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Effective VTeO/SBA-15 Catalyst Prepared by Precursor Method for the Selective Oxidation of Propane to Acrolein

FENG Mao-ying, HUANG Chuan-jing, WENG Wei-zheng, WAN Hui-lin[*],
XU Qin and ZHOU Zhao-hui

*College of Chemistry and Chemical Engineering, State Key Laboratory for Physical Chemistry of Solid Surface,
National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters,
Xiamen University, Xiamen 361005, P. R. China*

Abstract   Precursor decomposition was used for the preparation of VTeO/SBA-15 catalyst for the selective oxidation of propane to acrolein. The catalyst shows a better performance compared with those prepared by conventional impregnant method. A yield of 9.3% of acrolein was achieved with 2% V loadings at 500 $^{\circ}$C. XRD, N_2-adsorption, H_2-TPR, Py-IR and XPS measurements were used to unclose the relationship between the structure and performance of the catalyst.

Keywords   Acrolein; Propane; Vanadium catalyst; Precursor decomposition

1   Introduction

In our previous communication[1], VTeO/SiO_2 catalyst was used for the oxidation of propane to acrolein with a maximal yield of 6.6% at 520 °C. It has been proposed that V^{5+} is responsible for the activation of propane as usual, and Te^{4+} can eliminate the α-H of propene and further insert oxygen in the ally. A catalyst with a high density of vanadium clusters showed a decrease in the acrolein selectivity and an increase in deep oxidation products. It is desirable to synthesize an effective catalyst with maximum density of isolated vanadium species. It has been noted that precursor method like molecular designed dispersion is used to produce highly evenly dispersed metal oxide[2,3]. There are also many publications contributed to the synthesis and characterization of SBA-15 with high thermal stabilities and large surface areas[4—6], while the use of VO$_x$-SBA/15 as catalyst for the selective oxidation of propane is relatively scarce. In this study, we used VTeO/SBA-15 catalyst prepared by the decomposition of vanadyl acetylacetonate for the selective oxidation of propane to acrolein. The catalytic performances were compared with those of the catalysts prepared by co-

impregnation and step-impregnation methods. A detailed characterization of the catalyst was performed.

2   Experimental

2.1   Sample Preparations and Treatments

2.1.1   Preparation of SBA-15

As the method of ref. [7], Plutonic P123 triblock copolymer surfactant EO_{20}-PO_{70}-EO_{20}(9.0 g) from Aldrich was dissolved in 300 mL of 2 mol/L hydrochloric acid. Tetraethyl orthosilicate(TEOS, 20.4 g, 141 mmol) was then added to the above solution. The resulting mixture was stirred for 24 h at 40 °C, and aged for another 24 h at 100 °C. A white solid was filtered, washed and dried. The product was then calcined at 600 °C for 10 h with a heating rate of 1 °C/min to obtain 5.5 g SBA-15(91 mmol, yield 65%).

2.1.2   Deposition of Vanadyl Acetylacetonate VO(acac)$_2$ on the Ordered Mesoporous Material SBA-15

SBA-15(1.0 g, 17 mmol) was impregnated with 8 mL of tellurium acid(19 mg, 83 μmol) for 4 h. The product was dried and calcined at 600 °C for 4 h with a heating rate of 1 °C/min. Vanadyl acetylacetonate

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saturated in toluene(50 mL) was added to the solid of TeO$_x$/SBA-15 and stirred for 1 h. The product was filtered and washed repeatedly with toluene until the filtrate was colorless, and then calcined in air at 600 °C for 4 h with a heating rate of 1 °C/min. The catalyst was named VTeO/SBA-15^M(Molecular designed deposition method).

