

The study of L-VPO catalysts prepared by microwave methods

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Abstract

The new catalysts of L-VPO with different dopants were prepared by microwave method and conventional heating method. These catalysts showed a definite activity for partial oxidation propane to acrylic acid. The catalyst with Ce and La prepared by microwave method, especially, showed the best activity with the yield and selectivity of acrylic acid being 43.0% and 85.4%. The catalysts were examined with BET, XRD, IR and LRS techniques. The catalysts prepared by microwave method showed larger specific surface area than the catalysts prepared by usual heating method. The Ce-doped VPO catalyst prepared by microwave method possessed $\text{CeP}_3\text{O}_{14}$ phase, which might be the important factor to improve the performance of the VPO catalysts.

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1. Introduction

One of the development trends of petrochemical engineering was using cheaper and more resourceful chemical feeds. One of the most promising reactions was partial oxidation of propane instead of propene to produce acrylic acid and acrolein. Acrylic acid and its derivatives were elementary chemical feeds used for chemical fiber, coatings, leather and adhesives. The primary method of producing acrylic acid was two-step process from propene, and the output of acrylic acid from the method was over 85%. Because of the current abundance and low cost of alkanes, recently, however, more and more interests have been generated in the oxidative catalytic conversion of alkanes other than olefins to produce oxygenates and nitriles in both petroleum and petrochemical industries, although it was well known that those alkanes were low reactive because they had no lone pairs of electrons, no empty orbital and the polarity of the C–H bonds was very little [1,2].

Ai [3,4] prepared some V_2O_5 – P_2O_5 -based catalysts and used them in the selective oxidation of propane. He brought forward the propane oxidation reaction kinetic: Start from the oxidative dehydrogenation of propane to form propene and water played a role in this reaction.

The component of the catalysts was one of the important factor determined the activity of the catalysts. The VPO with Ce dopant was one of the best catalysts used for partial oxidation propane to acrylic acid [5]. It was found that not only the component but also the preparation method of the catalyst could greatly affect the structure or species of formed oxides. Microwave heating method was usually applied to prepare many catalysts and these catalysts showed better performance in the reaction of selective oxidation alkyl to olefin and other chemical feed [6–10]. But few papers related to VPO catalysts prepared by microwave method when they used for selectivity oxidation propane to acrylic acid. In present paper, we would like to report the catalyst prepared by microwave method in addition to the effect of different dopant on the VPO catalysts. These catalysts were characterized by FT-IR, BET, XRD and LRS. The result illuminated that VPO catalysts with Ce prepared by microwave heating method showed best activity.

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2. Experimental

2.1. Catalysts preparation

All the reagents were commercially obtained and used without further purification.

The catalyst used in this study was a V_2O_5 – P_2O_5 . The molar ratio of V, P and other dopants was listed in Table 1. L-VPO was prepared by the method reported elsewhere [11,12] (the major dopants was lanthanide series metal oxides, and the catalysts was named L-VPO). V_2O_5 (5 g, AR, 99%) was reduced in mixture of *iso*-butyl alcohol (100 cm³, AR, 99.5%) and benzyl alcohol (100 cm³, AR, 99.5%) at refluxing temperature for 6 h. Then a definite amount dopant: $La(NO_3)_3$, $Ce(NO_3)_2$, $((NH_4)_6Mo_7O_{24}) \cdot 4H_2O$ or $Bi(NO_3)_3$ was added into the suspended mixture following phosphorus acid (85%). A black solid was got after the mixture refluxed for 2 h and separated by filtration.

The black solid was divided into two parts. One was heated for 2 min by microwave method. The heating conditions were: frequency: 2450 MHz, output power: 160 W. The other was heating for 4 h at 393 K under atmosphere condition in an oven. All the dried catalysts were calcined at 723 K for 6 h.

The catalysts heated by microwave were named A-1, B-1, C-1 and D-1, and the catalysts with the same composition heated at oven were named A-2, B-2, C-2 and D-2.

2.2. Catalytic activity test

Selective oxidation of propane to acrolein was carried out in a tubular fixed bed flow reactor made of stainless steel (i.d. = 6 mm) under atmospheric pressure. Analysis of reactants and products were carried out by on-line gas chromatography, using two parallel connection column types: (i) Porapak Q (2.0 m × 1/8 in.) to analyze CO_2 , acrolein and acrylic acid, (ii) molecular sieve 13A (2 m × 1/8 in.) to analyze CO , N_2 , O_2 , C_2H_4 , C_3H_8 , C_3H_6 .

