

Oxidative dehydrogenation of propane over a series of low-temperature rare earth orthovanadate catalysts prepared by the nitrate method

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A series of high-purity rare earth orthovanadates were prepared by the nitrate method and found to be effective low-temperature catalysts for the oxydehydrogenation of propane at 320 °C, at which no reactions occurred over the catalysts reported in the literature, and, thus, may be of practical significance. The catalytic performances of LnVO_4 ($\text{Ln} = \text{Y}, \text{Ce–Yb}$) at 500 °C were much better than those of rare earth orthovanadate catalysts and also slightly exceeded that of magnesium orthovanadate $\text{Mg}_3(\text{VO}_4)_2$ reported in the literature. LnVO_4 ($\text{Ln} = \text{Y}, \text{Ce–Yb}$) materials were tetragonal active phases which could stabilize the existence of active sites for the oxydehydrogenation of propane. Some catalysts with a certain amount of LnVO_3 reduced from LnVO_4 ($\text{Ln} = \text{Ho–Yb}$) under reaction atmosphere exhibited better redox properties and catalytic performances possibly due to the existence of biphasic catalytic synergy. LaVO_4 was a monoclinic unstable active phase, although its bulk structure did not change after reaction. The remarkable deactivation of the LaVO_4 catalyst was probably due to that LaVO_4 could not stabilize the existence of surface active sites.

Keywords: low-temperature catalysts, rare earth orthovanadate catalysts, oxidative dehydrogenation of propane, nitrate method

1. Introduction

The oxidative dehydrogenation of propane (ODP) to propene is one of the potentially important catalytic processes for the effective utilization of light alkanes. Some kinds of catalysts were developed for this reaction at about 500 °C or more [1–8]. The VMgO catalysts which have better catalytic performances for the reaction have given rise to much interest. Kung et al. [1–3] proposed that Mg orthovanadate was the active phase, and Mg pyrovanadate was as selective for the OD of propane as Mg orthovanadate but nonselective for the OD of butane. Volta et al. [4,5] suggested that Mg pyrovanadate was the active phase, and Mg orthovanadate was responsible for total oxidation. The presence of V^{4+} ions which were associated with the formation of oxygen vacancies and of the corner-sharing VO_4 tetrahedra for the simultaneous formation of water were responsible for the high propene selectivity over Mg pyrovanadate, while in Mg orthovanadate, the nonexistence of V^{4+} ions and the occupation of vanadium in isolated tetrahedral sites were unfavorable for selective oxidation. Further study by Kung et al. [2] showed that the residual potassium degraded the propene selectivity over Mg orthovanadate prepared from KOH, as applied in the literature [4,5].

To study the active phase of the VMgO catalysts and the possible biphasic catalytic synergy between Mg orthovanadate and pyrovanadate, three pure Mg vanadates were prepared by the citrate method and citrate precursors

[6–10]. With these methods, the formations of desired Mg vanadates can be easily achieved by controlling the Mg/V mole ratio in the solution and by calcining very homogeneous citrate precursors at the lower calcination temperature of 550 °C for 6 h, with no contamination from other residual elements. Under the same propane conversion, the propene selectivities followed the order $\alpha\text{-Mg}_2\text{V}_2\text{O}_7 > \text{Mg}_3\text{V}_2\text{O}_8 > \beta\text{-MgV}_2\text{O}_6$, indicating that $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ was the active phase with high propene selectivity [6–8]. Under the same reaction conditions, $\text{Mg}_3\text{V}_2\text{O}_8$ was more active but less selective than $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$, while $\beta\text{-MgV}_2\text{O}_6$ demonstrated the worst catalytic activity. These results suggested that $\text{Mg}_3\text{V}_2\text{O}_8$ was probably beneficial to the activation of propane and $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ to the selective formation of propene [7,8]. Based on the fact that the selectivity of Mg orthovanadate could be promoted by the coexistence of Mg pyrovanadate, Delmon et al. [6] and Fang et al. [7,8] suggested that biphasic catalytic synergy probably existed between Mg orthovanadate and pyrovanadate phases.

In order to prepare catalysts for the ODP with better catalytic performances than magnesium vanadates, few examples have been reported by replacing magnesium with rare earth, and their catalytic performances of ODP were lower than magnesium vanadates [11–15], although some rare earth orthovanadates have been shown to be almost as selective as the Mg vanadates for the oxidation of butane [16]. In this paper, the preparation of rare earth orthovanadate catalysts by the nitrate method is reported, together with characterization and good catalytic performance of catalysts for the ODP to propene at low temperature.

