

State Key Laboratory of Genetics of Fudan University and State Key Laboratory of Bioorganic Chemistry of Shanghai Institute of Organic Chemistry.

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Active site of praseodymium orthovanadate catalyst in oxidative dehydrogenation of propane

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Abstract The pure phase of praseodymium orthovanadate (PrVO₄) has been prepared by the citrate method. The active site of PrVO₄ was studied by ESR, NO-TPD, O₂-TPD and ¹⁸O₂-isotope exchange methods. The results of ESR and NO-TPD confirmed the presence of V⁴⁺ in the catalyst. ¹⁸O₂-isotope exchange was through a single exchange procedure. From the result of O₂+TPD and the kinetic study of ¹⁸O₂-isotope exchange, one can reach a conclusion that the V⁴⁺ species associated with oxygen vacancies are the site for O₂ activation. The adsorbed O₂ or O⁻ are the active oxygen species in propane oxidative dehydrogenation.

Keywords: praseodymium orthovanadate active site propane oxidative dehydrogenation catalyst.

VANADIUM-BASED catalysts are the catalysts for most important oxidation reactions. For example, in the industrial production of sulphuric acid, the oxidation of SO₂ to SO₃ is catalyzed by alkali promoted V₂O₅ catalysts. The oxidation of *n*-butane and *n*-butene to produce maleic anhydride is based on VPO catalysts^[1]. In recent years, VMgO catalysts have been reported to be effective in the oxidative dehydrogenation of light alkane such as propane and butane^[2-3]. Some of the supported vanadium catalysts have also been used in the selective oxidation of light alkane^[4-6]. The vanadium-based catalysts are complex since the vanadium ions have many kinds of valences and can form many kinds of vanadates such as orthovanadate, pyrovanadate and metavanadate. In order to design more effective catalysts for the selective oxidation of light alkane, we must investigate the active phase and active species in vanadium-based catalysts. We have prepared pure phase of rare earth orthovanadates and studied their catalytic action on propane oxidative dehydrogenation^[7]. Here we report the studies on the active site of praseodymium orthovanadate (PrVO₄) catalyst by means of electron spin resonance (ESR), temperature programmed desorption (NO-TPD and O₂-TPD) and ¹⁸O₂-isotope exchange methods.

1 Experimental

The PrVO₄ catalyst was prepared by citrate method. The starting materials were analytical grade Pr(NO₃)₃·5H₂O and NH₄VO₃. Equal mole ratio of the two reagents was first dissolved in hot deionized water and extra amount of citric acid was then added. The resulting solution was heated with stirring to obtain the solid which was heated at 400 °C for 24 h to decompose the organic precursor and then calcined at 550 °C for 6 h. The phase composition of the prepared sample has been confirmed to be pure phase of

tetrahedral PrVO_4 by XRD and Raman spectrum.

ESR was conducted on a Bruker 200D-SRC meter. The $^{18}\text{O}_2$ -isotope exchange experiment was conducted in a flow system connected to a Hewlett Packard G 1800A GCD mass quadrupole spectrometer. 200 mg of each sample was pretreated in a flow of pure He at 500°C for 2 h and cooled down to 200°C and 10 mL $^{18}\text{O}_2$ was pulsed into the reactor. The procedures were repeated at 300, 400, 500 and 600°C . The $^{16}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}_2$ were monitored at the exit of the reactor to detect the oxygen exchange ability of the catalyst. The temperature programmed desorption (NO-TPD and O_2 -TPD) was performed in the system as oxygen isotope exchange.

2 Results and discussion

Figure 1-1 shows the ESR spectrum of the fresh PrVO_4 catalyst. It shows an intensive signal with g value at about 1.98 which has been assigned to V^{4+} ions^[8]. It shows hyperfine structure due to V^{4+} ($S = 1/2$; $I = 7/2$) in a distorted tetrahedron structure. The hyperfine structure is not particularly well resolved indicating that the V^{4+} ions in the catalyst are not sufficiently apart from each other. In other words, the concentration of V^{4+} ions is not low. The V^{4+} ions in the catalyst can be easily oxidized by O_2 . Fig. 1-2 is the ESR spectrum of PrVO_4 treated with O_2 at 550°C for 10 min and then sealed in a glass tube. The spectrum shows that the ESR signal at $g = 1.98$ was greatly reduced. The V^{4+} also appears in the catalyst after reaction (figure 1-3).