Other reaction conditions such as feed gas molar ratio and GHSV were measured and chose the best one with the flow of $N_2/O_2/C_3H_8 = 17.5/3.2/5.1$ ml/min, amount of the catalysts = 200 mg in the present paper. Water was introduced by its saturated vapor at 338 K (water vapor pressure was 25.0 kPa). The catalysts were not any further reduced

or diluted prior to reaction. The reaction temperature was 723 K.

2.3. Catalyst characterization

X-ray diffraction (XRD) analysis was carried out using a Thermo-X'TRA automated power X-ray diffractometer with a graphite filter by the continuous scanning (4°/min) with $Cu K\alpha$ radiation (400 kV, 120 mA).

The specific area was measured by a NOVA 1000E Material Physical Structure Determinator. The sample was pre-treated at 573K under the pressure being 0.67 Pa, then measured under liquid nitrogen temperature (77 K).

FT-IR was analyzed at a Nicolet AVATAR 370 FT-IR spectrometer.

All laser Raman spectra (LRS) were recorded with an Almega spectrometer (Thermo Nicolet Co., USA) equipped with a confocal microscope (50 × objective) and CCD detector. An Ar-laser (532 nm) was used for the excitation of the Raman spectra.

3. Results and discussion

3.1. BET results

The specific area of the catalysts was showed in Table 1. The specific surface area of the catalysts heated by microwave was commonly larger than that of the catalysts heating at oven, as Table 1 showed. The specific area of sample B-1 and D-1 was almost was two times of that of B-2 and D-2 and it of sample A-1 attained 27.28 m²/g.

The mechanics of heat diffusing in the traditional heating process was that heat gradually diffused from outer to inner. Gas and liquid coexist in the pore of the gel and form a meniscus following solvent evaporation. The meniscus gradually shrunk into the pore for the effect of surface tension. The capillary force drew the pore framework and made it breakdown accompany with the temperature, and then the specific surface area and volume of the catalysts became very little. Surface tension and capillary force would disappear because the outer and inner of catalyst was heat simultaneously when it was dried by microwave. It would prevent the collapse of the gel and the framework (three-dimensional net structure) of it could be preserved. Then the specific area and pore volume of the catalyst got larger.

On the other hand, microwave was a non-ionizing electromagnetic energy and showed special electric field effect. So it could apace heat the catalysts and could shorten heating time. At the same time, the characteristic of microwave could render the active constituent more homogeneous and took on better dissemination.

3.2. XRD

The effect of preparation method on the XRD patterns of catalysts was different. As Fig. 1 showed, a main phase

Table 1
Specific surface area of the catalysts with BET

Catalysts	Molar ratio	Heating	BET (m ² g ⁻¹)
A-1	P:V:La = 1.1:1:0.04	Oven	26.0
A-2	P:V:La = 1.1:1:0.04	Microwave	27.3
B-1	P:V:La:Ce = 1.1:1:0.04:0.04	Oven	12.5
B-2	P:V:La:Ce = 1.1:1:0.04:0.04	Microwave	21.1
C-1	P:V:La:Mo = 1.1:1:0.04:0.04	Oven	10.9
C-2	P:V:La:Mo = 1.1:1:0.04:0.04	Microwave	12.5
D-1	P:V:Bi = 1.1:1:0.04	Oven	7.7
D-2	P:V:Bi = 1.1:1:0.04	Microwave	12.2

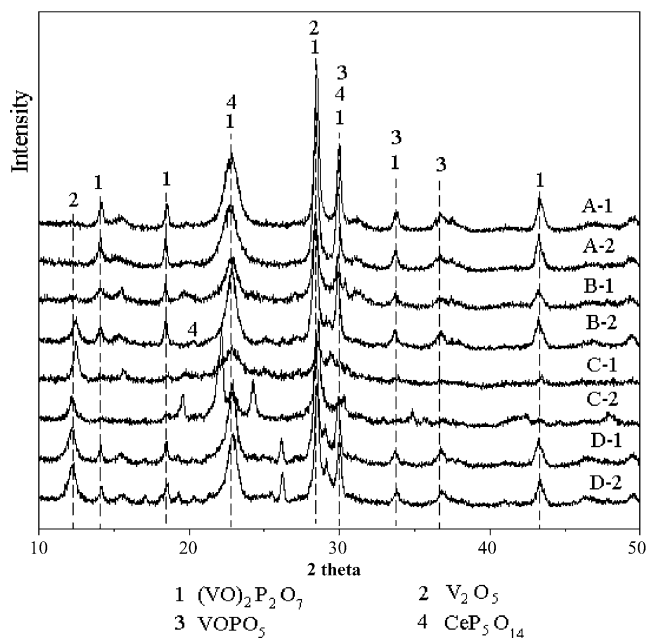
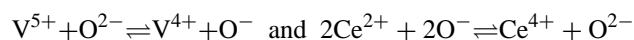