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2. Experimental

2.1. Catalyst preparation

The rare earth orthovanadate catalysts were prepared by the nitrate method (-N). The rare earth oxide (AR) was dissolved in HNO_3 (AR) solution, then added into a transparent aqueous solution of NH_4VO_3 (AR) at 80°C . The resulting precipitate was evaporated to dryness while being stirred, and then dried at 120°C for 1 h. The resulting solid was ground into a fine powder and calcined in air at 600°C for 6 h.

2.2. Catalyst characterization

XRD was performed on a Rigaku Rotaflex D/Max-C using $\text{Cu K}\alpha$ radiation with $\lambda = 1.5406 \text{ \AA}$. The target/filter

(monochro) was graphite. The voltage was 40 kV, and the current was 30 mA.

FT-IR spectra were recorded on a PE Spectrum 2000 FTIR spectroscope at a resolution of 4 cm^{-1} . The detector was MCT-B. The sample was diluted with KBr (5/100 by weight) and pressed into a thin wafer.

2.3. Catalyst evaluation

The catalyst evaluation was performed in a fixed-bed quartz microreactor in a flow system. Normally, the flow rate of feed was 60 ml/min with the ratio of $\text{C}_3\text{H}_8:\text{O}_2$ being 2:1, the weight of catalyst was 0.30 g with particle fractions between 60 and 100 mesh, and the reaction temperature was 320 and 500°C , respectively. The propene selectivity versus propane conversion was studied at 500°C by changing the $\text{C}_3\text{H}_8:\text{O}_2$ mole ratios from 4:1 to 1:1.

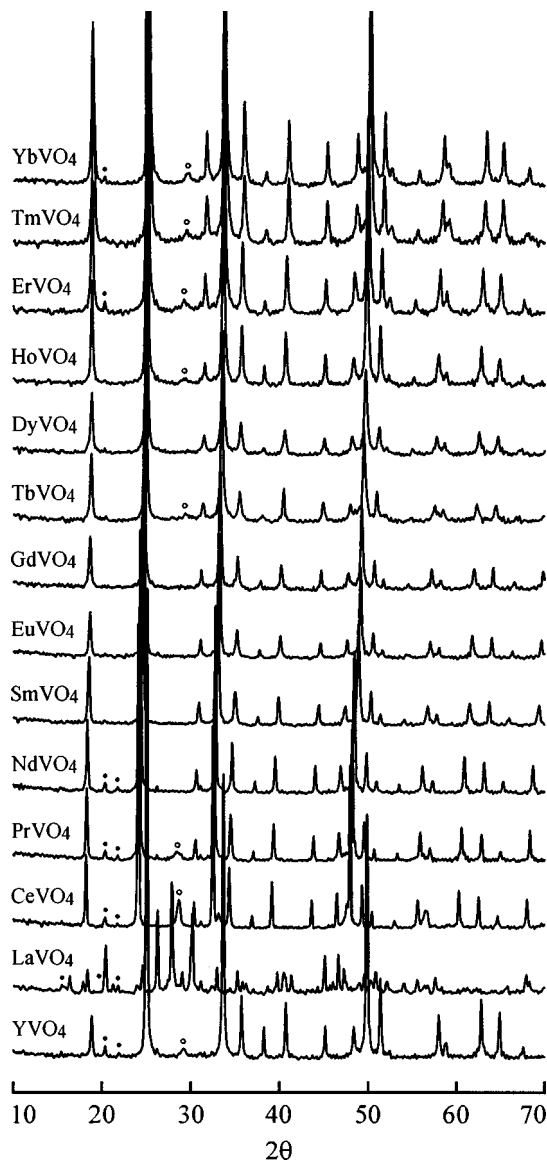


Figure 1. XRD diagrams of fresh $\text{LnVO}_4\text{-N}$ catalysts: (●) V_2O_5 , (○) Ln_xO_y .

