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# Rare earth (Y, La, Ce)-promoted V-HMS mesoporous catalysts for oxidative dehydrogenation of propane

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## Abstract

The effect of rare earth (Y, La, Ce) oxides on hexagonal mesoporous silicas (HMS) silica supported vanadia catalysts for the oxidative dehydrogenation of propane was investigated. The doping of Y, La oxides into the V-HMS catalyst affords a significant promotion in the selectivity to propylene while the Ce oxide exhibits a reverse effect for the oxidative dehydrogenation process. The characterization results show that the doping of rare earth oxides results in a significant modification of the redox and acid properties of the V-HMS catalysts. In addition, the formation of a new active phase of rare earth orthovanadates over the modified V-HMS catalysts was also identified. The correlation between the structural changes and the selectivity of the catalysts implied that the formation of new active phase of $LaVO_4$ and $YVO_4$ might be responsible for the improved catalytic performance.

*Keywords:* Rare earth oxides; Oxidative dehydrogenation of propane; HMS silica; Redox and acid properties

## 1. Introduction

The oxidative dehydrogenation (ODH) of propane provides an attractive alternative to produce industrially important propylene. The reaction is preferable due to the low energy consumption and low reaction temperature relative to the traditional thermal dehydrogenation process. A large number of recent reports have shown that vanadia catalysts based on the supported vanadium oxide are likely to be available for ODH of propane [1–6]. However, one continuously challenging problem in this area is to suppress the undesirable deep oxidation of propane and propylene during the ODH of propane.

Enormous efforts have been dedicated to developing new catalyst systems or finding new additives to enhance the propylene yield in the oxidative dehydrogenation of propane. The incorporation of alkali or alkali earth metals into vanadium-based catalysts has been shown to be promising to improve the selectivity to propylene [7–9]. It has been reported that the vanadium–magnesium mixed oxides (VMgO) are the most selective and active catalyst systems [10]. On the other hand, several recent investigations have demonstrated that the utilization of rare earth as additives for vanadia catalysts can also be very attractive for oxidative dehydrogenation of light alkanes [11,12]. Au and coworkers [12] have systematically studied the ODH of propane over a series of pure rare earth orthovanadates prepared by the citrate method. Their results show that these rare earth materials have catalytic performance comparable with that of their magnesium counterparts. This observation implies that the rare

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earths are promising promoters for the conventional vanadium-based catalysts in the ODH of propane.

Very recently, we have reported that a simple catalytic system which consists of vanadia supported on hexagonal mesoporous silicas (HMS) exhibited a high catalytic activity for oxidative dehydrogenation of propane [6]. However, the HMS supported vanadia catalysts have only presented a moderate selectivity to propylene in ODH of propane due to the weak acidic nature of the HMS silica. In the present work, we report the investigation of the effect of rare earth addition on the catalytic performance of the HMS silica supported vanadia catalysts in ODH of propane. The promotional effect of the Y-modified catalyst in relative to the La and Ce doped catalyst are studied. For comparison reasons, the doping effect of yttrium on vanadia supported conventional supports of $Al_2O_3$, $ZrO_2$, $TiO_2$ and $SiO_2$ is also presented.

## 2. Experimental

### 2.1. Catalyst preparation

Mesoporous HMS silica has been prepared by hydrolysis of tetraethyl silicate (TEOS) in the presence of dodecylamine ($C_{12}H_{25}NH_2$), water, and ethanol as a cosolvent. The commercial supports of $Al_2O_3$ ($143.8\,m^2\,g^{-1}$), $TiO_2$ ($22.8\,m^2\,g^{-1}$), $ZrO_2$ ($40.1\,m^2\,g^{-1}$) and $SiO_2$ ($226.9\,m^2\,g^{-1}$) were used as received. The vanadium-impregnated catalysts have been prepared by impregnating the support with an aqueous solution of ammonium metavanadate, $NH_4VO_3$, at 80 °C [6]. After the material was dried in air at 110 °C overnight, the V-supported catalysts were obtained by calcination at 600 °C for 2 h. The resultant samples were impregnated with solutions of different rare earth nitrates, followed by calcination at 600 °C for 2 h to obtain the rare earth modified catalysts. Since the V-HMS catalyst with 5.6 wt.% V content has given the best catalytic performance for ODH of propane [6], the RE/V atomic ratio was varied on the 5.6V-HMS catalyst to prepare the modified catalysts with different rare earth doping levels. The resultant samples were denoted as RE-V-HMS (1/X, X is the molar ratio of V in respect to RE). For comparison reasons, the Y/V ratio was fixed at 1/2 on V-HMS, V-$SiO_2$, V-$Al_2O_3$, V-$ZrO_2$ and V-$TiO_2$ catalysts. A relative lower vanadia loading (2.8 wt.% V) was employed to make sure that active component could be well dispersed on various supports with relatively lower surface areas.

