The Active Sites of the Reference Phase of SmVO₄ as Catalyst for Propane Oxidative Dehydrogenation*

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The active sites of samarium orthovanadate(SmVO₄) were studied by means of ESR, NO-TPD and temperature programmed $^{18}O_2$-isotope exchange(TPIE) methods. The results of ESR and NO-TPD confirm the presence of V^{4+} in the catalyst. The TPIE revealed that the $^{18}O_2$-isotope exchange was carried out through a single exchange procedure. The V^{4+} species associated with oxygen vacancies are the sites for O_2 activation.

Keywords Samarium orthovanadate, Active site, V^{4+} species, Oxidative dehydrogenation

Introduction

The utilization of alkane to produce intermediate chemicals is always attractive. The functionalization of light paraffin by catalytic oxidation to produce alkene and oxygenates is a preferable method[1]. The oxidation of n-butane to produce maleic anhydride catalyzed by VPO catalyst is the unique example which has been commercialized in this field[2]. VMgO catalysts have been claimed to be effective in the oxidative dehydrogenation of propane[3], butane[4] and cyclohexane[5] to produce the corresponding alkene. Kung and his colleagues suggested $Mg_3V_2O_8$ as the active phase in the oxidative dehydrogenation reaction, while Volta and co-workers pointed out that α-$Mg_2V_2O_7$ was the active phase whereas the $Mg_3V_2O_8$ was responsible for the total oxidation[6]. We have prepared the pure phase of rare earth orthovanadates and studied their catalytic action on propane oxidative dehydrogenation[7]. The present paper covers the studies on the active sites of samarium orthovanadate catalyst by means of ESR, NO-TPD and $^{18}O_2$-isotope exchange methods.

Experimental

The preparation of samarium orthovanadate(SmVO₄) has been described elsewhere[7]. The prepared sample has been confirmed by IR, Raman and XRD to be a pure phase of tetrahedral samarium orthovanadate. The temperature programmed $^{18}O_2$-isotope exchange(TPIE) experiment was conducted in a flow system connected to a Hewlett Packard G1800A GCD mass quadrupole spectrometer. The sample(200 mg) was pretreated in a flow of pure He at 500 for 2 h and cooled down to 30 . The sample was plugged with a mixture gas of 1.0% $^{18}O_2$ and 99.0% He(in volume) for 30 min and then was heated to 800 at a rate of 10 /min. The $^{16}O_2$ and $^{18}O^{16}O$ were measured to detect the exchange ability of lattice oxygen in the catalyst with the gaseous molecular oxygen. The NO-TPD was performed in the

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system as oxygen isotope exchange and the sample was pretreated in the same way. The ESR was conducted on a BRUKER 200D-SRC meter.

Results and Discussion

Fig. 1*a* shows the ESR spectum of fresh SmVO$_4$ catalyst. It shows an intensive singal at g= 1. 98 which has been assigned to V^{4+} ions[8]. The hyperfine structure due to V^{4+} (S = 1/2; I= 7/2) also appears in a distorted tetrahedron structure, but it does not show a very good resonance. The V^{4+} ions in the catalyst can be easily oxidized by O$_2$. The ESR spectrum of SmVO$_4$ treated by O$_2$ at 550   for 20 min and then sealed in a glass tube (Fig. 1*b*) shows that the signal at g= 1. 98 is greatly reduced. The signal of V^{4+} in the ESR spectra also appears after the reaction (Fig. 1*c*). The result indicates that V^{4+} species existed in the catalyst in the reacting procedure.
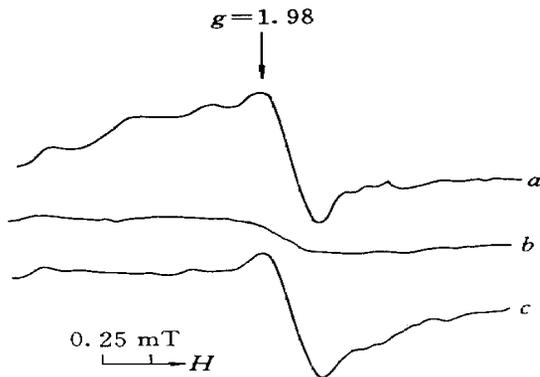
Fig. 1   ESR spectra of SmVO$_4$.
    a. fresh catalyst; *b*. the catalyst was pretreated
    with O$_2$ at 550   for 20 min; *c*. after reaction.
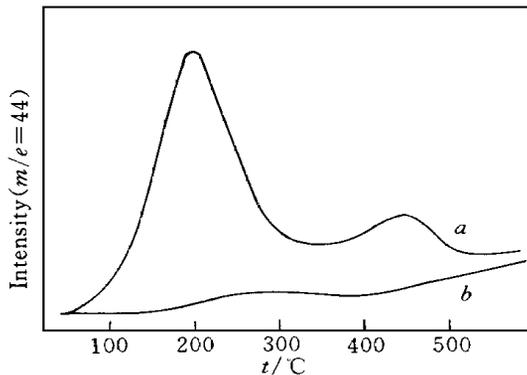
Fig. 2   NO-TPD profiles of SmVO$_4$ catalyst.
    a. pretreated with He at 550   for 2 h; *b*. pre-
    treated with O$_2$ at 550   for 1 h.