Co-impregnation method was performed by impregnating SBA-15(1.0 g, 17 mmol) with 8 mL of a solution of tellurium acid(19 mg, 83 µmol) and ammonium metavanadate(39 mg, 333 µmol) for 4 h. The product was calcined in air at 600 °C for 4 h, and named VTeO/SBA-15^C(Co-impregnation method). In a similar way, step-impregnation method was performed by impregnating SBA-15(1.0 g, 17 mmol) with 8 mL of tellurium acid(19 mg, 83 µmol) for 4 h, and the product was calcined at 600 °C for 4 h. The solid was re-impregnated with a solution of ammonium metavanadate(39 mg, 333 µmol) for 4 h, followed by calcining in air at 600 °C for 4 h. The obtained catalyst was named VTeO/SBA-15^S(Step-impregnation method).

2.2 Characterization of Catalyst

The contents of V in the samples were determined by ICP on a Perkin-Elmer OPTIMA 3000 instrument. The above catalysts were dissolved in a solution of nitric, hydrochloric and hydrofluoric acids. The mixture was evaporated at 180 °C to remove Si. The solid was then redissolved in 5 mL of nitric acid, and the solution was diluted to a V concentration less than 30 µL/L. The molar ratios of V, Te and SBA-15 in the catalysts were about 2:0.5:100 by the ICP measurements.

X-Ray diffraction patterns(XRD) were collected on a Rigaku Rotflex D/Max-C powder diffractometer with C-filtered Cu $K\alpha$ radiation(λ=0.15064 nm). Py-IR was measured on a Nicolet Nexus-XT spectrometer. 32 scans were taken with a resolution of 4 cm^{-1}. The catalysts were heated at 500 °C for 1 h, followed by vacuuming and cooling. When the temperature was cooled to 150 °C, a spectrum was collected. The temperature was further down to 100 °C, pyridine was adsorbed for 15 min. After vacuum-pumping, the temperature was raised to 150 °C and IR spectrum was re-collected. N$_2$ adsorption was performed on a Tristar 3000 autosorb instrument.

The H$_2$-TPR measurement was carried out using

a flow quartz reactor. The catalyst(20 mg) were pretreated at 400 °C for 3 h in a flow of argon(20 mL/min), which was cooled to room temperature, and contacted with a dilute hydrogen gas in argon(1%, volume fraction). The heating rate was 10 °C/min from room temperature to 800 °C. The hydrogen consumption was monitored by a TCD detector after removing the water formed.

X-Ray photoelectron spectra(XPS) were taken on VG ESCLABMK-II(Al $K\alpha$, 10.1 kV). Spectra were recorded for V$_{2p3/2}$, Te$_{3d5/2}$ regions. The binding energies were referred to 284.8 eV for C$_{1s}$. Transmission electron microscopy was performed on a Phillips FEI Tecnai 30 high resolution analytical electron microscope operated at 300 kV.

3 Results and Discussion

3.1 Characterization of Precursors

Fig.1 shows the XRD patterns of VTeO/SBA-15 samples. The peaks of (100), (110) and (200) indexed to hexagonal regularity of SBA-15 were clearly observed for the four samples. However, the shifts of the diffraction peaks to higher 2θ values were found for the V grafted SBA-15 catalysts, which was possibly caused by the contraction of their frameworks with vanadium and tellurium loading during the calcination procedure. Furthermore, the peak of d(100) was reduced with vanadium loading compared with that of pure SBA-15 supporter. This is possibly due to a degradation of the hexagonal arrangement of SBA-15 pores[8,9]. However, the detail forms of the vanadium and tellurium oxides remain unresolved. The XRD shows no peak related to vanadium and tellurium oxides, which may be caused by the very low contents of the catalysts. Fig.2 shows the X-ray diffraction peaks in high 2θ region, which also indicates highly dispersed VTeO species on SBA-15 or the contents or
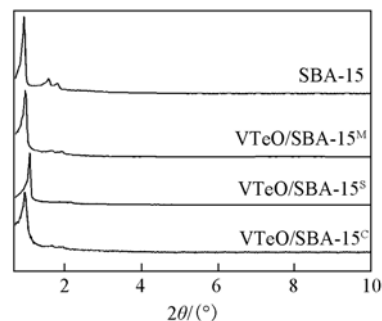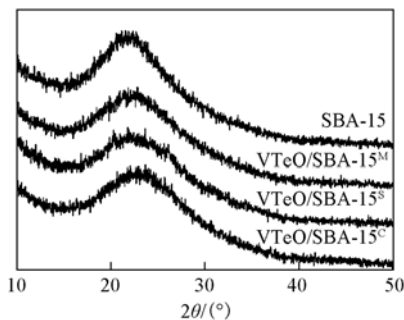

