Preparation and characterization of rare earth orthovanadates for propane oxidative dehydrogenation

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Received 3 July 1995; accepted 21 November 1995

High purity rare earth orthovanadates (R_EVO_4), YVO_4, $LaVO_4$, $CeVO_4$, $NdVO_4$, $SmVO_4$ and $EuVO_4$, were prepared by the citrate method. XRD, FT-IR, LRS and TPR techniques were employed to characterize these orthovanadates. The catalytic performance of $SmVO_4$, $LaVO_4$ and YVO_4 in the oxidative dehydrogenation of propane can compete with that of $Mg_3V_2O_8$. The selectivity of propene over $CeVO_4$, $NdVO_4$ and $EuVO_4$ was relatively lower. The correlation between the reducibility and the selectivity of the catalysts implied that the V^{4+}/V^{3+} couple might be involved in the dehydrogenation process.

Keywords: rare earth orthovanadates; citrate method; propane oxidative dehydrogenation; redox property

1. Introduction

Alkanes are relatively abundant in natural gas and liquefied petroleum gas and the utilization of them to produce alkenes or oxygenated compounds has been receiving great attention. The selective oxidation of alkanes is one of the promising routes. Catalysts have been developed for this process. For example, VPO catalysts have been commercialized in the oxidation of butane to maleic anhydride [1]. Recently, VMgO catalysts have been reported to be active and relatively selective in the oxidative dehydrogenation (OXD) of propane to propene [2–5]. The vanadium-based catalysts are complex and the kinetic and active phase are not easy to define due to the multiple oxidation states of vanadium and the formation of multiple phases of vanadates with other metal ions. In the case of the oxidation of *n*-butane to maleic anhydride with a V–P mixed oxide, Trifirò and coworkers pointed out that the dehydrogenation of butane to butene requires the V^{4+}/V^{3+} couple, whereas the insertion of oxygen requires the V^{5+}/V^{4+} couple [6]. In another case of oxidehydrogenation of propane to propene on VMgO catalysts, Kung and colleagues attributed the active phase to magnesium orthovanadate ($Mg_3V_2O_8$) [3], but Volta and coworkers suggested that magnesium pyrovanadate (α-$Mg_2V_2O_7$) was the active phase and $Mg_3V_2O_8$ was responsible for total oxidation [4]. Recently, Gao et al. prepared three pure phases of magnesium vanadates and confirmed that in the OXD of propane, α-$Mg_2V_2O_7$ was the most selective and MgV_2O_6 was the worst [7]. They also found that the existence of α-$Mg_2V_2O_7$ or MgO with $Mg_3V_2O_8$ could promote the selectivity of $Mg_3V_2O_8$ [8].

Rare earth is not rare. The utilization of rare earth in catalysis is attractive, especially in oxidation reactions [9]. Very few examples have been reported for the use of rare earth vanadates in the OXD of light alkanes [10]. In this paper we report the preparation of rare earth orthovanadates by the citrate method. The characterization and performance of the catalysts in propane OXD to propene were also investigated.

2. Experimental

2.1. Catalyst preparation

The R_EVO_4 (R_E = Y, La, Ce, Nd, Sm, Eu) catalysts were prepared by the citrate method [11]. The starting materials were analytical grade $R_{E2}O_3$ (except for $CeVO_4$ where $Ce(NO_3)_4 \cdot 6H_2O$ was used) and NH_4VO_3 (atomic ratio = 1 : 1). The main steps are as follows:

(a) The $R_{E2}O_3$ were dissolved in 1 M HNO_3 solution, then NH_4VO_3 was added, followed by heating to dissolve.

(b) Citric acid was added in such a manner that the molar number of equivalent anions (3 ions per molecule of citric acid) equaled that of cations (total amount of R_E^{3+} and V^{5+}).

(c) The resulted solution was heated by steam bath to obtain the solid.

(d) The obtained solid was heated at 400°C for 24 h to decompose the organic precursor and then calcined at 550°C for 6 h.

2.2. Catalyst characterization

The structures of the prepared catalysts were con-

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firmed by X-ray diffraction (XRD)-Rigaku D/Max-RC equipped with Cu Kα radiation.