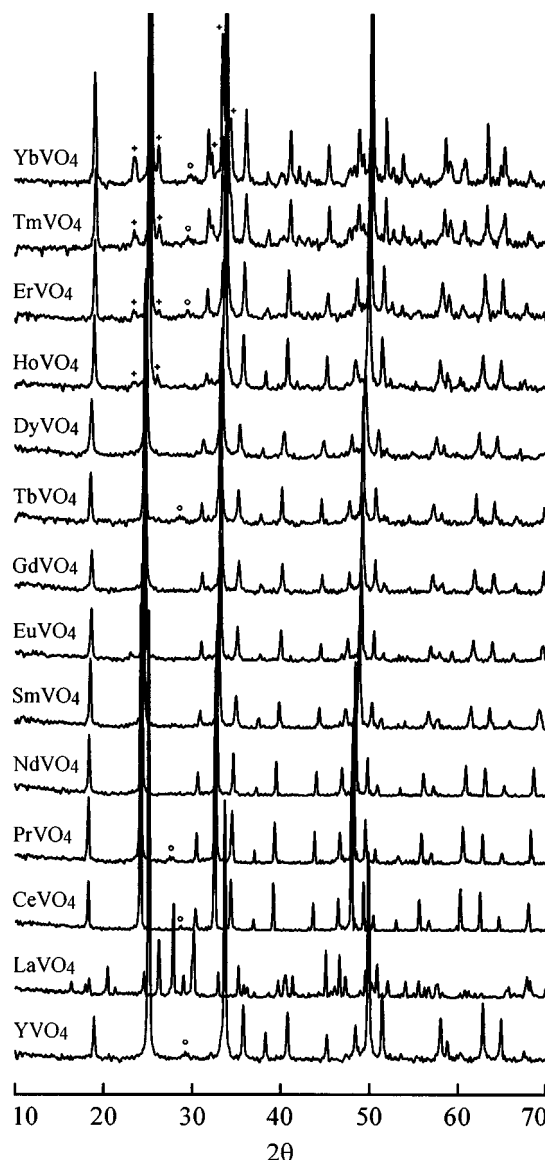


Figure 2. XRD diagrams of used $\text{LnVO}_4\text{-N}$ catalysts: (○) Ln_xO_y , (+) LnVO_3 .

The reaction products were analyzed with an on-line 102-GD gas chromatograph with a squalane/active alumina column for C_3H_8 , C_3H_6 , C_2H_4 , and C_2H_6 analyses, and a 601 carbon molecular sieve column for O_2 , CO , CO_2 and CH_4 analyses.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD

$LaVO_4$ was monoclinic with trace V_2O_5 impurity. The other rare earth orthovanadates $LnVO_4$ ($Ln = Y, Ce-Yb$) were tetragonal with trace V_2O_5 impurities (for $Ln = Y, Ce, Pr, Nd, Er, Yb$) and trace corresponding rare earth oxide impurities (for $Ln = Y, Ce, Pr, Tb, Ho, Er, Tm, Yb$), as shown in figure 1. This indicated that high-purity rare earth orthovanadates could be prepared by the nitrate method. After reaction the trace V_2O_5 impurities vanished and the crystal structures of most catalysts did not change except that orthorhombic $LnVO_3$ phases reduced from $LnVO_4$ phases appeared in some $LnVO_4$ ($Ln = Ho, Er, Tm, Yb$) catalysts and accounted for ca. 9, 17, 23 and 28%, respectively, increasing with the atomic number of the rare earth ion, as shown in figure 2.

3.1.2. FTIR

Six well resolved peaks at 782, 802, 820, 835, 850 and 881 cm^{-1} appeared in the strongest VO_4 absorbance

band of $LaVO_4$ with low monoclinic symmetry (figure 3). $LaVO_4$ contained a small V_2O_5 impurity feature at 1023 cm^{-1} . The strongest and broad unresolved VO_4 absorbance bands of the other rare earth orthovanadates with high tetragonal symmetry appeared around 798–831 cm^{-1} , and on the whole, their peak wavenumber increased with the atomic number of the rare earth metal. Some $LnVO_4$ ($Ln = Y, Ce, Pr, Nd, Tb, Er, Yb$) materials contained trace V_2O_5 impurities at 1020–1027 cm^{-1} .

3.2. Catalytic evaluation

3.2.1. Catalytic performance

Table 1 lists the performances of oxydehydrogenation of propane over rare earth orthovanadates at 500 °C. Oxidative dehydrogenation and combustion were the major reactions. Small amounts of cracking products were also produced. No oxygenates were found. V_2O_5 was of worse catalytic performance. Although the propane conversion was 17.3%, the propene selectivity and yield were only 32.2 and 5.6%, respectively. The catalytic performance of V_2O_5 was improved remarkably by combining V_2O_5 with rare earth oxides to form rare earth orthovanadates.