Fig.1 Low-angle X-ray diffraction patterns of VTeO catalysts prepared by different methods

Fig.2　High-angle X-ray diffraction patterns of catalysts prepared by different methods

the concentrations of the metal oxides are below the level that can be detected.

Further evidence was obtained by the TEM images, which clearly reveal well-ordered hexagonal arrays of SBA-15 characteristic mesopores in Fig.3. In this case, vanadium oxide particles cannot be observed on the surface of the SBA-15. This reveals that the vanadium oxide was incorporated into the channels of the support.
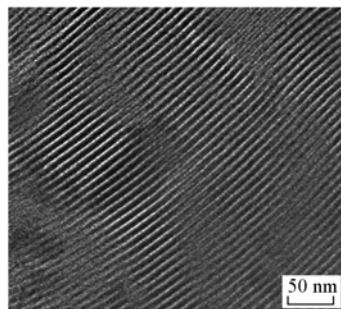

Fig.3　TEM image of sample after grafting of V and Te

Table 1 shows the results obtained from N_2 adsorption measurements. BET surface area was 777 $m^2 \cdot g^{-1}$ for SBA-15. The surface area, pore diameter and volume of VTeO/SBA-15 decreased due to the introduction of VTeO into SBA-15. However, the catalyst prepared by MDD method showed much larger surface area than the other two catalysts, which may indicate that VTeO is loaded not only on the surface, but also inside the pores of SBA-15.

Table 1　N_2 adsorption measurements for the SBA-15 samples

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	Pore volume/ $(m^3 \cdot g^{-1})$	Pore diameter/ nm
SBA-15	777	1.05	8.6
VTeO/SBA-15^M	654	0.73	6.0
VTeO/SBA-15^C	432	0.62	6.12
VTeO/SBA-15^S	496	0.52	4.10

To investigate the influence of reducibility on the catalytic reaction, H_2-TPR was performed and the results are shown in Fig.4. All the SBA-15 supported samples have one main reduced peak with a weak shoulder at 400—450 K. Compared to the TPR profiles of the other two samples, the downshift of the main peak was observed in the TPR profile of VTeO/SBA-15^M. The other two catalysts have similar H_2-TPR profiles, and the main reduction temperature of VTeO/SBA-15^C is a little lower than that of VTeO/SBA-15^S.
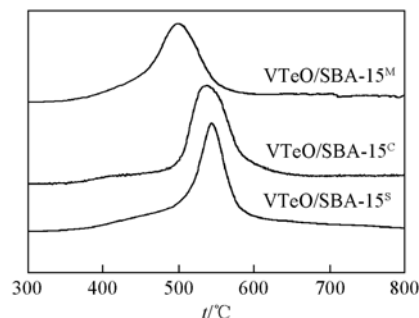
Fig.4　H_2-TPR results of SBA-15 supported VTeO catalysts prepared by different methods

The results of TPR experiment show that the reducibility order of the three catalysts is as follows: VTeO/SBA-15^M>VTeO/SBA-15^C>VTeO/SBA-15^S,for which the reduction peaks are at 499, 539 and 545 °C. According to the studies on the reducibilities of VO/SiO$_2$ and VO/SBA-15[10,11], the peak at the higher temperature is attributed to the reduction of polymeric V^{5+} species, while the peak at the lower temperature is attributed to dispersed tetrahedral vanadium species. Our previous study shows that TeO$_2$ has two reductive peaks at ~465 °C and ~590 °C, corresponding to the reduction of TeO$_2$ to Te and the Te^{4+} species strong interaction with support, respectively[12]. The present H_2-TPR results indicate that VTeO$_x$ species on VTeO/SBA-15^M are more dispersed and thus more reducible than those in the other two catalysts. MDD method is better for the preparation of catalyst with highly dispersed active sites than conventional impregnant method.