FT-IR spectra were recorded between 400 and 1200 cm^{-1} with a Nicolet 740 FT-IR spectrometer. The sample was mixed with KBr and pressed into a thin wafer.

Laser Raman spectroscopic (LRS) studies were performed on a Jobin Yvon U-1000 Raman spectrometer.

Temperature programmed reduction (TPR) was conducted by using a mixture of 7% H_2 and 93% N_2 (in volume). The flow rate of the carrier gas was 20 ml/min. A TCD detector was used. The amount of sample was 40 mg and the heating rate was 10°C/min.

2.3. Catalyst performance

The catalytic test was conducted in a flow system. The sample with particle size between 35 and 75 mesh was placed in a fixed bed (inner diameter 5 mm) quartz microreactor. Under standard conditions, the feed was composed of 10% O_2, 20% C_3H_8 and 70% He in volume. The total flow rate was 50 ml/min. The catalyst weight was 0.05 g. The empty reactor showed no activity. All data were collected after 4 h of reaction time.

The reaction products were analyzed by on-line gas chromatography (Shimazu GC-8A equipped with a C-R6A data processor) with helium as carrier gas. Two columns were used in parallel. A Porapak Q (60–80 mesh, Aldrich) was used to separate the hydrocarbons and CO_2. A molecular sieve 5A was used to separate O_2 and CO. The column temperature was 100°C. The conversion of propane was defined as

$$\frac{\text{mole of propane consumed}}{\text{mole of propane in feed}} \times 100\%.$$

The selectivity of product A was defined as

$$\frac{\text{mole of product A}}{\text{mole of propane consumed}} \times \frac{1}{R_C} \times 100\%,$$

where R_C is the ratio of the number of carbon atoms in propane to the number of carbon atoms in product A.

3. Results

3.1. X-ray diffraction

Fig. 1 shows the XRD profiles of the R_EVO_4. The results indicated that high purity YVO_4, $LaVO_4$, $CeVO_4$, $SmVO_4$ and $EuVO_4$ were obtained. However, a small amount of V_2O_5 was observed as impurity in $NdVO_4$. Except for $CeVO_4$ which is monoclinic, the others are tetragonal (zircon structure). The XRD spectra are in good agreement with the standard spectra of YVO_4 [12], $LaVO_4$ [13], $CeVO_4$ [14], $NdVO_4$ [15], $SmVO_4$ [16] and $EuVO_4$ [17].

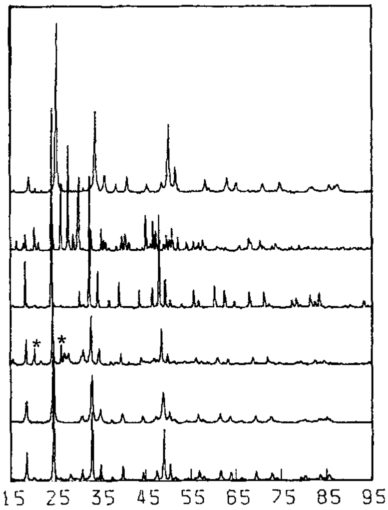

Fig. 1. XRD profile of R_EVO_4 (from top to bottom: YVO_4, $LaVO_4$, $CeVO_4$, $NdVO_4$, $SmVO_4$ and $EuVO_4$).(*) V_2O_5 impurity.

3.2. FT-IR study

Fig. 2 shows the FT-IR spectra of the prepared R_EVO_4. For all of the R_EVO_4 studied, the strongest absorbence IR peak appears around 800–850 cm^{-1}. The strongest IR peaks for $CeVO_4$, $SmVO_4$ and $EuVO_4$ are close in position (~ 802 cm^{-1}). The most intense IR peak of YVO_4 is at 812 cm^{-1} while $NdVO_4$ at 843 cm^{-1}. The

