



Catalytic performance of $V_2O_5/ZrO_2-Al_2O_3$ for methanol oxidation

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ABSTRACT

A bifunctional $V_2O_5/ZrO_2-Al_2O_3$ catalyst of oxidation and dehydration was prepared by wet impregnation method and used in methanol oxidation. The redox, acidity and texture properties of the catalyst were characterized by N_2 sorption, H_2 -TPR, NH_3 -TPD, and XRD. Under mild reaction conditions, $V_2O_5/ZrO_2-Al_2O_3$ possesses reasonable acidic and redox properties and exhibits excellent catalytic performance in methanol oxidation with dimethoxymethane, methyl formate and formaldehyde as main products. The catalytic performance of $V_2O_5/ZrO_2-Al_2O_3$ is dependent on the catalyst compositions and reaction temperature. V_2O_5 (16.5 wt.%)/ ZrO_2 (8.5 wt.%)– Al_2O_3 exhibits a good synergistic effect of the redox and acidic properties in the methanol oxidation; over it the selectivity to dimethoxymethane reaches 89.0% with the methanol conversion of 11.1% at 165 °C, while the selectivity to methyl formate is 30.0% with the methanol conversion of 66.1% at 215 °C.

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1. Introduction

With the rapid growth of methanol production from coal-derived syngas, the research and development of new processes to transform methanol to valuable down stream products has attracted extensive attention. Through oxidation and/or dehydration, methanol can be converted to formaldehyde (FA), dimethyl ether (DME), dimethoxymethane (DMM), methyl formate (MF), and so on. Among them, DMM is an excellent solvent and chemical intermediate in industry; moreover, it was found recently that DMM can also be a potential procetane because of its high oxygen content and cetane number [1]. DMM was conventionally produced by the dehydration of FA with methanol over acidic catalysts, in which FA is obtained through methanol oxidation over Ag or Fe–Mo catalysts [2]. MF is also an important chemical; it is generally produced from the dehydrogenation of methanol on Cu catalysts or the carbonylation of methanol with CO on sodium methoxide [3]. The conventional processes may face the demerits like the critical reaction conditions, complicated procedures, high energy consumption, and possible equipment corrosion and environmental problems. Therefore, one-step synthesis of DMM and MF through the selective oxidation of methanol under mild reaction conditions, as one of the energy-saving processes for methanol conversion and utilization, is of great importance in both theoretical and practical aspects.

Many researches have been reported in this area. Yuan and Iwasawa found that α - Fe_2O_3 or γ - Fe_2O_3 supported ReO_2 exhibits good catalytic activity in the methanol oxidation with a DMM selectivity of 90–94% at a methanol conversion of 15–49% [4]. Iglesias et al. reported that the Keggin structure heteropolyacid like $H_{3+n}V_nMo_{12-n}PO_{40}$ and the amorphous oxide $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}O_x$ were active in the selective oxidation of methanol [5–7]. Other catalysts such as MoO_3/ZrO_2 , Sn–Mo–O, and V_2O_5/TiO_2 were also used in this reaction [8–10]. It was generally accepted that a catalyst suitable for the selective oxidation of methanol with DMM or MF as products should possess both redox sites and acid sites. The redox sites are in charge of transferring the lattice oxygen to adsorbed methanol to form formaldehyde and formic acid, while the acid sites catalyze the condensation of the intermediates with methanol to form DMM and MF [11]. Therefore, to enhance the efficiency of such a process, it is necessary to investigate the synergistic effect of the redox and acidic properties of a catalyst as well as their dependence on the catalyst composition and reaction conditions.

Supported V_2O_5 catalysts were widely used in the selective oxidation of alcohol, oxidative dehydrogenation of alkane and selective catalytic reduction of NO [12–14]. Under mild reaction conditions, $V_2O_5/ZrO_2-Al_2O_3$ possesses reasonable acidic and redox properties and exhibits excellent catalytic performance in methanol oxidation. Therefore, in this work, the effects of ZrO_2 contents, V_2O_5 loadings, and reaction temperature upon the catalytic performance of $V_2O_5/ZrO_2-Al_2O_3$ for methanol oxidation were investigated. The reducibility, acidity and texture properties of the

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catalyst were studied by means of H₂-TPR, NH₃-TPD, N₂ sorption, and XRD. The influence of catalyst composition and reaction conditions on the catalyst redox and acidic properties were then discussed.