Fig. 1. XRD patterns of different L-VPO catalysts with different dopants.

of $(\text{VO})_2\text{P}_2\text{O}_7$ (JCPDS 34-1381) appeared in catalyst A prepared by both microwave and general heating method. A new phase, $\text{CeP}_5\text{O}_{14}$ (JCPDS 34-0021), V_2O_5 (JCPDS 45-1074) and $(\text{VO})_2\text{P}_2\text{O}_7$ were the main phases when VPO was intermingled with La and Ce. As to catalysts C-2 and D-2, which was heated by microwave, V_2O_5 was the only other phase accompany with $(\text{VO})_2\text{P}_2\text{O}_7$ phase, but VOPO_4 (JCPDS 27-0948) simultaneously appeared in the catalysts C-1 and D-1 when the catalysts C and D was heated in oven. This probably illuminated that the structure of catalysts containing rare-earth elements was impervious to microwave and kept uniform when they were heated either by microwave or oven. Mo and Bi, however, could promote the formation of high valence of V when the catalysts were heated in dry oven, and VOPO_4 phase emerged.

$\text{CeP}_5\text{O}_{14}$ phase was the only phase which was not composed by V and/or P. Ce ion showed two valence state, i.e., Ce^{2+} and Ce^{4+} . Ce and V could form two kinds of electron couples, i.e., $\text{Ce}^{2+}/\text{Ce}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$. Such couples could be formed by a charge transfer:



The O^- species had been indeed shown to be active in activation of the C–H bond both in alkane and olefin molecules. The electron couples were propitious to activation of the C–H bond. The synergic effect between Ce and V, to the contrary, could make the active phase, $(\text{VO})_2\text{P}_2\text{O}_7$, more stable.

3.3. FT-IR

Fig. 2 showed the FT-IR patterns of catalysts A-1, A-2, B-1 and B-2. The band situated at about 3375, 970, 620, 500 cm^{-1} was ascribed to benzyl alcohol. And the band sit-

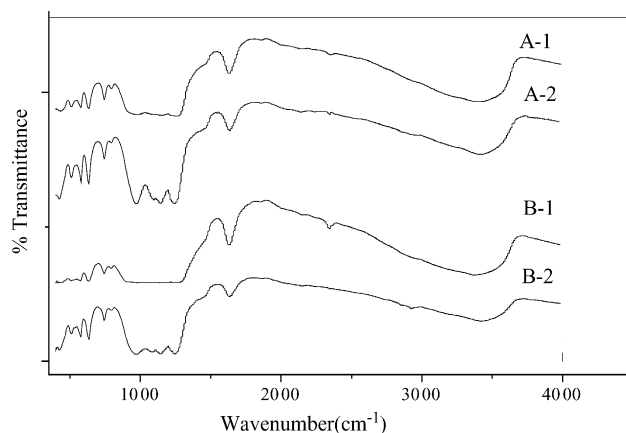


Fig. 2. FT-IR patterns of the catalysts A-1, A-2, B-1 and B-2.

uated at about 1240, 1140, 740 cm^{-1} was identical with the flexible frequency of P–O band in the $(\text{VO})_2\text{P}_2\text{O}_7$ phase. The FT-IR peak at about 1645 cm^{-1} was contributed to the absorbance band of the coordinate water. According to both the result XRD and FT-IR, it could be confirmed that the main active phase of the catalysts being $(\text{VO})_2\text{P}_2\text{O}_7$.

3.4. Laser Raman spectra (LRS)

Laser Raman spectra of catalysts A-1, B-1, C-1, D-1 and A-2, B-2, C-2, D-2 were showed in Fig. 3. The main band was situated in the 930–940 cm^{-1} region with one peak situated at 1188 cm^{-1} for catalysts A-1, B-1 and A-2. They could be assigned to $(\text{VO})_2\text{P}_2\text{O}_7$ phase [13,15]. Some peaks besides the above-mentioned were situated in the 434–654 cm^{-1} were observed for catalysts B-2, C-1, D-1, C-2 and D-2 and they could be attributed to V_2O_5 [16]. Four peaks were situated in the 897–1073 cm^{-1} region for catalyst D-2. A new peak was situated at 1040 cm^{-1} could be assigned to VOPO_4 phase [15] for catalysts B-2, C-1, D-1, C-2 and D-2, respectively.