### 2.2. Catalyst characterization

The powder X-ray diffraction (XRD) characterization of the catalysts was carried out on a Germany Bruker D8 Advance X-ray diffractometer using nickel filtered Cu Kα radiation ($\lambda = 1.5418$ Å) in the $2\theta$ ranges from 10 to 80°. The textural parameters have been measured using the BET method by $N_2$ adsorption and desorption at 77 K in a Micromeritics TriStar system. Thermal-programmed desorption of ammonia ($NH_3$-TPD) was used to determine the total acidity of the catalysts. Before the adsorption of ammonia at 100 °C the samples (150 mg) were heated at 500 °C in a He flow ($35\,ml\,min^{-1}$) for 1 h. The $NH_3$-TPD was performed between 100 and 500 °C, with a heating rate of $10\,°C\,min^{-1}$. The evolved ammonia was analyzed by TCD and collected by a cold-trap containing liquid nitrogen. The collected ammonia is warmed by hot water and is brought to a TCD detector to determine the amount of ammonia. Raman spectra were obtained using a confocal microprobe Raman system (SuperLabRam, Dilor). The excitation wavelength was 632.8 nm from an internal He–Ne laser with a power of 13 mW. Spectra were recorded with a resolution of $2\,cm^{-1}$. $H_2$-temperature programmed reduction ($H_2$-TPR) was performed as follows: the catalyst samples (150 mg) were loaded in a U-tube quartz reactor and pretreated at 600 °C for 2 h in flowing air in order to ensure complete oxidation. The temperature was then ramped linearly from 100 to 700 °C at a heating rate of $5\,°C\,min^{-1}$ in a flow consisting of 5% $H_2$/Ar (v/v) with a rate of $30\,ml\,min^{-1}$. The water formed or desorbed during the TPR was removed by molecular sieve 5 A before the flow passes the thermal conductivity detector (TCD).

### 2.3. Catalytic tests

The ODH reactions were carried out in a fixed-bed quartz micro catalytic flow reactor at atmospheric pressure with 250 mg catalyst loading. To avoid undesired overheating in the catalytic bed, the catalysts were diluted with 300 mg quartz powder. The gas reactant mixture was constituted of 16.6 mol% propane in air and a total gas flow of 25 ml $\mathrm{min}^{-1}$, giving a space velocity of 6000 ml $\mathrm{h}^{-1}$ $\mathrm{g}^{-1}$. The reaction temperature is 500 °C. The feed and the product gases were analyzed on-line with a gas chromatograph (Type GC-122, Shanghai). Permanent gases ($N_2$, $O_2$, CO, $CO_2$) were separated by using a TDX-01 column connected to a TCD detector and other reaction products were analyzed by employing a Propak Q column connected to a FID detector. All data were collected after 1 h of reaction time.

## 3. Results and discussion

### 3.1. Catalyst characterization

The powder X-ray diffraction patterns for HMS show the characteristic low-angle diffraction peak attributable to the $d_{100}$ reflection, assuming a hexagonal lattice typical of HMS solids. We have previously demonstrated that the vanadium oxide species can be well dispersed with particle sizes less than 4 nm on 5.6V-HMS with vanadium content at 5.6 wt.% [6]. The Raman results show that only the spatially isolated vanadia species were detected on the 5.6V-HMS catalyst.

