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Characterization and performance of V_2O_5–TiO_2 catalysts prepared by rapid combustion method

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ABSTRACT

The VO_x–TiO_2 (VT) catalysts were prepared by the rapid combustion (RC) method and characterized by SEM, XRD, Raman, XPS, NH_3-TPD and H_2-TPR techniques. The catalytic performance was evaluated in the methanol oxidation reaction. The SEM result showed that the VT catalysts were consisted of nanoparticle with mean grain size about 30 nm. The RC process enhanced the formation of $Ti_{(1-x)}V_xO_2$. The XRD and Raman results revealed that the vanadia transformed from the isolated VO_x to polymeric VO_x and then as crystalline V_2O_5 on the surface of $V_xTi_{(1-x)}O_2$. The polymeric VO_x was predominant when V_2O_5 content was 30 wt.%. The H_2-TPR and NH_3-TPD results showed that the polymeric VO_x exhibited more acidic sites and stronger reducibility than isolated VO_x and crystalline V_2O_5. The catalytic activity result showed that the polymeric VO_x was more active in methanol oxidation. The product distribution showed that the VT catalysts had redox-acidity bifunctional properties suitable for dimethoxymethane (DMM) synthesis, and the DMM selectivity was closely related to the reducibility and acidic sites.

1. Introduction

VT catalysts are widely used for many selective oxidation reactions. For example, they are used for ammoxidaion of alkyl aromatics [1,2], selective oxidation of methanol to formaldehyde (FA) [3] and methyl formate (MF) [4], selective oxidation of ethanol to acetaldehyde [5], selective oxidation of toluene to benzaldehyde and benzoic acid [6], selective oxidation of o-xylene to phthalic anhydride [7,8], etc.

It was well known that the structure, surface properties as well as catalytic performance of VT catalysts could be greatly influenced by the preparation method [9–11]. Several publications are available on the studies of these physico-chemical properties of VT catalyst prepared by coprecipitation, deposition and incipient wetness impregnation methods [12–15]. While, the study of these properties on VT catalyst prepared by the rapid combustion (RC) method has been rarely reported.

The RC method is a novel preparation method to produce the nanoscale catalysts, which typically involves a reaction in solution of metal nitrates and different fuels at high temperature [16–19]. These fuels reacting with oxygen-containing species, formed during the nitrates decomposition, provides rapid high-temperature interaction in the system. During this combustion reaction, various gas-phase products could be formed which inhibits particle size growth and increases specific surface area. Moreover, being the liquid state the initial reaction media (e.g., aqueous solution) allows mixing of the reactants on the molecular level, thus enhances the interaction between active species. And this might lead to the unique properties of the catalysts. Several publications are available on the preparation and characterization of iron-based, cobalt-based, cerium-based, etc., catalysts by RC method [16–21]. However, little attention has been paid to prepare the VT catalysts by this method. Therefore, the present work is focused on the study of the physico-chemical properties of VT catalysts prepared by RC method. In order to precisely characterize these properties, the methanol oxidation reaction is chosen as the probe reaction. That is because, in this reaction, the activity of the catalysts can reflect the existing state of vanadia [22–24], and the distribution of products can reflect the nature of the surface active sites: methanol is converted to formaldehyde (FA) and methyl formate (MF) on redox sites, to dimethyl ether (DME) on acidic sites and to dimethoxymethane on acidic and redox bifunctional sites (DMM) [21,25].

In the present work, the VT catalysts were prepared by RC method and the physico-chemical properties were characterized by SEM, BET, XRD, Raman, XPS, H_2-TPR and NH_3-TPD techniques. The catalytic performance was probed by the methanol oxidation in the presence of O_2. The purpose of this work is to determine the typical properties of VT (RC) catalysts.

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Table 1
The textural properties, surface and bulk composition of the catalysts as well as the dispersion of vanadia.

Sample	S_{BET} ($m^2\ g^{-1}$)	Pore size (nm)	Pore volume (cm^3/g)	V/Ti[a]	V/Ti[b]	(V/Ti[a])/(V/Ti[b])	V density calculated [c] ($1/nm^2$)	%w/w TiO_2 (cell volume A)	
								Anatase	Rutile
TiO_2 (anatase)	151.34	6.07	0.23	–	–	–	–	100(137.62)	–
TiO_2 (rutile)	34.54	6.20	0.05	–	–	–	–	–	100(62.51)
10VT	29.29	10.42	0.08	0.34	0.078	4.35	18.6	31.2 (134.80)	68.8 (61.76)
20VT	94.53	6.38	0.15	0.46	0.190	2.44	12.4	100(134.70)	–
25VT	103.8	5.25	0.14	0.58	0.262	2.21	14.0	100(135.20)	–
30VT	119.98	6.13	0.18	0.71	0.332	2.14	15.1	100(134.51)	–
40VT	63.35	8.37	0.13	0.74	0.425	1.74	38.4	100(135.80)	–
50VT	40.04	10.05	0.10	0.85	0.769	1.27	77.2	100(135.20)	–

[a] Surface atomic ratio calculated from XPS data.
[b] Bulk atomic ratio calculated from ICP-AES data.
[c] Supposing that all the vanadium atoms locate on the surface.