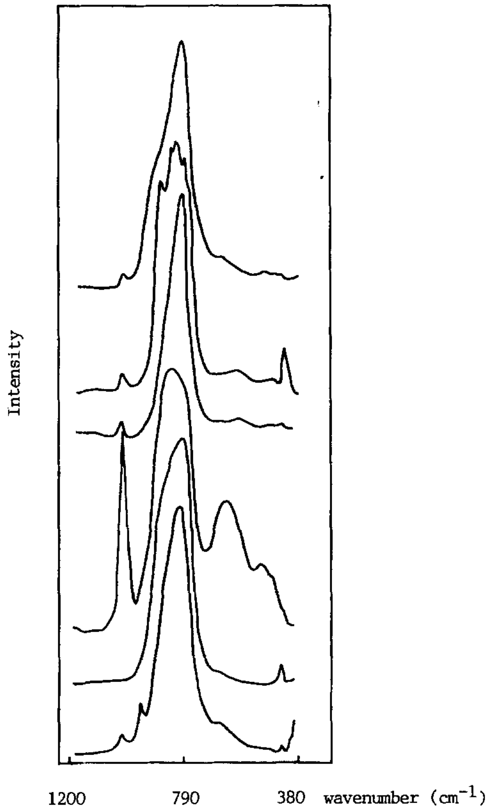

Fig. 2. FT-IR spectra of R_EVO_4 (from top to bottom: YVO_4, $LaVO_4$, $CeVO_4$, $NdVO_4$, $SmVO_4$ and $EuVO_4$).

$NdVO_4$ has another strong peak at 1016 cm^{-1}. The spectrum of $LaVO_4$ is different from the rest in that the most intense absorbence IR band around 800–890 cm^{-1} exhibits four peaks at 802, 831, 850, 886 cm^{-1}. The IR peaks and their assignments are illustrated in table 1.

3.3. Raman study

The Raman spectra of the six rare earth orthovanadates are presented in fig. 3. The Raman peaks are tabulated in table 2. The Raman peaks are different in intensity. The peak of the Raman spectrum of YVO_4 is the strongest, in contrast to that of $CeVO_4$ which is the weakest. Similar to the Raman spectrum of $Mg_3V_2O_8$ [7] which presents a very strong peak at 861 cm^{-1}, the Raman spectra of YVO_4, $LaVO_4$, $NdVO_4$, $SmVO_4$ and $EuVO_4$ also show a strong peak at 862–896 cm^{-1}. Very different from the other orthovanadates, the spectrum of YVO_4 shows four strong peaks at 280, 320, 398 and 422 cm^{-1}. The others either do not have or only have weak peaks.

3.4. Temperature programmed reduction of the rare earth orthovanadates

In order to examine the reducibility of the rare earth orthovanadates, TPR experiments were conducted. The results are shown in fig. 4. It can be seen that all of the TPR profiles have a significant peak positioned around 680–760°C. $NdVO_4$ has another strong peak at 650°C. The final products of the TPR treatment were R_EVO_3. This result can be confirmed by XRD. Fig. 5 is the XRD profile of catalysts after TPR. The XRD results also revealed that no apparent reduction of R_E ions had occurred in the TPR process.

3.5. Catalyst performance

The catalytic behavior of the six rare earth vanadates in the oxidative dehydrogenation of propane was monitored. The major products were propene, CO and CO_2; no oxygenated product was found. The carbon balance was found to be 97.5–102%. Table 3 shows the result of the catalytic OXD of propane at 500°C. This result indicated that the R_EVO_4 catalysts were quite selective to propene. The conversion of propane varied between 2.31 and 16.6%. The selectivity of propene was from 57.0 to 75.8%. $SmVO_4$ was the most active (the propane conversion reached 16.6%), while $CeVO_4$ was the most inactive (the conversion of propane was only 2.31%). The selectivity as a function of conversion is illustrated in fig. 6. It