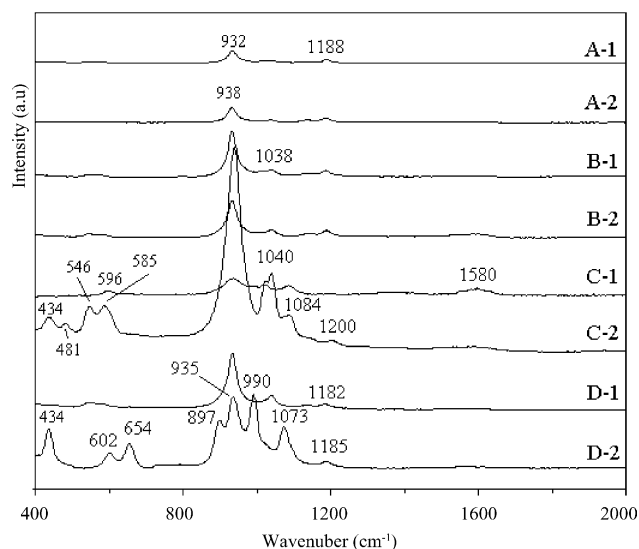


Fig. 3. Laser Raman spectra of different L-VPO catalysts with different dopants.

Table 2
The catalytic performance of VPO catalysts

Catalysts	Conversion of propane (%)	Selectivity (%)				
		CO	CO ₂	C ₃ H ₆	Acrolein	Acrylic acid
A-1	6.5	23.0	10.8	–	3.2	63.0
A-2	7.5	21.3	9.3	–	2.7	66.7
B-1	49.0	13.8	7.5	0.2	4.9	73.6
B-2	50.3	8.5	4.0	–	2.0	85.5
C-1	27.2	29.8	8.8	–	13.6	47.8
C-2	27.4	30.3	13.1	0.4	11.3	44.9
D-1	24.0	20.0	11.3	0.4	12.0	55.7
D-2	29.2	17.5	14.5	0.3	8.9	58.8

Reaction condition: N₂/O₂/C₃H₈ = 17.5/3.2/5.1 ml/min; amount of catalysts = 200 mg; reaction temperature: 723 K.

The Raman result was coincided with that of XRD. The CeP₅O₁₄ could not be observed in the Raman spectrum probably for its inert sensitivity to the Raman signal.

3.5. Catalytic performance

The reaction results of selective oxidation from propane to acrylic acid under different preparation method of the catalysts with different dopant were showed in Table 2. As Table 2 showed, the performance did not present large discrepancy between the catalysts prepared by different method. The activity of catalyst A-2 was very low although its high specific surface area. The conversion of propane was high for catalysts C and D. it might be explained by the strong oxidizing property of V₂O₅ phase. All the catalyst contained V₂O₅ phase except catalysts A, according to XRD and Raman results. Catalyst C-2 showed lower selectivity of acrylic acid because it contained minor (VO)₂P₂O₇ phase. The catalysts B, especially B-2 showed the highest selectivity and yield for acrylic acid. The content of V₂O₅ in catalyst B-2 was lesser than catalysts C and D, and the content of (VO)₂P₂O₇ phase was lesser than catalyst A, logically, the conversion of propane might be lower than catalysts C and D and the selectivity of acrylic acid might be lower than catalysts A. Combination with XRD and Raman results, the experimental result might be the synergic effect between CeP₅O₁₄ and (VO)₂P₂O₇ phase which promoted the stabilization of catalyst B and conversion of propane, and enhanced the selectivity of acrylic acid. Catalysts C and D all showed lower activity than catalyst B. This meant that the addition of La and Bi might promote the overall oxidation of propane.

4. Conclusion

It was concluded by the results of reaction from selective oxidation propane to acrylic acid and the BET, XRD,

FT-IR and LRS characterization of the catalysts prepared by different methods that different preparation methods of the catalysts could greatly affect the specific surface area and active phase. V₂O₅ was the main effect on the conversion of propane and (VO)₂P₂O₇ phase was the main effect on the selectivity of acrylic acid. Specific surface area showed few effect on the performance of the catalyst though the catalysts prepared by microwave method took on higher specific area. The catalyst containing Ce composed by CeP₅O₁₄ and (VO)₂P₂O₇ phase, and could promote the catalyst performance for the synergic effect between these two phases.

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