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Short Communication

Promoting effect of SiO_2 on the K_2WO_4/Al_2O_3 catalysts for methanethiol synthesis from methanol and H_2S

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ABSTRACT

Silicon-promoted K_2WO_4/Al_2O_3 catalysts for methanethiol synthesis from methanol and H_2S were prepared and characterized by XRD, in situ pyridine adsorption FT-IR and NH_3/CO_2-TPD, etc. techniques. With increasing the amount of Si added, the crystallite sizes of the catalysts decreased, while the surface area increased at first and then decreased. When the content of Si in the catalyst increased in the range from 1 to 5%, the acidity of the catalyst increased, while the basicity decreased. The highest catalytic activity of the catalyst for the reaction can be obtained when Si content in the catalyst is as high as 5%.

1. Introduction

Methanethiol is an important chemical raw material and organic synthesis intermediate, in particular, methionine, a widely used feed additive or medicine. To date, methanethiol can be produced by methanol hydrosulfurization over acid–basic catalysts [1–11] or direct synthesis from H_2S-containing syngas [12–14]. At present, the synthesis of methanethiol from methanol and hydrogen sulfide is an effective process and more favorable for industrial production due to the high productivity.

It has been reported that the introduction of SiO_2 to alumina-supported catalysts could increase the hydrogenation properties by affecting acidic nature and the phase-support interaction [15–18]. Rajagopal et al. [15] showed an increase of Brønsted and Lewis acidity as the silica content in the silica–alumina increased from 10 to 90%. The high loading of silica on alumina leaded to the rapid increase of Brønsted acidity. Minero et al. [18] claimed that 10% loading of silica on alumina leaded to the decrease in Lewis acidity. As for the methanethiol catalysts, the authors [4,5] compared the catalytic activities of the catalysts of Al_2O_3 and SiO_2 promoted with K_2WO_4, and found that K_2WO_4/SiO_2 showed much lower catalytic activity than K_2WO_4/Al_2O_3. Owing to the Brønsted acidity, zeolites were more active in methanethiol synthesis with lower selectivity [6,7]. The literatures mentioned above mainly focused on introducing alkali metal salts to support matrix having high surface area in order to improve the selectivity toward methanethiol. Less work has been done on the mixed oxide support for the synthesis of methanethiol. The aim of present work is to determine the effect of silica incorporation to alumina-supported K_2WO_4 catalysts with low silica loading (1, 3, 5 and 7%) and the catalytic performances of the as-prepared catalysts were studied. XRD, N_2 adsorption–desorption, in situ pyridine adsorption FT-IR and NH_3/CO_2-TPD techniques were used to characterize the modified catalysts.

2. Experimental

2.1. Catalyst preparation

The Si-promoted K_2WO_4/Al_2O_3 catalysts were prepared by the multi-step impregnation method, which consists of the following two processes; firstly, appropriate amount of commercial pseudo-boehmite was suspended in a mixed solution of 50 mL which was consist of 97% ethanol, 2% deionized water and 1% ammonia aqueous solution under vigorous stirring at 50 °C, then a given quantity of silicon tetraethoxide was added drop wise to the suspending liquid under stirring, keeping it at the same temperature for 24 h, followed by washing, drying at 120 °C for 8 h and calcining at 550 °C for 4 h. Secondly, the precursor prepared above was impregnated in an aqueous solution of K_2WO_4 with a desired loading of 20 wt.%, then dried, followed by calcining at 550 °C in air for 3 h. The resulted catalysts were expressed as K_2WO_4/S_xA, where x denotes the molar ratio of Si to Al, x = 1, 3, 5 and 7%. For comparison, 20 wt.% K_2WO_4/Al_2O_3 catalyst also prepared by traditional impregnation (denoted by K_2WO_4/S_0A).

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2.2. Catalyst characterization

The crystalline structure was analyzed on a Panalytical X'pert PRO X-ray diffractometer (XRD) utilizing monochromatic Cu kα radiation and scanning 2θ range from 10° to 90°, scanning step length of 0.0167°.

Nitrogen adsorption–desorption experiments were performed at 77 K on a Micromeretics Tristar 3000 system. Prior to the measurements, all samples were degassed at 300 °C for 3 h. The specific surface area was determined via the Brunauer–Emmett–Teller (BET) method in 0.05–0.3P/P_0 range and the pore volume was assessed by the Barret–Joyner–Halenda (BJH) desorption cumulative pore volume of the pores with the pore sizes ranging from 0.85 to 150 nm.

In situ IR spectra of adsorbed pyridine were conducted on a Nicolet Nexus FTIR spectrometer and a homemade quartz in situ IR cell with CaF_2 windows. The catalyst was pressed into self-supporting wafer (approximatively 10 mg/cm^2) and pretreated by evacuation at 400 °C for 1 h in the IR cell. After cooling down to 50 °C, pyridine vapor was switched into in situ-cell with contact time of 7 min. After evacuation for 5 min, all the IR spectra were recorded in situ at the destination temperatures. The spectra were scanned in the range of 1700–1400 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

The acidity and basicity of the catalysts were obtained from the temperature-programmed desorption of ammonia and carbon dioxide (NH_3/CO_2-TPD) on a self-constructed instrument equipped with a quadra-pole mass spectrometer model QIC-20 (Hiden Analytical Ltd.). Before adsorption, the catalyst was pretreated at 400 °C in dry Ar flow for 1 h, then, cooled down to 40 °C and saturated with a mixed gas of 10% NH_3/Ar (or CO_2/Ar). The sample was heated to 550 °C at a heating rate of 10 °C/min under Ar flow. The desorption signals were recorded by the software provided by the QIC-20 system.