The NO-TPD method can also be used to confirm the presence of V^{4+} ions[6]. The catalyst was first treated with pure He for 2 h at 600   in order to eliminate the interference of CO$_2$ which has the same m/e(44) as N$_2$O. The NO-TPD profile of SmVO$_4$ pretreated by He at 550   for 2 h shows two peaks at 205 and 450   (Fig. 2*a*). The peak at 205   is due to the reaction of NO with the oxygen defect in the catalyst. The peak at *ca*. 440   corresponds to the release of N$_2$O produced by the reaction of NO with V^{4+} ions. On the other hand, the NO-TPD profile of SmVO$_4$ pretreated by O$_2$ at 550   for 1 h has no peak at the range, indicating that the oxygen vacancies in the catalyst and the V^{4+} ions have been oxidized by O$_2$ in the pretreatment process. This result is in good agreement with that of ESR.

Temperature programmed ^{18}O$_2$-isotope exchange(TPIE) was employed to determine the degree of isotope exchange between gas phase oxygen and the lattice oxygen of the solid catalyst. The type of isotope species formed(*i.e.*, ^{18}O^{16}O and ^{16}O$_2$) in the procedure was monitored. Our results of oxygen isotope exchange on SmVO$_4$ are shown in Fig. 3. The results show that the ^{18}O^{16}O profile starts at 570   and increases with temperature increase. Also, a small peak appears at 738   . Because the blank experiment(without catalyst) shows no occurrence of isotope exchange in the gaseous phase, ^{18}O^{16}O must be produced by gaseous ^{18}O$_2$ exchanged with catalyst lattice oxygen through a single exchange procedure, *i.e.*, there is only one atom of the gaseous oxygen molecule exchanged for one lattice oxygen atom of the catalyst in a single step,

$$^{16}O + {}^{18}O_2(g) \longrightarrow {}^{18}O + {}^{18}O^{16}O(g) \qquad (1)$$

where ^{16}O and ^{18}O stand for lattice oxygen in the catalyst. The small peak at 738   cor-responds to an active site of the catalyst which can exchange with gaseous oxygen at this temperature.

The onset temperature for $^{16}O_2$ profile is about 610   . The content of $^{16}O_2$ is smaller than that of $^{18}O^{16}O$ below 657   , but it increases extremely above 650   and reaches the maximum at 747   , $i.e.$, at a high temperature, the content of $^{16}O_2$ is much bigger than that of $^{18}O^{16}O$. The content of $^{16}O_2$ did not increase in step with that of $^{18}O^{16}O$ and the

Fig. 3   TPIE profiles of SmVO₄.

shape of $^{16}O_2$ profile is not similar to that of $^{18}O^{16}O$. The results indicate that $^{16}O_2$ was pro-duced due to the lattice oxygen desorption. It did not conceive with the isotope exchange pro-cedure. Because of the low concentration of $^{18}O^{16}O$ in the gaseous phase, the $^{16}O_2$ produced by the exchange of $^{18}O^{16}O$ with lattice oxygen(^{16}O) must be extremely low, thus the continu-ous exchange of the produced $^{18}O^{16}O$ in the first step with the lattice oxygen can be omitted.

The ESR and NO-TPD results clearly show that there exist V^{4+} species on the SmVO₄ catalyst. In the V-based catalysts, there are usually oxygen vacancies associated with V^{4+}. The reaction of NO with the catalyst is as follows:

$$-O-V^{4+}-[e]- + 2NO \longrightarrow -O-V^{5+}-O- + N_2O \qquad (2)$$
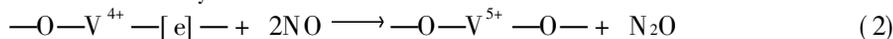
The $^{18}O_2^-$ isotope exchange is carried out as the following process:

$$- {}^{16}O-V^{4+}-[e]- + {}^{18}O_2 \longrightarrow -{}^{16}O-V^{4+}-[e]- \longrightarrow$$

$$-{}^{16}O-V^{5+}-O^{18} \longrightarrow -[e]-V^{4+}-{}^{18}O- + {}^{18}O^{16}O \qquad (3)$$
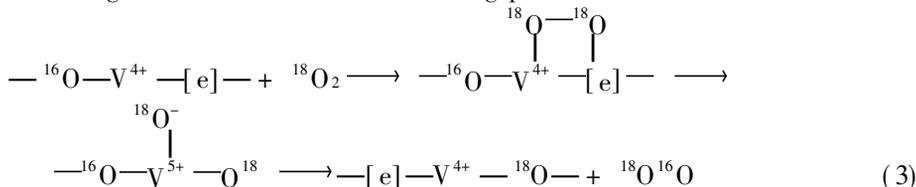
where [e] stands for oxygen vacancies in the catalyst. Based on the kinetic scheme, one can reach a conclusion that the activation of O₂ is on the site of V^{4+} associated with oxygen va-cancies. The adsorbed molecular oxygen and O^- species might be the active oxygen species in the oxidative dehydrogenation of propane.

References

[1] Bell, A. T., Boudard, M. and Ensley B. D. $et\ al.$, Catalysis Looks to the Future, National Aca-demic Press, Washington D. C., 1992: 21
[2] Hodnett, B. K., Catal. Rev. Sci. Eng. , **27**, 373(1985)
[3] Nguyen, K. T., Kung, H. H., J. Catal. , **122**, 415(1990)
[4] Patel, D., Andersen, P. J. and Kung, H. H., J. Catal. , **125**, 132(1990)
[5] Kung, M. C. and Kung, H. H., J. Catal., **128**, 287(1991)
[6] Guerrero-Ruiz, A., Rodriguez-Ramos, I. and Fierro, J. L. G. $et\ al.$, Studies in Surface Science and Catalysis, Ed. by Ruiz, P. and Delmon, B., Elsevier, Vol. 72, 1992: 203
[7] Au C. T., Zhang W. D., Wan H. L., Catal. Lett., **37**, 241(1996)
[8] Martini, G., Trifiro, F. and Vaccarl, A., J. Phys. Chem., **86**, 1 573(1982)