Upon rare earth introduction, dramatic spectral changes have been identified in the XRD patterns for the modified samples. Fig. 1 presents the XRD patterns for the 5.6V-HMS catalysts after different amounts of yttrium introduction. When yttrium was introduced into 5.6V-HMS, even at a very low Y/V ratio of 1/6, the characteristic diffraction peaks corresponding to a tetragonal $YVO_4$ crystal were detected. With increasing Y/V ratio, the peak intensity of the $YVO_4$ phase is gradually increased. It is noticeable that in all yttrium-doped samples, no crystalline phases from $Y_2O_3$ or $V_2O_5$ were detected, suggesting the presence of a strong interaction between yttrium and vanadium species on the surface of the catalyst. Similar spectral changes have been found on the samples with La-addition. For lanthanum-doped samples, very weak diffraction peaks of $LaVO_4$ phase were detected until La/V attained a value as high as 1/1 (Table 1). In contrast, the absence of $CeVO_4$ phase

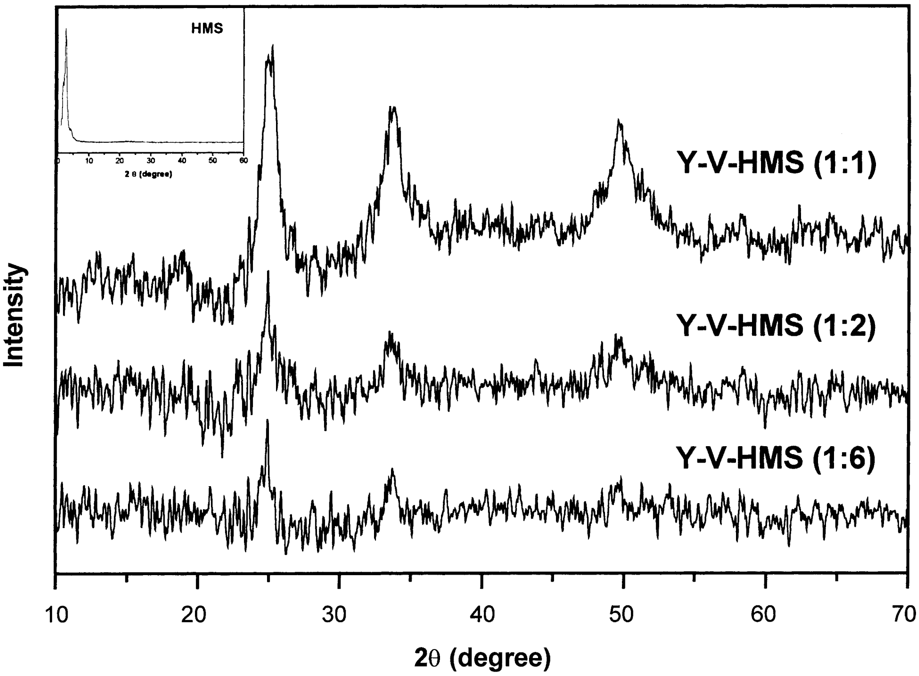

Fig. 1. XRD patterns of V-HMS catalysts doped with a rare earth (RE/V = 1/1).

Table 1
Physico-chemical properties of V-HMS catalysts doped with a rare earth

| Catalysts | SA ($m^2\,g^{-1}$) | XRD crystalline phase | Acid amount ($mmol\,g^{-1}$) | $NH_3$-desorption temperature (°C) |
|---|---|---|---|---|
| V-HMS | 647.1 | Non | 0.204 | 248 |
| Y-V-HMS(1/6) | 544.2 | $YVO_4$ | 0.219 | 235 |
| Y-V-HMS(1/2) | 510.3 | $YVO_4$ | 0.193 | 261 |
| Y-V-HMS(1/1) | 419.4 | $YVO_4$ | 0.195 | 261 |
| La-V-HMS(1/6) | 616.5 | Non | 0.163 | 248 |
| La-V-HMS(1/2) | 520.6 | Non | 0.143 | 298 |
| La-V-HMS(1/1) | 427.6 | $LaVO_4$ | 0.113 | 323 |
| Ce-V-HMS(1/6) | 560.3 | $CeO_2$ | 0.184 | 261 |
| Ce-V-HMS(1/2) | 546.5 | $CeO_2$ | 0.131 | 273 |
| Ce-V-HMS(1/1) | 474.8 | $CeO_2$ | 0.132 | 268 |

and the appearance of $CeO_2$ crystalline phase in all Ce-doped samples display a different doping behavior in terms of rare earth–vanadium interaction.