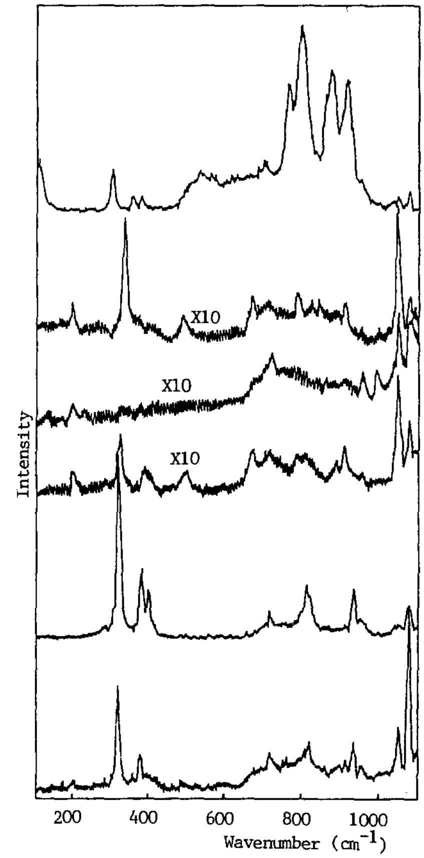

Fig. 3. Raman spectra of R_EVO_4 (from top to bottom: YVO_4, $LaVO_4$, $CeVO_4$, $NdVO_4$, $SmVO_4$ and $EuVO_4$).

Table 1
Rare earth orthovanadates FT-IR peaks and their assignments [7]

YVO_4	$LaVO_4$	$CeVO_4$	$NdVO_4$	$SmVO_4$	$EuVO_4$	Assignment
	439			448.9	446	$\nu_S(VO_4)$
			520			$\nu_S(VOV)$
	613		648		672	$\nu_{AS}(VOV)$
812	802 831 850 886	802	843	802	806	$\nu_{AS}(VO_4)$
1015	1020	1021	1016		947 1016	$\delta_S(VO_4)$ and $\delta(V{=}O)$

Table 2
Raman peaks of rare earth orthovanadates

YVO_4	$LaVO_4$	$CeVO_4$	$NdVO_4$	$SmVO_4$	$EuVO_4$
122m	122s	120s	122s	124s	122vs
150w	150vs	148vs	150vs		150s
		202m			
280vs	290w	244m	290m	266s	269m
320vs			310w		
398vs	410w		412vw	388s	384w
422s		482w	482w	482m	482w
494m	528w		528m		
662w	705w		700w		
			812w	802s	
820w				820s	824m
842w	862vs		874s	882vs	882vs
896s					
1090s	1000s	1012vw	1000m		

shows that, at similar propane conversion, the selectivity of catalysts YVO_4, $SmVO_4$ and $LaVO_4$ is higher than that of $NdVO_4$, $CeVO_4$ and $EuVO_4$. The catalytic behavior of YVO_4, $SmVO_4$ and $LaVO_4$ is comparable with that of $Mg_3V_2O_8$ [8].

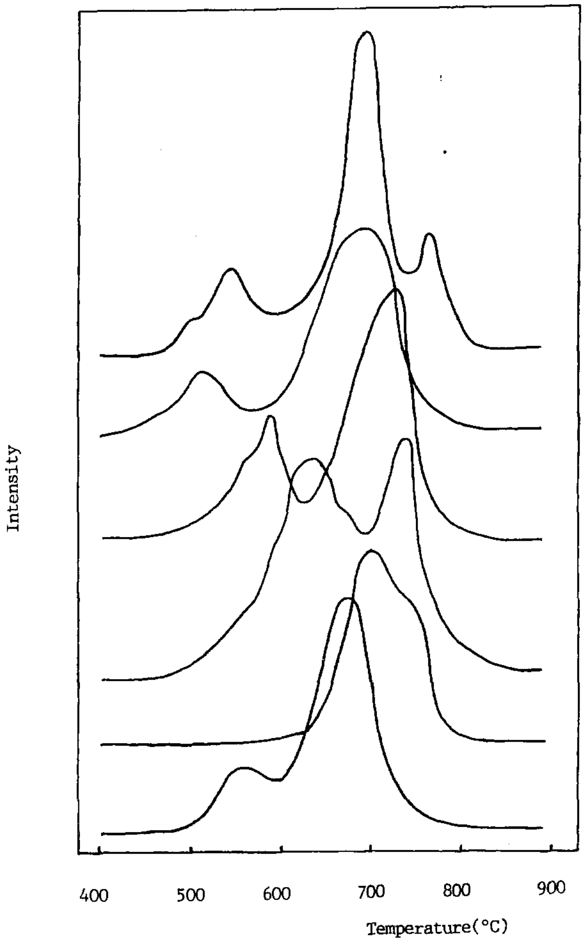

Fig. 4. TPR profile of R_EVO_4 (from top to bottom: YVO_4, $LaVO_4$, $CeVO_4$, $NdVO_4$, $SmVO_4$ and $EuVO_4$).