To investigate the influence of acidity on the catalytic reaction, Py-IR experiment was performed and the results are shown in Fig.5, Fig.6 and Table 2. The peaks at 1540 and 1450 cm^{-1} were used to represent B and L acid sites, respectively. From Fig.5, it can be seen that all the catalysts show Lewis and Broensted acid sites on the surface[13].

The molar ratios of L to B acid sites in the three catalysts are shown in Table 2. The L/B ratio is in the following sequence: VTeO/SBA-15^C>VTeO/SBA-15^M> VTeO/SBA-15^S, which indicates that the catalyst

prepared by step impregnation method has a much larger density of B acid sites than that of L acid sites, and the catalyst prepared by MDD method has a medium larger density of B acid sites than that of L acid sites.
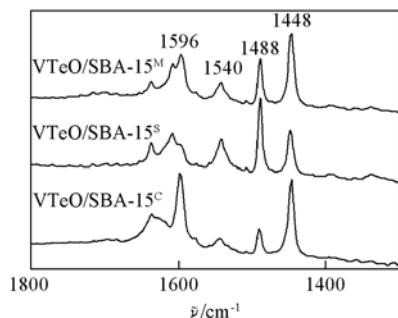

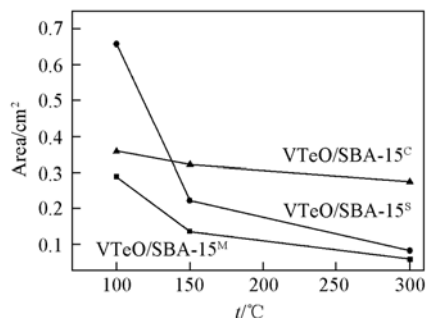**Fig.5　IR spectra of pyridine adsorption on the catalysts prepared by different methods**

Fig.6　Desorption areas of pyridine at different temperatures from the IR peak at 1540 cm^{-1}

Table 2　Distribution of L and B acid sites on the catalysts obtained by Py-IR experiments

Catalyst	Peak area		Molar ratios of L to B acid sites
	L py(1450 cm^{-1})	B py(1542 cm^{-1})	
VTeO/SBA-15^M	1.098	0.287	3.82
VTeO/SBA-15^S	0.609	0.658	0.93
VTeO/SBA-15^C	1.141	0.274	4.16

The intensity of the desorption peak of pyridine at different temperatures reflects the acidity of catalysts. Basic species on weak acid sites desorb at a comparative low temperature. The desorptions of pyridine in different temperature regions were characterized by the IR peak at 1540 cm^{-1} in Fig.6. The greater the area decreases, the weaker the acidity is. Within the temperature range, the desorption area of VTeO/SBA-15^C catalyst has no distinct change. From 100—150 °C, VTeO/SBA-15^S catalyst has the sharpest slope, then VTeO/SBA-15^M has a medium slope, and VTeO/SBA-15^C catalyst has the smallest descend slope. It is obvious that the acidity sequence of the catalysts is VTeO/SBA-15^C>VTeO/SBA-15^M>VTeO/SBA-15^S. VTeO supported on SBA-15 by MDD method has Bronensted acid sites with medium acidic

strength, compared with the catalysts prepared by the other two methods.

According to Pearson Hard Soft Acid Base (HSAB) principle, the interaction of hard B acid sites with hard C—C bond is preferred to that of it with the softer C—H bond. These will predominantly lead to the cracking of propane. On the contrary, the interaction of mild B acid sites with softer C—H bond will lead to the dehydrogenation. Bandiera et al.[14] also showed that strong acid sites favored cracking whereas the B acid sites with medium strength favored proteolytic dehydrogenation.