The catalytic performance of $LaVO_4$ decreased remarkably within 40 min reaction with propene yield from 9.6 to 0.9% (table 2). The other $LnVO_4$ ($Ln = Y, Ce-Yb$) catalysts were quite active, selective and stable for the oxydehydrogenation of propane during 4 h reaction (table 3). Propane conversions of 19.1–23.9% with propene selectivities of 46.5–51.1% and propene yields of 9.1–12.0%

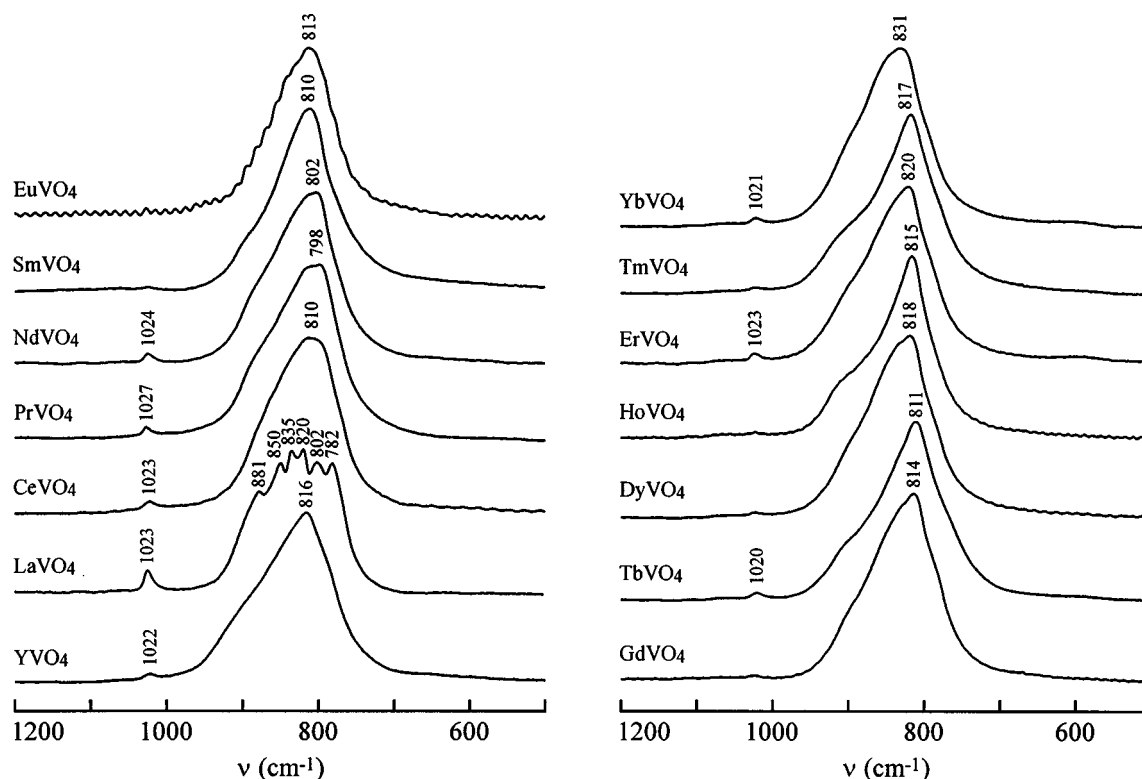


Figure 3. FTIR spectra of fresh $LnVO_4$ -N catalysts.

Table 1
Catalytic performances of rare earth orthovanadates for oxydehydrogenation of propane.^a

Catalyst	C ₃ H ₈ conversion (%)	Selectivity (%)					C ₃ H ₆ yield (%)
		C ₃ H ₆	Crack ^b	CO	CO ₂	CO _x ^c	
EQR ^d	0.4	85.0	3.2	4.0	7.8	11.8	0.3
V ₂ O ₅	17.3	32.2	1.2	38.0	28.6	66.6	5.6
YVO ₄	23.0	49.5	11.3	25.8	13.4	39.2	11.4
LaVO ₄	1.3	71.6	2.0	13.8	12.6	26.4	0.9
CeVO ₄	19.2	48.1	6.3	26.3	19.3	45.6	9.2
PrVO ₄	20.0	46.5	7.5	26.1	19.9	46.0	9.3
NdVO ₄	19.1	47.7	6.2	27.3	18.8	46.1	9.1
SmVO ₄	22.1	52.1	8.9	26.3	12.7	39.0	11.5
EuVO ₄	20.6	49.2	7.6	28.7	14.5	43.2	10.1
GdVO ₄	20.1	51.1	7.1	27.8	14.0	41.8	10.3
TbVO ₄	23.9	47.6	14.5	23.2	14.7	37.9	11.4
DyVO ₄	21.7	50.4	8.7	24.0	16.9	40.9	10.9
HoVO ₄	21.6	50.1	8.4	26.4	15.1	41.5	10.8
ErVO ₄	22.3	48.7	10.8	26.7	13.8	40.5	10.9
TmVO ₄	23.2	49.2	12.1	25.2	13.5	38.7	11.4
YbVO ₄	23.7	50.5	12.3	24.3	12.9	37.2	12.0

