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Article

Chemistry

Selective oxidation of methanol to dimethoxymethane over $V_2O_5/TiO_2–Al_2O_3$ catalysts

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Abstract This paper describes the effect of the preparation method of binary oxide supports ($TiO_2–Al_2O_3$) on catalytic performance of $V_2O_5/TiO_2–Al_2O_3$ catalysts for methanol selective oxidation to dimethoxymethane (DMM). The $TiO_2–Al_2O_3$ supports are synthesized by a number of methods including mechanical mixing, ball milling, precipitation, co-precipitation, and sol–gel method, which is followed by incipient wetness impregnation to produce $V_2O_5/TiO_2–Al_2O_3$ catalysts. Among these samples, the $V_2O_5/TiO_2–Al_2O_3$ catalyst prepared by the sol–gel method has the best catalytic performance with a maximum methanol conversion of 48.9 % and a high DMM selectivity of 89.9 % at 393 K, showing superior performance than V_2O_5/TiO_2 and V_2O_5/Al_2O_3. The excellent catalytic performance of $V_2O_5/TiO_2–Al_2O_3$ is attributed to the effective interaction between the active component and the mixed support. Such interaction changes the chemical states of supported active V components, produces an increased amount of V^{4+} species, and facilitates the electron transfer between support and active component. Additionally, the incorporation of titanium cation into the alumina structure could also help produce an appropriate amount of acidic sites, which increases the DMM selectivity. The coordinated environment of the dispersed vanadia on $TiO_2–Al_2O_3$ mixed support improves the catalytic efficiency on methanol oxidation to DMM.

Keywords Methanol selective oxidation · Dimethoxymethane · $V_2O_5/TiO_2–Al_2O_3$ · Binary oxide support

1 Introduction

Dimethoxymethane (DMM) has successfully attracted increasing attention as a downstream chemical product of methanol in industrial practice. DMM is a useful intermediate in organic synthesis and an excellent solvent in perfume and pharmaceutical industries. It can also act as an environmentally friendly fuel with high efficiency and low toxicity [1]. Moreover, it has been used as a starting monomer in the synthesis of polyoxymethylene dimethylether (POMM) [2]. The traditional method for DMM synthesis includes two consecutive steps: gas-phase methanol partial oxidation to formaldehyde (FA) and the subsequent acetalization of methanol and formaldehyde over acid catalysts [3]. However, this reaction scheme suffers from high reaction temperatures, complicated procedures, and severe equipment corrosion [2]. In addition to the target product DMM in methanol oxidation, several byproducts could form, including methyl formate (MF), dimethyl ether (DME), FA, and oxycarbide. An alternative synthetic pathway by one-step selective oxidation of methanol to DMM under mild reaction conditions becomes more desirable with both environmental and economic advantages. To obtain a high DMM yield in one step, the design of the catalyst is followed by the principle of appropriately balanced redox ability and acidity [4]. Excessive redox sites of the catalyst could lead to the abundant amount of FA, MF, and oxycarbide, while superfluous acidic sites result in a large amount of DME.

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Several catalytic systems have been reported to be active for the methanol oxidation to DMM by carefully coupling the redox sites with suitable supports. For example, Re oxide has been considered as a potential active site for methanol oxidation, and the supported Re oxide like Re/γ-Fe_2O_3 catalyst has a DMM selectivity of 91 % and a methanol conversion of 48.4 % at 513 K [5]. But a bulk ReO_3 catalyst without support has a rather low methanol conversion, only ~12.4 % [5]. The V_2O_5/TiO_2-based catalysts by acidic modification have shown superior performance. For instance, $V_2O_5/TiO_2/SO_4^{2-}$ achieved a 47 % methanol conversion at 393 K, which is much better than the conventional V_2O_5/TiO_2 catalyst with 17 % methanol conversion [4, 6, 7]. The bulk $H_5PV_2Mo_{10}O_{40}$ only showed a 41.1 % methanol conversion with a 40.2 % DMM selectivity at 453–513 K, while the supported heteropoly acid catalysts exhibited 60.3 %–68.4 % methanol conversion with 67 %–51 % DMM selectivity. This is benefitted from the Keggin structures of $H_{3+n}PV_nMo_{12-n}O_{40}$ providing both redox and Bronsted acid sites required for producing DMM [8]. Additionally, several other catalytic systems have been reported to be active for the methanol oxidation to DMM, including modified V/TS-1 catalysts [9], amorphous multi-metal oxides [10, 11], $Fe_2(MoO_4)_3$–MoO_3 catalysts [2, 12]. Among these catalysts, the supported V_2O_5 catalysts have shown excellent catalysis performance in the selective oxidation of methanol to DMM, owing to the outstanding redox properties of V_2O_5.

