was calculated by the BJH method by using the data of desorption branch. The sulfided catalysts and the used catalysts were characterized by XRD. A Japanese Rigaka's D/Max-1200 diffractometer (Cu Kα-radiation, λ = 0.154056 nm) operating at 40 kV and 30 mA was used for recording XRD. The evaluation of the diffractogram was made by MDI Jade 5.0 software to identify the crystalline phases within the catalysts. The sulfide catalysts were characterized by NO-TPD on a home-made apparatus equipped with a highly sensitive TCD detector. As for NO-TPD experiment, 0.1 g of catalyst sample was loaded in the reactor. Prior to TPD analysis, the sample was pre-treated at 400 °C for 1 h under the flow of helium (He) to remove adsorbed water as well as impurities, then cooled down to 30 °C, at which nitric oxide (NO) was absorbed by using 30 ml/min of high concentration NO for about 0.25 h. Weakly bound NO was removed by sweeping with the flow of high purity He at 30 °C, and then the temperature was increased to 400 °C at a heating rate of 10 °C/min under the flow of high purity He. A thermal conduction detector (TCD) was used to detect the desorbed NO. Raman spectrum was carried out by using a Via Reflex Raman spectrometer with 514 nm emission line from Ar^+ laser at room temperature. TEM images of the catalysts were equipped with a JEM-2100 microscope operated at 200 kV. XPS technique was employed to determine the composition and chemical state of different elements composing the solids using a PHI 5000 Versa Probe II with non-monochromatic Al K*a* radiation (1486.6 eV). CasaXPS software was used to fit the corresponding spectra and charge referencing was detected against adventitious carbon with the C 1 s at 284.6 eV.

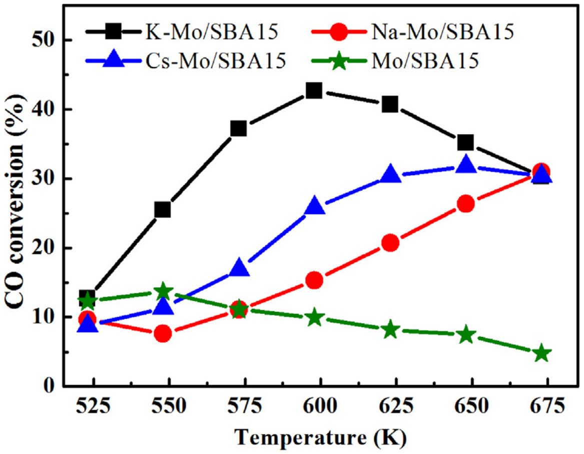

Fig. 1. CO conversion of ^{S}Mo/SBA-15 (olive), ^{S}Na-Mo/SBA-15 (red), ^{S}K-Mo/SBA-15 (black) and ^{S}Cs-Mo/SBA-15 (blue). Reaction conditions: 0.2 MPa,1000 h^{-1} and $CO/H_2S/H_2 = 1{:}5{:}4$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Catalytic activity test

The catalytic activity experiment was carried out in a 6 mm i.d. quartz fixed-bed reactor. 0.4 g catalyst (40–60 mesh) was loaded with quartz wool in the isothermal region of the reactor. Then, the reactant gas ($CO/H_2S/H_2 = 1{:}5{:}4$) was introduced into the reactor under the conditions of P = 0.2 MPa, GHSV = 1000 h^{-1} and under different reaction temperature (523k–673 K) and the used catalysts were denoted as ^{U}Mo/SBA-15, ^{U}Na-Mo/SBA-15, ^{U}K-Mo/SBA-15 and ^{U}Cs-Mo/SBA-15. Prior to each activity evaluation measurements, all of the samples were presulfided in the gas stream with $CO/H_2S/H_2 = 1{:}5{:}4$ (20 ml/min) at 553 K for 6 h, the catalysts after sulfidation were denoted as ^{S}Mo/SBA-15, ^{S}Na-Mo/SBA-15, ^{S}K-Mo/SBA-15 and ^{S}Cs-Mo/SBA-15. Reactor products were online detected using three GC fitted with one flame ionization detector (FID), two flame photometric detectors (FPD) and two thermal conductivity detectors (TCD). Carbon hydrogen components including CH_3SH, CH_4, little C_2H_4 and C_2H_6 were detected by FID with a porapak Q column. The FPD equipping with a HP-Plot/Q capillary column was employed to detect sulfur-containing matters including COS, CS_2, CH_3SH and H_2S. TCD equipped with TDX-01 carbon molecular sieve was used to detect H_2, CO and CO_2.

3. Results and discussion

3.1. The catalytic activity test

CO conversions of ^{S}Mo/SBA-15, ^{S}Na-Mo/SBA-15, ^{S}K-Mo/SBA-15 and ^{S}Cs-Mo/SBA-15 are displayed in Fig. 1. It is observed