2. Experimental

2.1. Catalyst preparation

To prepare the mixed support ZrO₂-Al₂O₃ with different ZrO₂ contents, γ -Al₂O₃ (BET surface area of 167.5 m²/g) were impregnated with aqueous solution of Zr(NO₃)₄·5H₂O, followed by drying in air at 80 °C for 10 h and calcination at 500 °C for 3 h. The catalysts V₂O₅/ZrO₂-Al₂O₃ were then obtained by wet impregnation of the mixed support ZrO₂-Al₂O₃ with an aqueous solution of NH₄VO₃ containing equimolar oxalic acid, followed by drying in air at 110 °C for 10 h and calcination at 500 °C for 3 h.

2.2. Catalyst characterization

BET surface area of the catalysts was measured by nitrogen sorption at -196 °C with a TriStar 3000 Gas Absorption Analyzer (Micromeritics Instrument Co., USA). The samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement.

X-ray diffraction (XRD) characterization was performed on a Bruker AXS D8 advanced X-ray diffractometer equipped with a graphite monochromator (Cu K α , λ = 0.15406 nm, 40 kV, 40 mA) in the step scanning mode (0.02° and 0.24 s per step) with the 2 θ range between 10° and 80°.

H₂-TPR measurement was performed in a quartz tubular microreactor. Catalyst sample (50 mg) was placed in the reactor and subjected to a gas flow of O₂ (10 vol.%) in Ar (30 ml/min) at 500 °C for 1 h, followed by cooling down to ambient temperature in pure Ar flow. After that, the sample was heated in H₂-Ar flow (30 ml/min, containing 10 vol.% H₂) from room temperature to 700 °C at the rate of 10 °C/min. The amount of H₂ consumption during the reduction was measured by a thermal conductivity detector (TCD).

NH₃-TPD was also conducted in the same microreactor. The catalyst sample was pretreated in Ar flow (30 ml/min) at 500 °C for 1 h followed by cooling down to room temperature; and then the sample was saturated with pulse NH₃ for 1 h, followed by purging with the Ar flow for 1 h to remove the physically adsorbed NH₃. After that, the sample was heated in the Ar flow from ambient temperature to 550 °C at a ramp of 10 °C/min. The amounts of NH₃ desorption were measured by the TCD.

2.3. Catalytic test and analytic procedure

The catalytic tests for methanol oxidation were carried out in a quartz tubular flow microreactor at atmospheric pressure. About 600 mg of catalyst sample (40–60 mesh) diluted with quartz sand of the same volume and size was loaded per run. The catalyst was first activated at 400 °C for 1 h in air with a flow rate of 30 ml/min and then the reactor was cooled down to the reaction temperature. After that, methanol and oxygen were fed into the reactor. The molar ratio of methanol to oxygen in the feed was 1 and the volume hourly space velocity (VHSV) was 1120 h⁻¹. The effluents, including oxidation products and unreacted methanol, were condensed in a trap with an ice water bath.

The liquid products including methanol, DMM, FA, MF, DME, and water were analyzed with a TCD gas chromatograph (Shimadzu GC-14C) equipped with a 3 mm × 3 m stainless-steel column packed with Porapark-T. The gaseous effluents (mainly CO₂, CO, and O₂) were analyzed with a TCD gas chromatograph (Shimadzu

GC-8A) equipped with a 3 mm × 3 m stainless-steel column packed with carbon molecular sieves.