The catalytic activity and selectivity of the catalyst would be improved by the use of an appropriate support. Due to its high specific surface area, weak acidity, and good thermal stability, γ-Al_2O_3 has been widely used as a support for a number of catalysts. Recently, some interesting results have been obtained for TiO_2 as a promoter on high surface area supports. The chemical states of supported metal or metal oxides, adsorption properties of the catalyst and their catalytic activity are influenced by the incorporation of TiO_2 with the support. Particularly, TiO_2–Al_2O_3 support has drawn special attention owing to its versatile catalytic properties for various commercially important reactions such as isomerization of alkenes, dehydration of alcohols, and hydrodesulphurization [13–15]. Particularly, the TiO_2–Al_2O_3 supported catalysts show better performance than single Al_2O_3 supported catalyst in the hydrodesulfurization (HDS) reaction [14]. It is also well established that the supported vanadium oxides are effective catalysts for partial oxidation of hydrocarbons and alcohols [13, 16, 17]. And the structure of the dispersed vanadium species is closely related to the nature of the specific oxide support, the loading amount, and the preparation procedure [18].

Considering versatile catalytic properties of TiO_2–Al_2O_3 support and good redox properties of V_2O_5, we have developed V_2O_5/TiO_2–Al_2O_3 catalysts for methanol oxidation to DMM. The aim of this study is to explore the influence of preparation method of mixed TiO_2–Al_2O_3 support on the catalytic activity of V_2O_5. The V_2O_5/TiO_2–Al_2O_3 catalysts prepared by five different methods have been employed in selective methanol oxidation to DMM, including mechanical mixing, ball milling, precipitation, co-precipitation, and sol–gel methods. The materials are characterized with the N_2 adsorption/desorption, X-ray diffraction (XRD), temperature-programmed reduction (H_2-TPR), Raman spectroscopy, temperature-programmed desorption of ammonia (NH_3-TPD), and X-ray photoelectron spectroscopy (XPS) techniques. A set of activity tests has been conducted in a fixed-bed micro-reactor for collecting and comparing their kinetic data. The relationship between catalytic activities and the behaviors of both redox and acidic sites of V_2O_5/TiO_2–Al_2O_3 catalysts is analyzed and discussed.

2 Experimental

2.1 Catalyst preparation

A series of $15V_2O_5/TiO_2$–Al_2O_3 catalysts were prepared by a wetness impregnation method with the TiO_2–Al_2O_3 complex support. The V_2O_5 content is all fixed at 15 % for well dispersion and effective comparison reason, as the monolayer coverage of V_2O_5/TiO_2 and V_2O_5/Al_2O_3 catalysts is about 12.5 % and 20 %, respectively [7, 19]. The TiO_2–Al_2O_3 complex support were prepared by five different methods—mechanical mixing, ball milling, precipitation, sol–gel, and co-precipitation method—with the uniform constitute of Al_2O_3 and TiO_2 (Al_2O_3:TiO_2 = 2:1 by weight). A γ-Al_2O_3 powder support and an industrial TiO_2 (P25) (80 % anatase and 20 % rutile) powder were calcined in air at 573 K for 2 h prior to the catalyst preparation. For the complex support with the mechanical mixing method (denoted as TiO_2–Al_2O_3-mix), the required amount of Al_2O_3 and P25 were mechanically mixed with each other until smooth powder was formed. For the support with the ball-milling method (denoted as TiO_2–Al_2O_3-mil), the required amount of Al_2O_3 and P25 were spread in the high energy ball-milling pot and milled for 12 h. The complex support with the precipitation method (denoted as TiO_2–Al_2O_3-imp) was prepared by the method of gel-supported precipitation [13]. In the case with the sol–gel method (denoted as TiO_2–Al_2O_3-sol), it was prepared by the procedure adapted from the literature [20]. For the complex support with the co-precipitation method (denoted