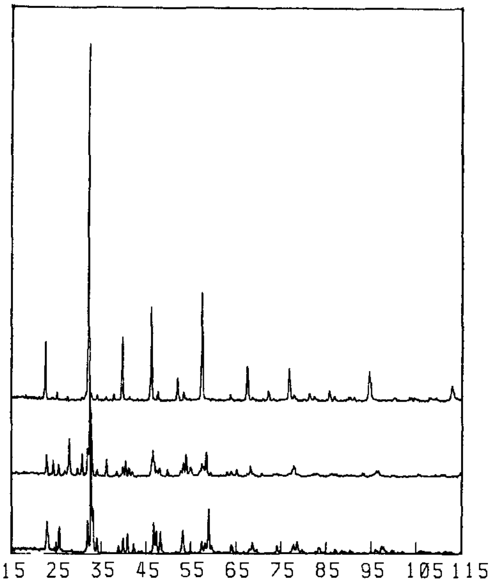

Fig. 5. XRD profile of R_EVO_4 after TPR (from top to bottom: $LaVO_4$, $NdVO_4$, $SmVO_4$).

4. Discussion

From the XRD results, one can see that pure rare earth metal orthovanadates could be prepared easily by the citrate method at relatively short time (~ 6 h) and low temperature (550°C); only a very small amount of V_2O_5 was found in $NdVO_4$ as impurity. This conclusion can be confirmed by FT-IR and LRS which are more sensitive than XRD. According to ref. [18], if both the IR peak at 1020(vs) cm^{-1} and LRS peaks at 700 and ~ 995 cm^{-1} appear, the presence of V_2O_5 can be confirmed. From tables 1 and 2, one can find that YVO_4, $LaVO_4$, $CeVO_4$, $NdVO_4$ and $EuVO_4$ have IR peaks at about 1000–1090 cm^{-1}, but only $NdVO_4$ and $LaVO_4$ have LRS peaks at about 700 and 1000 cm^{-1}. Since the Raman cross section of V_2O_5 was found to be much larger than that of vanadates [7,8], we conclude that the V_2O_5 impurity in $LaVO_4$ was very small and could not be detected by XRD. The amount of V_2O_5 impurity in $NdVO_4$ was larger than that in $LaVO_4$, but the amount

Table 3
The performance of rare earth orthovanadates in propane OXD at 500°C

Catalyst	C_3H_8 conv. (%)	Selectivity (%)			C_3H_6 yield (%)
		C_3H_6	CO_2	CO	
YVO_4	7.44	53.7	15.6	30.7	4.00
$LaVO_4$	2.86	75.8	7.80	16.4	2.17
$CeVO_4$	2.31	71.7	10.0	18.3	1.66
$NdVO_4$	5.10	47.8	32.5	19.7	2.44
$SmVO_4$	16.6	45.7	25.7	28.6	7.59
$EuVO_4$	6.80	49.4	27.4	23.2	3.36