^a 500 °C; SV = 12000 ml g⁻¹ h⁻¹; C₃H₈:O₂ = 2:1.

^b Crack = CH₄ + C₂H₄ + C₂H₆.

^c CO_x = CO + CO₂.

^d EQR: empty quartz reactor.

Table 2
Catalytic performance of LaVO₄ catalyst for oxydehydrogenation of propane.^a

Time on stream (min)	C ₃ H ₈ conversion (%)	Selectivity (%)					C ₃ H ₆ yield (%)
		C ₃ H ₆	Crack ^b	CO	CO ₂	CO _x ^c	
20	23.3	41.4	17.4	23.1	18.1	41.2	9.6
40	1.30	72.5	1.6	13.5	12.4	25.9	0.94
60	1.29	72.1	1.7	13.7	12.5	26.2	0.93
120	1.27	71.8	1.9	13.7	12.6	26.3	0.91
240	1.26	71.6	2.0	13.8	12.6	26.4	0.90

^a 500 °C; SV = 12000 ml g⁻¹ h⁻¹; C₃H₈:O₂ = 2:1.

^b Crack = CH₄ + C₂H₄ + C₂H₆.

^c CO_x = CO + CO₂.

Table 3
Catalytic performance of SmVO₄ catalyst for oxydehydrogenation of propane.^a

Time on stream (min)	C ₃ H ₈ conversion (%)	Selectivity (%)					C ₃ H ₆ yield (%)
		C ₃ H ₆	Crack ^b	CO	CO ₂	CO _x ^c	
20	22.3	50.7	9.2	26.6	13.5	40.1	11.3
40	22.3	51.4	9.0	26.5	13.1	39.6	11.5
60	22.1	51.6	9.0	26.4	13.0	39.4	11.4
120	22.2	51.9	8.9	26.4	12.8	39.2	11.5
240	22.1	52.1	8.9	26.3	12.7	39.0	11.5

^a 500 °C; SV = 12000 ml g⁻¹ h⁻¹; C₃H₈:O₂ = 2:1.

^b Crack = CH₄ + C₂H₄ + C₂H₆.

^c CO_x = CO + CO₂.

were achieved. These results were much better than those over rare earth orthovanadate catalysts reported in the literature [11–15]. Among the catalysts in table 1, the propene yields over YVO₄, SmVO₄, TbVO₄, TmVO₄ and YbVO₄ slightly exceeded the propene yield of 11.2% over magnesium orthovanadate Mg₃(VO₄)₂ at 500 °C with propane conversion and propene selectivity 24.0 and 46.6%, respectively [6].

Figure 4 shows the plots of propene selectivity versus propane conversion for YVO₄, SmVO₄ and YbVO₄ catalysts at 500 °C. The propene selectivity decreased with increasing propane conversion over these catalysts. At the given propane conversion, the propene selectivities for these catalysts were higher than those over rare earth orthovanadates and magnesium orthovanadate catalysts reported in the literature [1–15].

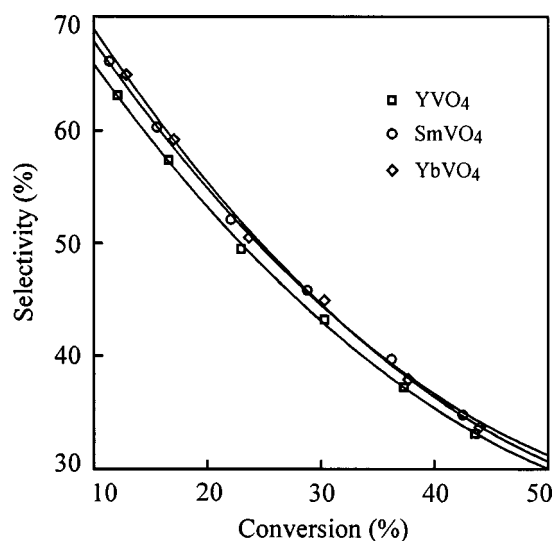


Figure 4. Propene selectivity as a function of propane conversion.