3. Results and discussion

3.1. Redox and acidic properties of the V₂O₅/ZrO₂-Al₂O₃ catalyst

XRD patterns of the catalysts V₂O₅/ZrO₂-Al₂O₃ with different ZrO₂ contents and V₂O₅ loadings are shown in Figs. 1 and 2. The diffraction peaks at 2 θ of 37.6°, 39.5°, 45.9°, and 67.0° are attributed to the crystalline γ -Al₂O₃ [15]. The peaks at 2 θ of 30.5°, 51.0°, and 60.5° are corresponding to the tetragonal ZrO₂ phase [16]. The diffraction peaks at 2 θ of 20.2°, 26.5°, and 31.0° are ascribed to the crystalline V₂O₅. As shown in Fig. 1, amorphous or well dispersed tetragonal ZrO₂ are present on the V₂O₅/ZrO₂-Al₂O₃ catalysts when the ZrO₂ content in the support is less than 8.5 wt.%. In Fig. 2, the diffraction peaks of V₂O₅ are not distinct when its loading is lower than 12.5 wt.%. When V₂O₅ loading exceeds 12.5 wt.%, the diffraction peaks corresponding to crystalline phase V₂O₅ appear and their intensity increases with the V₂O₅ loading, indicating an increase of the crystalline size. These suggest that amorphous or well dispersed ZrO₂ and crystalline V₂O₅ are present on V₂O₅/ZrO₂-Al₂O₃ catalysts when ZrO₂ content and V₂O₅ loading are less than 8.5 wt.% and 12.5 wt.%, respectively.

The effect of ZrO₂ content in the support on the acidity of the catalysts is shown by the NH₃-TPD profiles in Fig. 3. With the increase of ZrO₂ coverage on the alumina surface, the acid strength of the catalyst becomes weaker. As shown in Fig. 4, the loading of V₂O₅ also exhibits significant influence on the catalyst acidity; the acidity density is enhanced greatly by increasing the loading of V₂O₅. With the increase of V₂O₅ loading, the NH₃ desorption peaks shift toward lower temperature; the reason is that the crystal V₂O₅ possess Lewis acid sites with the NH₃ desorption peak located at 150–200 °C [17,18].

As shown in Table 1, the BET surface area and relative acidity density of the catalyst V₂O₅/ZrO₂-Al₂O₃ are largely dependent on the ZrO₂ content and V₂O₅ loading. With the increase of ZrO₂ content in the support (V₂O₅ loading is 16.5 wt.%), the surface area of the catalyst decreases considerably. When ZrO₂ content in the support is 8.5 wt.%, highest surface area is obtained at a V₂O₅ loading of 8.0 wt.%. For the catalysts with different ZrO₂ contents in the support, the change in the relative acidity density (the NH₃-TPD desorption area divided by the catalyst surface area) is mainly ascribed to the decrease of surface area by addition of ZrO₂. For the

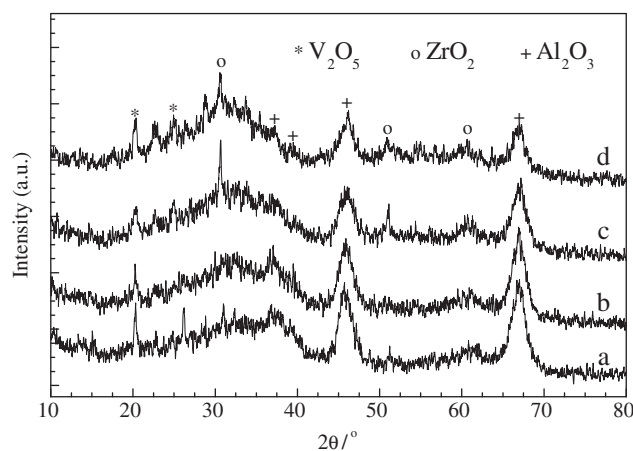


Fig. 1. XRD patterns of the V₂O₅/ZrO₂-Al₂O₃ (V₂O₅ loading is 16.5 wt.%) catalysts with different ZrO₂ contents: (a) 4.0 wt.%; (b) 8.5 wt.%; (c) 20.1 wt.% and (d) 34.2 wt.%.

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