The NO-TPD method can also be used to reveal the presence of V^{4+} ions^[4]. If there are V^{4+} ions in the catalyst, the chemically adsorbed NO can react with them at elevated temperatures. Two NO molecules could react with one V^{4+} ion so produce one molecule of N_2O . Since the desorption of N_2O ($m/e = 44$) can be masked by CO_2 , we first characterized the CO_2 desorption profile of the catalyst. Fig. 2-1 shows the CO_2 spectrum of the fresh PrVO_4 sample. The threshold for major CO_2 desorption is at 530°C . Fig. 2-2 is the N_2O spectrum of PrVO_4 pretreated with He at 600°C for 2 h. It has a peak positioned at 440°C , corresponding to the release of N_2O when NO reacts with V^{4+} . On the other hand, the NO-TPD profile of PrVO_4 pretreated with O_2 at 550°C for 1 h has no peak in this range (fig. 2-3), indicating that the V^{4+} ions in the catalyst have been oxidized by O_2 in the pretreatment process.

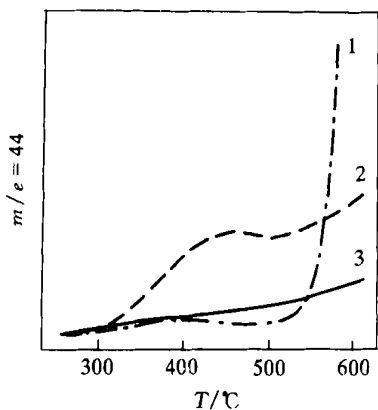


Fig. 1. ESR spectra of PrVO_4 . 1, Fresh; 2, pretreated with O_2 at 600°C ; 3, after reaction.

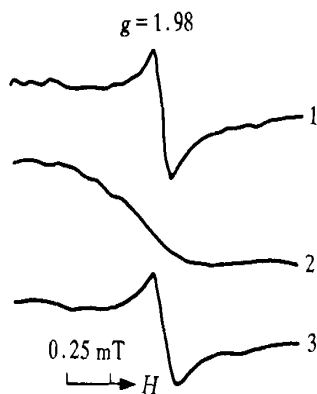
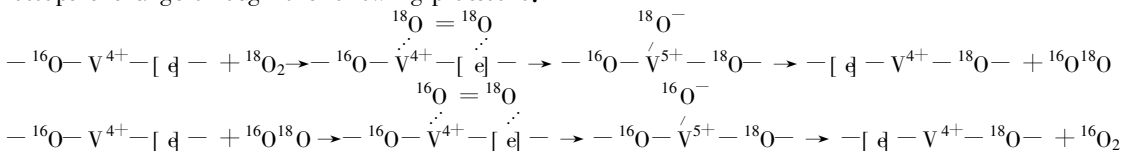


Fig. 2. NO-TPD profiles of PrVO_4 . 1, CO_2 spectrum; 2, N_2O spectrum, pretreated with He at 600°C for 2 h and then adsorbed NO at 30°C ; 3, N_2O spectrum, pretreated with O_2 at 600°C for 2 h and then adsorbed NO at 30°C .

Figure 3 shows that O_2 desorption starts at ca. 410°C . There is a shoulder at 510°C , which is corresponding to the desorption of adsorbed oxygen. The main desorption peak appears at ca. 690°C . This is due to the desorption of lattice oxygen.

$^{18}\text{O}_2$ -isotope exchange was employed to determine the degree of isotope exchange between gas phase oxygen and the lattice oxygen of the solid catalysts and the type of isotope species formed (i. e. $^{18}\text{O}^{16}\text{O}$

and $^{16}\text{O}_2$). The blank experiment (without catalyst in the reactor) showed no occurrence of isotope exchange in the temperature range (200–600 °C) adopted in our investigation. The result of oxygen isotope exchange on PrVO_4 was shown in fig 4. One can see that the threshold temperature for the exchange of gaseous oxygen with lattice oxygen was about 380 °C. At any temperature above 380 °C, the amount of $^{16}\text{O}_2$ was much higher than that of $^{18}\text{O}^{16}\text{O}$, signifying that double exchange was dominant. The amount of $^{16}\text{O}_2$ increased linearly with the increase in temperature while that of $^{18}\text{O}^{16}\text{O}$ optimized at 500 °C and then decreased. In the V-based catalysts, there are usually oxygen vacancies associated with V^{4+} . The $^{18}\text{O}_2$ -isotope exchange through the following process is:



where [e] stands for oxygen vacancies. From the kinetic scheme, one can reach a conclusion that the activation of oxygen is on the site of V^{4+} associated with oxygen vacancies. The adsorbed O_2 and O^- species might be the active oxygen species in the oxidative dehydrogenation of propane.