Laser Raman spectroscopy has been employed to elucidate the nature of the supported vanadium species on the rare earth-doped samples (see Fig. 2). The 5.6V-HMS catalyst without rare earth doping exhibited a single peak at 1034 $cm^{-1}$ which indicates the existence of isolated vanadium species on the surface of the V-HMS catalyst [6]. According to the literature assignments, the 1034 $cm^{-1}$ band is attributed to the stretching frequency of a terminal V=O group bonding to the HMS silica. The absence of characteristic peaks of crystalline $V_2O_5$ in Raman spectra indicates that the vanadium species were well dispersed as isolated vanadium species, which matches well with the absence of characteristic peaks of crystalline $V_2O_5$ on XRD patterns. In contrast to the V-HMS catalyst without rare earth addition, the yttrium-doped sample shows a new vibrational feature at 890 $cm^{-1}$ as shown in Fig. 2, which is characteristic of the typical Raman band from $YVO_4$ [14]. Moreover, the lack of 1034 $cm^{-1}$ on the Raman pattern of yttrium sample indicates that almost all the isolated vanadium species interact with yttrium and eventually result in the formation of $YVO_4$ species. Slightly different from the yttrium-doped sample, both lanthanum and cerium doped samples exhibit a peak at 860 $cm^{-1}$; the spectra are similar to the spectrum obtained on $Mg_3V_2O_8$ [15]. Although the 860 $cm^{-1}$ band for the Ce-V-HMS sample is much weaker than that for the La-V-HMS sample in terms of the peak intensity, one can still conclude that $LaVO_4$ and $CeVO_4$ species were formed on the doped samples.

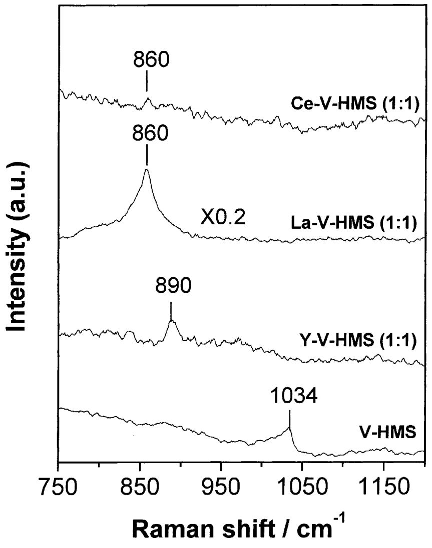

Fig. 2. Raman spectra of V-HMS catalysts doped with a rare earth (RE/V = 1/1).

The acid–base nature is one of the most important factors affecting the performance of the alkane selective oxidation catalysts. Basic catalysts have been suggested to be more selective catalysts for oxidative dehydrogenation of propane. To clarify the acid nature of the rare earth doped catalysts, $NH_3$-TPD experiments have been performed. The results of the total acidity of the catalysts have been assembled in Table 1. It is seen that the loading of lanthanum and cerium results in a dramatic decrease in surface acidity on the doped V-HMS samples. In comparison, the doping of the catalyst with yttrium can only decrease the surface acidity of the sample in a very slight way. Such results suggest that the strongly basic nature of a rare earth is responsible for the decrease in surface acidity on the rare earth modified catalysts. In addition, it is also observed that the ammonia desorption maxima shift to higher temperatures with rare earth loading, which is more evident for the lanthanum-doped samples. This indicates that the doping with rare earth oxides may eliminate the surface acid centers with a weaker or moderate acidity in the V-HMS catalysts.