2.3. The evaluation of the catalysts

The reaction of methanol with H_2S was performed in a flowing system, the reaction products were analyzed by chromatographic technique. The activity measurement of the catalyst with a grain size of 30–60 mesh was conducted under the reaction conditions: p = 0.6 MPa, H_2S/MeOH = 1.5, GHSV = 1900 h^{-1}, T = 340 °C. Before the reaction, the sample (1 mL) was sulfurized with H_2S at 400 °C for 1 h. The reaction products were analyzed on line using a gas chromatograph (model GC9560) equipped with TCD detector.

The conversion of methanol (X) and selectivity toward products (S) were defined as

$$X = \frac{\sum x_i n_i}{x + \sum x_i n_i}$$

$$S = \frac{x_i n_i}{\sum x_i n_i}.$$

Where χ_i and χ are the mole fraction of product i and methanol, respectively, and n_i is the number of carbon atoms in each molecule of product i.

Table 1
Textural properties of the catalysts.

Catalysts	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Crystallite size (nm)
K_2WO_4/S_0A	216	4.7	0.53	6.2
K_2WO_4/S_1A	254	3.9	0.56	5.6
K_2WO_4/S_3A	232	4.2	0.52	5.3
K_2WO_4/S_5A	232	3.8	0.48	5.1
K_2WO_4/S_7A	211	4.4	0.44	4.7

3. Results and discussion

The XRD patterns of the catalysts are given in Fig. 1, in which the characteristic peaks at 2θ = 19.29°, 32.25°, 37.28°, 39.42°, 45.76°, 60.66°, and 66.78° can be assigned to (111), (220), (311), (222), (400), (511) and (440) planes of γ-alumina, respectively [JCPDS File no. 00-029-0063]. There are no detectable bulk phases of silicon or tungsten species, this indicates that the supported species are amorphous or in the form of nanocrystallite. The crystallite sizes of the samples calculated by Deby–Scherer formula are listed in Table 1. It can be seen from Table 1 that the crystallite sizes of the catalysts decrease as increasing the amount of silicon. Therefore it can be concluded that the addition of Si can restrain the aggregation of the catalyst crystallites.

Textural properties of the catalysts are also listed in Table 1. As described in Table 1, the addition of a small amount of Si to K_2WO_4/Al_2O_3 catalyst increases the BET surface area and pore volume, hereafter they decrease from 254 to 211 m^2/g and 0.56 to 0.44 cm^3/g, respectively as the Si content increased from 1 to 7%, because Si clogged the mouths of small pores and occupied the space of big pores. The average pore diameter remains constant of around 4 nm.

The surface acidity properties of K_2WO_4/S_xA were tested by in situ pyridine adsorption FTIR spectroscopy. The results are displayed in Fig. 2. Five peaks at 1440, 1487, 1574, 1588 and 1608 cm^{-1} are attributed to hydrogen-bonded pyridine and pyridine species coordinating to Lewis acid sites, this suggests that more than one type of Lewis acid sites exists on the surface of the catalysts. But the absence of 1540 cm^{-1} indicates that Brønsted acid sites do not exist on the surface of the catalysts owing to the reaction of alkali metal salts

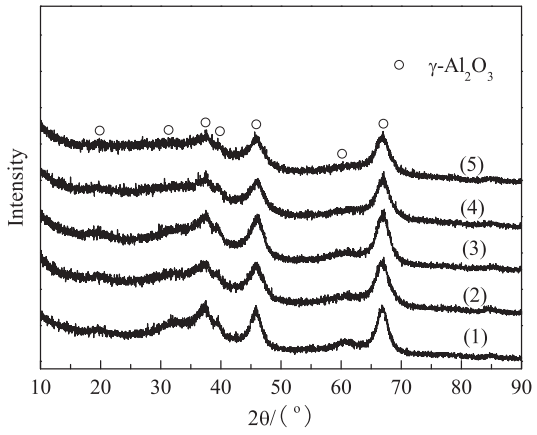

Fig. 1. XRD patterns of the catalysts. (1) K_2WO_4/S_0A, (2) K_2WO_4/S_1A, (3) K_2WO_4/S_3A, (4) K_2WO_4/S_5A, (5) K_2WO_4/S_7A.

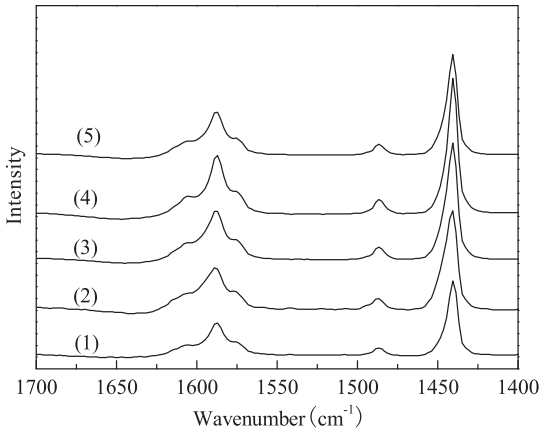

Fig. 2. In-situ IR spectra of pyridine adsorption on the K_2WO_4/S_xA catalysts at 50 °C. (1) K_2WO_4/S_0A, (2) K_2WO_4/S_1A, (3) K_2WO_4/S_3A, (4) K_2WO_4/S_5A, (5) K_2WO_4/S_7A.