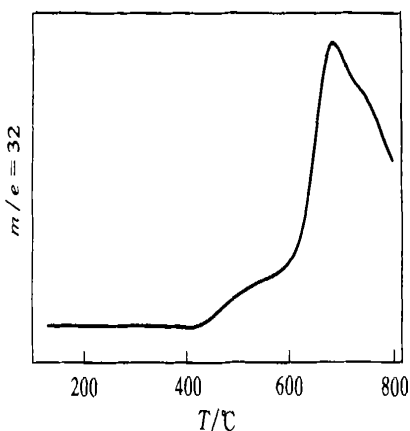


Fig. 3. O_2 -TPD profile of PrVO_4 .

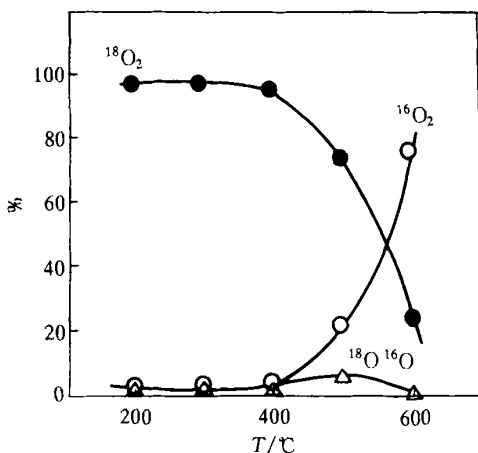


Fig. 4. $^{18}\text{O}_2$ -isotope exchange over PrVO_4 .

3 Conclusion

ESR and NO-TPD methods have been employed to study the active phase of PrVO_4 catalyst in oxidative dehydrogenation of propane. The results indicate that V^{4+} ions are present on the surface of the catalyst which is favorable for the production of active oxygen species. O_2 -TPD and $^{18}\text{O}_2$ -isotope exchange results reveal that the adsorbed O_2 or O^- are the active oxygen species in oxidative dehydrogenation of propane.

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Optical resolution ability of optically active poly(N-diphenylmethyl maleimide)

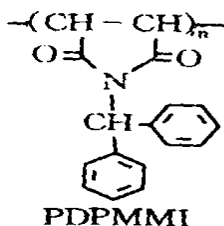
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Abstract A new optically active polymer, (+)poly(N-diphenylmethyl maleimide), was coated on macroporous silica gel and used as a chiral stationary phase for high performance liquid chromatographic resolution of enantiomers. The chiral polymer showed efficient resolution ability to some polar racemates, and eleven pairs of racemates are resolved effectively.

Keywords optical resolution, chiral stationary phase, high performance liquid chromatography, N-diphenylmethyl maleimide, optically active polymer.

OPTICALLY active compounds have attracted great attention because living systems are chiral. Living organisms usually show different biological responses to one or the other of a pair of enantiomers, whether they are drugs, pesticides or wastes. It is well known that optically inactive reagents always yield optically inactive products. However, racemates can be separated in a chiral environment. Recently, chiral resolution by high-performance liquid chromatography (HPLC) has already become an important, practically useful method for the separation of optical isomers, and various optically active polymers have been tested as chiral stationary phase (CSP)^[1-3]. Especially, optically active poly(triphenylmethyl methacrylate) (PTrMA) and its derivatives^[4-9] with chirality mainly due to the helical conformation show excellent chiral recognition ability for various racemic compounds in HPLC. However, the PTrMA column will lose its optical resolving ability slowly when methanol is used as an eluent because the ester group of PTrMA undergoes solvolysis in methanol^[4]. This defect has been improved by replacing one or two of the phenyl groups of PTrMA with one or two 2-pyridyl groups. The polymers have been tested as CSP^[6,8].



In this paper, a new optically active polymer, (+)poly(N-diphenylmethyl maleimide) (PDPMMI), is coated on macroporous silica gel and first tested as a CSP for HPLC. The optically active (+)PDPMMI with its chirality from the excessive chiral centers of (S,S) or (R,R) formed by *trans* opening of the double bond is prepared by the asymmetric polymerization of non-chiral N-diphenylmethyl maleimide (DPMMI) with chiral anionic initiators^[10]. The polymer is stable to solvents, acids and bases. The optical resolution ability of the chiral polymer is tested and discussed.

1 Experimental

(1) Materials. (+)PDPMMI obtained by the asymmetric polymerization of DPMMI with