Figs.7 and 8 show the XPS of V$_{2p}$ and Te$_{3d}$ regions for the catalysts. The binding energies of V$_2$O$_5$ and VO$_2$ are 517.0 and 516.0 eV, and that of Te^{4+} is 576.2 eV, respectively[13]. The V valence state in the three catalysts is +5, and V(V) species contribute to a high conversion of propane. Moreover, the Te$_{3d}$ peak appeared at (576.6±0.1) eV, corresponding to Te^{4+}. The Te ions in the catalyst were reduced from Te^{6+} to Te^{4+} during the procedure of calcination[15].
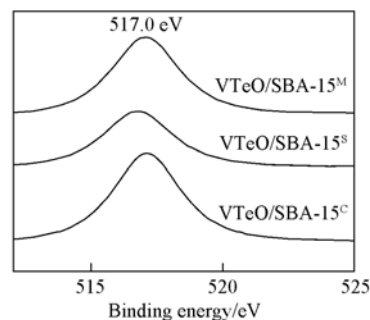

Fig.7　XPS of V$_{2p}$ for the catalysts prepared by different methods
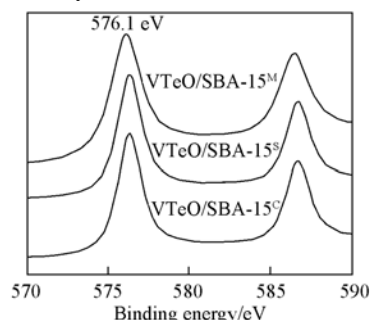

Fig.8　XPS of Te$_{3d}$ for the catalysts prepared by different methods

3.2　Catalytic Tests in Selective Oxidation of Propane to Acrolein

Table 3 shows the catalytic performances of the catalysts for propane selective oxidation at different temperatures. No gas reaction occurred under the

reaction conditions. For the VTeO/SBA-15 catalysts, the samples prepared by vanadyl acetylacetonate exhibited a higher propane conversion and a higher selectivity to acrolein than those by co-impregnant and step-impregnated method. From the result of selective oxidation of propane to acrolein combined with the results of BET, Py-IR and TPR experiments, it is considered that mild Broensted acidity and high dispersed V species on VTeO/SBA-15[M] lead to propane dehydrogenation to propene, subsequently Te^{4+} abstracts α-H of propene to allyl and makes insertion of oxygen into allyl to form acrolein. Better catalytic performances are achieved by well synergy effect of each active site.

Table 3   Catalytic performances of supported VTeO for propane selective oxidation to acrolein[*]

Catalyst	React. temp./°C	Conversion of C_3H_8(%)	Selectivity(%)				Yield(ACR, %)
			ACR	Propene	CO_x	Others	
VTeO/SBA-15[M]	500	29.2	31.7	13.8	50.2	3.8	9.3
	520	31.2	27.4	15.6	50.7	5.3	8.5
VTeO/SBA-15[S]	500	23.2	21.0	16.1	60.2	2.1	4.9
	520	28.3	23.2	15.9	57.6	2.6	6.6
VTeO/SBA-15[C]	500	25.6	30.3	16.9	49.3	3.2	7.8
	520	32.2	23.0	22.4	49.9	3.9	7.4

* Reaction conditions: mass: 0.2 g, GHSV: 3000 mL·g^{-1}·h^{-1}; other products: acetaldehyde, methane, ethane, CO_2 and CO.

4   Conclusions

An effective catalyst with 2% V loadings for the conversion of propane to acrolein with a yield of 9.3% has been obtained by precursor method. Detailed characterizations reveal that the well-organized mesoporous structures of SBA-15 are sustained after the introduction of V. The resulted catalyst possesses high surface area and moderate Broensted acid sites and acidity, facile reducibility, highly dispersed V active sites which are probably the main reasons for its superior catalytic behavior in the selective oxidation.

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