3.2.2. Low-temperature catalytic performance

Table 4 lists the catalytic performances of rare earth orthovanadates for oxidative dehydrogenation of propane at 320 °C. The results indicated that rare earth orthovanadate catalysts could catalyze oxydehydrogenation of propane effectively at 320 °C, considerably lower than the temperature of 480 °C for VMgO catalysts [1–8]. At 320 °C, no reactions occurred over the catalysts for the OD of propane reported in the literature. Therefore, the rare earth orthovanadate catalysts prepared in this work were low-temperature catalysts, and may be of practical significance. Moreover, it may be possible to extend the study of these catalysts to oxydehydrogenation of isobutane to isobutene and selective oxidation of propane to acrolein at lower temperature to avoid cracking and the total oxidation of acrolein over LnVO₄-based catalysts.

Since the oxygens in the feeds were completely consumed in the reactions over the active rare earth orthovanadate catalysts at both 320 and 500 °C, the propane conversions increased unremarkably from 320 to 500 °C due to the limitation of oxygen. Without oxygen, propane does not react obviously over the catalysts, resulting in the relatively low propane conversion at 500 °C.

4. Conclusions

- (1) A series of high-purity rare earth orthovanadates could be prepared by the nitrate method, and were shown to be low-temperature catalysts. These catalysts could catalyze the oxydehydrogenation of propane effectively at 320 °C, at which no reactions occurred over the catalysts reported in the literature, and they may be of practical significance.
- (2) The catalytic performances of LnVO₄ (Ln = Y, Ce–Yb) at 500 °C were much better than those of rare earth orthovanadate catalysts and slightly exceeded that of magnesium orthovanadate Mg₃(VO₄)₂ reported in the literature.
- (3) LnVO₄ (Ln = Y, Ce–Yb) materials had tetragonal active phases which could stabilize the existence of active sites for oxydehydrogenation of propane. Some catalysts with a certain amount of LnVO₃ reduced from LnVO₄ (Ln = Ho–Yb) under reaction atmosphere presented better redox properties and catalytic performances, probably due to the existence of biphasic catalytic synergy. LaVO₄ was a monoclinic unstable active phase, although its crystal structure did not change after reaction. The remarkable deactivation of the LaVO₄ catalyst was probably due to that LaVO₄ could not stabilize surface active sites.

Table 4
Low-temperature catalytic performances of rare earth orthovanadates.^a

Catalyst	C ₃ H ₈ conversion (%)	Selectivity (%)					C ₃ H ₆ yield (%)
		C ₃ H ₆	Crack ^b	CO	CO ₂	CO _x ^c	
YVO ₄	21.7	46.5	10.2	27.9	15.4	43.3	10.1
LaVO ₄	0.9	68.2	1.8	15.8	14.2	30.0	0.6
CeVO ₄	18.1	45.0	5.8	29.9	19.3	49.2	8.1
PrVO ₄	19.1	43.7	6.7	29.8	19.8	49.6	8.3
NdVO ₄	18.0	44.7	5.5	29.9	19.9	49.8	8.0
SmVO ₄	21.3	47.8	8.1	28.4	15.7	44.1	10.2
EuVO ₄	20.0	45.0	7.0	29.5	18.5	48.0	9.0
GdVO ₄	19.4	46.8	6.2	29.3	17.7	47.0	9.1
TbVO ₄	23.0	43.4	13.4	26.5	16.7	43.2	10.0
DyVO ₄	20.9	46.9	8.0	27.7	17.4	45.1	9.8
HoVO ₄	20.7	46.7	7.5	28.2	17.6	45.8	9.7
ErVO ₄	21.6	45.9	10.0	28.3	15.8	44.1	9.9
TmVO ₄	21.9	46.2	11.2	27.1	15.5	42.6	10.1
YbVO ₄	22.6	47.6	11.3	26.2	14.9	41.1	10.8

^a 320 °C; SV = 12000 ml g⁻¹ h⁻¹; C₃H₈:O₂ = 2:1.

^b Crack = CH₄ + C₂H₄ + C₂H₆.

^c CO_x = CO + CO₂.

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