2. Experimental

2.1. Catalyst preparation

The VT catalysts were prepared by RC method. In the typical synthesis, 8.92 ml $TiCl_4$ was added to 24.26 ml 67 wt.% HNO_3 under vigorously stirring, and then 3.58 g NH_4VO_3 and 47.26 g carbamide were added to the solution. The obtained mixture was stirred until the NH_4VO_3 and carbamide were completely dissolved, and then calcined at 773 K for 10 min. According to V_2O_5 content in the final catalysts from ICP-AES (10, 20, 25, 30, 40 and 50 wt.%), the obtained catalysts were marked as 10VT, 20VT, 25VT, 30VT, 40VT and 50VT, respectively. For comparison, the pure anatase TiO_2 (TiO_2-A) and V_2O_5 were also prepared by RC method. And the rutile TiO_2 (TiO_2-R) was prepared by calcination of TiO_2-anatase at 873 K for 4 h.

2.2. Catalyst characterization

XRD patterns were measured on a Bruker Advanced X-Ray Solutions/D8-Advance scanning from 3° to 80° (2θ) at a rate of 0.02°/s, using a Cu Kα radiation ($\lambda = 0.15418$ nm) source. The applied voltage and current were 50 kV and 35 mA, respectively. Raman spectra were measured using a Renishaw-UV–Vis Raman System 1000 Raman spectrometer (Kaiser Optical) and a frequency-doubled He:Cd laser at a wavelength of 325 nm. Raman spectra were measured using a Renishaw-UV–Vis Raman System 1000 Raman spectrometer. The excitation was provided by 514.5 nm line of an Ar^+ ion laser (Spectra Physics) employing a laser power of 7 mW. Surface areas of the catalysts were measured by a BET nitrogen adsorption method at 77.35 K using an ASAP 2000 machine. Prior to a measurement, the sample was degassed to 10^{-3} Torr at 473 K. The particle morphology (SEM) of the catalyst was observed by means of LEO 438VP scanning electron microscopy. The elemental analyses (Ti, V and S) were performed by inductively coupled plasma-optic emission spectroscopy (ICP-AES). The XPS measurements were performed in a Physical Electronics Company Quantum-2000 Scanning ESCA Microprobe equipped with an Al X-ray source (23.3 mA and 1.5 kV), a solid angle acceptance lens and a hemispherical electron analyzer. Samples were compressed in small cup under the pressure of 5 kg/cm^2 for 30 s and supported on a holding ceramic carousel. The positive charge, developed on the samples due to the photoejection process was compensated by a charge neutralizer (low energy electron and low energy ion beam). The residual pressure in the spectrometer chamber was 5×10^{-7} Pa during data acquisition. The analyzed area of the sample was 100 μm and the energy region of the photoelectrons was scanned at a pass energy of 29.35 eV. The resolution was 0.68 eV. The binding energies were referenced to the C 1s band at 284.8 eV. The data were treated on Phi Multipack Program, Gaussian/Lorentzian = 80%. Atomic concentration ratios were calculated by correcting the measured intensity ratios with the manufacturer supplied sensitivity factor. The H_2-TPR measurements were carried out in continuous mode using a U-type quartz micro-reactor. A sample of about 25 mg was contacted with a H_2:N_2 mixture (5.13% volume of H_2 in N_2) at a total flow rate of 60 ml min^{-1}. The sample was heated at a rate of 10 K min^{-1} from room temperature to 1173 K. The hydrogen consumption was monitored using a thermal conductivity detector (TCD). The NH_3-TPD spectra were recorded in a fixed-bed reactor system equipped with a gas chromatograph. The catalyst (200 mg) was pretreated at 773 K under Ar flow (60 ml min^{-1}) for 2 h and then cooled to 373 K under Ar flow. Then NH_3 was introduced into the flow system. The TPD spectra were recorded at a temperature rising rate of 10 K min^{-1} from 373 to 900 K. The desorbed NH_3 was collected and titrated by 0.01 mol/l HCl. The amount of desorbed NH_3 was corresponding to the total number of acidic sites. According to the desorption temperature of NH_3, the acidity intensity could be determined. And based on the areas of desorption peaks, the number of acidic number for each type of acidity can be calculated.

3. Results and discussion

3.1. Physico-chemical characterization

The SEM photographs of the catalysts are shown in Fig. 1. The catalysts consisted of nanoparticle with an equable distribution except for a little aggregated particulate, and the morphology of the catalysts was homogeneous and had narrow distribution in grain size. The mean grain size was about 30 nm. The small particle size obtained on these catalysts might be due to the formation of gas-phase products during the high-temperature combustion reaction, which inhibited the growth of particle size.

The textural properties of the catalysts are shown in Table 1. The surface area of TiO_2-A was 151.34 m^2 g^{-1}, while that for TiO_2-R was only 34.54 m^2 g^{-1}, which might be due to the phase transformation of TiO_2-A to TiO_2-R at higher calcination temperature [25,26] (the TiO_2-R in the present study was prepared by calcination of TiO_2-A at 873 K for 4 h). For VT catalyst, with the increasing V_2O_5 content, the surface area of the obtained catalyst firstly increased then decreased, which reached the maximum on 30VT catalyst. The highest surface area obtained on 30VT catalyst might be responsible for the high dispersion of VO_x on this catalyst (as discussed below).

The XRD patterns of the catalysts are shown in Fig. 2 and the typical diffraction peaks of TiO_2-A were observed for all the catalysts. For 10VT catalyst, the TiO_2-R phase was also observed, which disappeared with the increase of V_2O_5 content [27]. This indicated that the increase of V_2O_5 content inhibited the formation of TiO_2-