To gain a more detailed insight into the effect of the rare earth addition on the reducibility of the vanadia species supported on HMS, we conducted temperature-programmed reduction experiments. In Fig. 3, the $H_2$-TPR profiles of the V-HMS catalysts with different yttrium loading in the temperature range of 100–700 °C are presented. The $H_2$-TPR profile for the V-HMS catalyst shows a reduction peak at around 558 °C and a broad shoulder spread to above 700 °C. A similar reduction peak and a shoulder were also observed on the temperature programmed reduction studies of vanadium modified MCM-41 and conventional silica supported samples [5,16–18]. Based on the literature assignments, the low temperature peak at 558 °C can be attributed to the reduction process of isolated surface $VO_x$ species from V(V) to V(III).

When yttrium was introduced into V-HMS, the intensity of reduction at 558 °C decreased dramatically and a new reduction peak was found above 700 °C as shown in Fig. 3. This observation suggests that there is a strong interaction between yttrium and the isolated surface vanadium species over the Y-promoted HMS catalyst. Based on the literature assignments, the reduction peak can be ascribed to the reduction of $YVO_4$ [12]. For the lanthanum-doped sample (see Fig. 4), there is also a new reduction shoulder around 700 °C. Moreover, it is also observed that the reduction temperature of the low temperature peak shifts to a high temperature on the lanthanum-doped sample, which is quite different from the yttrium-doped sample where almost no change in the position is found for the low temperature reduction peak. It is reasonable to attribute the shoulder around 700 °C to the reduction of $LaVO_4$ present on the doped samples, while the shift of temperature of LT peak may be associated with the presence of stronger interaction between lanthanum and isolated vanadium species. In addition to the two reduction features mentioned above, another reduction shoulder located at about

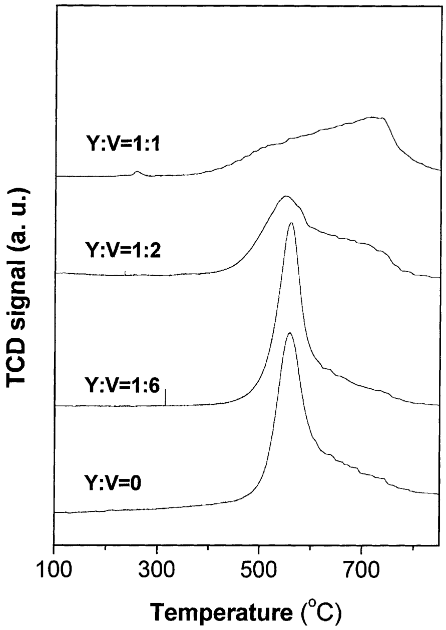

Fig. 3. TPR patterns of V-HMS catalysts doped with yttrium.

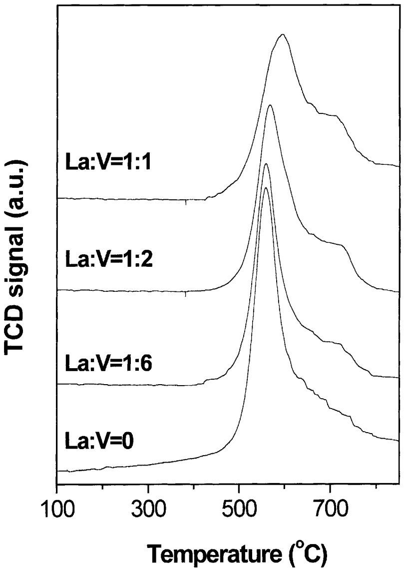

Fig. 4. TPR patterns of V-HMS catalysts doped with lanthanum.