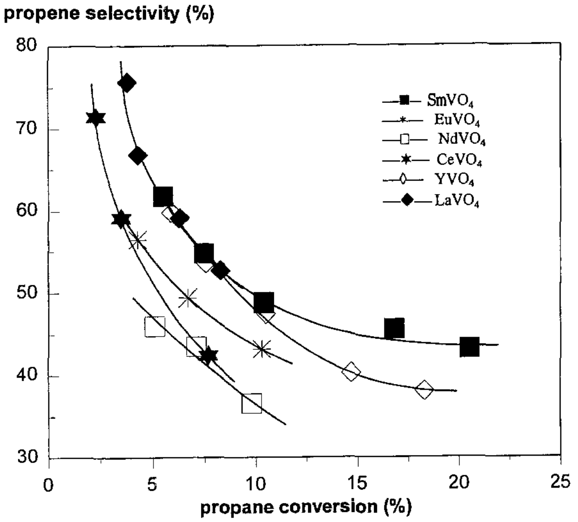

Fig. 6. The relation of propene selectivity and the conversion of propane. Conditions are: catalyst weight = 0.05 g, $T = 500°\mathrm{C}$, $C_3H_8 : O_2 : He = 20 : 10 : 70$, total flow rate varied from 20 to 130 ml/min.

was also very small because the LRS peaks at 700 and 1000 cm^{-1} were weak.

In the oxidation reaction, vanadium-based catalysts contain V^{5+}/V^{4+} and V^{4+}/V^{3+} redox couples. In the reaction of propane oxidehydrogenation over orthovanadates, we cannot confirm conclusively which couple is the one for the dehydrogenation, but the TPR results implied that it might be the V^{4+}/V^{3+} couple because the main peak of the TPR profile could be related to the reduction of V^{4+} to V^{3+}. Similar result has been obtained by Trifirò et al. in the oxidation of *n*-butane over VPO catalysts [6]. At the end of the reaction, we observed that the original color of the catalysts had changed from white or yellowish white (except for $CeVO_4$ which was black originally) to grey. The XRD profile of the catalyst after reaction indicated that the rare earth orthovanadates preserved their original structures, i.e. the catalysts were stable in the reaction. We do not deny that a small amount of V^{5+} could have been reduced to V^{4+} or even V^{3+}. The amount of low oxidation state vanadates could be so small that they were not detectable by XRD.

The different catalytic action of the orthovanadates can be correlated with their redox property. It has long been postulated that the catalytic activity and selectivity of an oxide in selective oxidation are related to the reduction rate of the oxide. Over the oxide which is very difficult to be reduced, the activity will be low; over the oxide which is very easy to be reduced, the activity is high but the selectivity will be low. An active and selective catalyst should have a suitable rate of reduction [19]. This principle can explain our result. We take the peaks between 680 and 760°C in the TPR profiles (fig. 4) to be the V^{4+}/V^{3+} redox couple. These peaks are compared with the selectivity of propene at a propane conversion of about 8% (achieved by varying the reactant flow rate) at 500°C (fig. 7). The correlation between the selectivity and the reducibility of the orthovanadates can be seen. The peaks of $EuVO_4$, $SmVO_4$, YVO_4 and $LaVO_4$ were lower in temperature than that of $NdVO_4$ and $CeVO_4$. The selectivity of propene over the former four catalysts was higher than that over the latter two, indicating that the easier the orthovanadates can be reduced, the higher the selectivity.

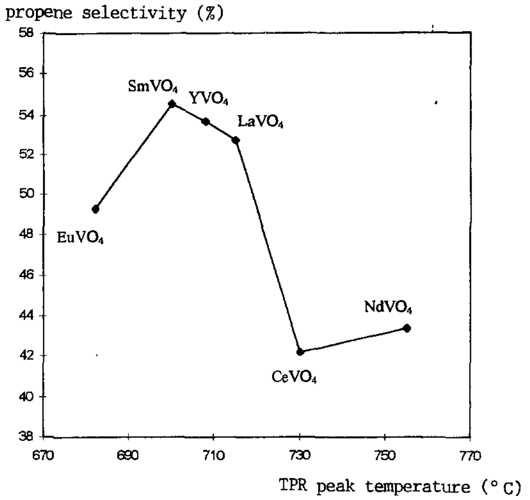

Fig. 7. The correlation of the position of the TPR peaks between 680 and 760°C) of R_EVO_4 with the propene selectivity at a propane conversion of about 8% at 500°C.

Acknowledgement

The authors gratefully acknowledge the support of this work by the Hong Kong Research Grants Council, UGC and the Chinese State Key Laboratory for Physical Chemistry of Solid Surface in Xiamen University for the facilitation of the XRD, FT-IR and LRS measurements.

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