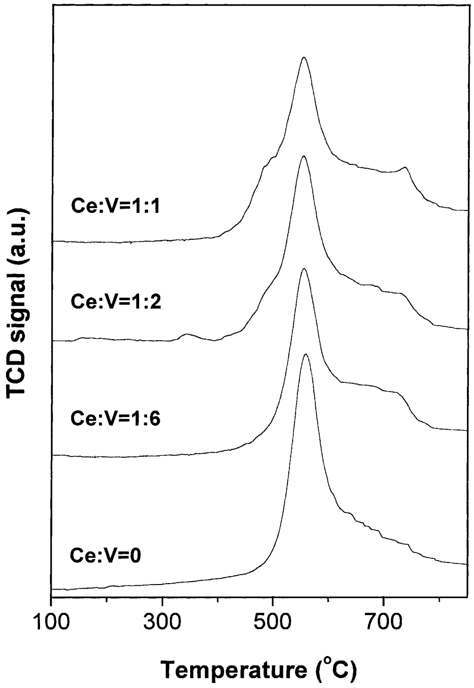

Fig. 5. TPR patterns of V-HMS catalysts doped with cerium.

480 °C was identified in the TPR spectrum (Fig. 5) of the Ce-V-HMS catalyst. This implies a much more complicated reduction behavior of the surface species on the Ce-doped sample in comparison to those of the samples doped with Y and La additives. According to previous literature results [19,20], the 480 °C shoulder can be considered to be associated with the reduction of $CeO_2$, with the high temperature shoulder around 700 °C assigned to the reduction of $CeVO_4$ [12].

The analysis of the hydrogen consumption of the catalysts may provide additional useful information regarding the nature of the active center of vanadia-based catalysts. Table 2 summarizes the hydrogen consumption results based on the present TPR measurements. The hydrogen consumption of V-HMS decreased remarkably after the doping of Y or La oxides. The average oxidative state (AOS) [9] of samples was estimated by assuming that the original vanadia species are all V(V) species. Ce-doped samples were not calculated due to the easy reduction of $CeO_2$. The results show that the AOS of Y, La doped samples is higher than those of rare earth-free samples. It appears that vanadia species on rare earth doped samples can only be reduced to a relatively higher oxidative state than V-HMS. Although V(V) species have been regarded as the dominating species in vanadia based catalysts [9], the existence of V(IV) species was also reported by several groups [11,13,16]. Particularly, Zhang et al. proposed that V(IV) sites are enriched on the surface of $V_2O_5/Y_2O_3$. Therefore, the presence of substantial amounts of V(IV) species may well explain the observation of the low hydrogenation consumption of the rare earth doped catalysts.

Table 2
Summary of the TPR results for V-HMS catalysts doped with a rare earth

| Catalysts | $T_{max}$ (°C) | $H_2$ consumption ($mmol\,g^{-1}$) | Average of oxidation state |
|---|---|---|---|
| V-HMS | 558 | 0.813 | 3.52 |
| Y-V-HMS(1/6) | 560 | 0.758 | 3.62 |
| Y-V-HMS(1/2) | 548 | 0.691 | 3.74 |
| Y-V-HMS(1/1) | 718 | 0.677 | 3.77 |
| La-V-HMS(1/6) | 548 | 0.622 | 3.87 |
| La-V-LIMS(1/2) | 567 | 0.652 | 3.81 |
| La-V-HMS(1/1) | 594 | 0.663 | 3.79 |
| Ce-V-HMS(1/6) | 554 | 0.656 | – |
| Ce-V-HMS(1/2) | 553 | 0.770 | – |
| Ce-V-HMS(1/1) | 552 | 0.844 | – |

### 3.2. *Catalytic tests*

Fig. 6 compiles the catalytic data for conversion of propane and selectivity to propylene over the catalysts with different rare earth doping level. As shown in Fig. 6, the rare earth-free 5.6V-HMS catalyst exhibited a high propane conversion but a low selectivity to propylene. With yttrium loading, the conversion of propane is dramatically decreased accompanied by a significant enhancement of the selectivity to propylene, which results in a slight increase in the yield of propylene. The selectivity to propylene increases continuously with increasing Y/V ratio, while the conversion of propane changes in a different way. It is seen that, when the Y/V ratio reaches 1/2, the yield of propylene attains a maximum value of 15% with a high selectivity to propylene of 61.2 at 24.5% of propane conversion. Further increase of the Y/V ratio to 1/1 results in an even higher selectivity to propylene of 66.7% over the yttrium-promoted catalyst. However, the yield of propylene starts to decrease due to the low propane conversion of 21.3%. Lanthanum-promoted

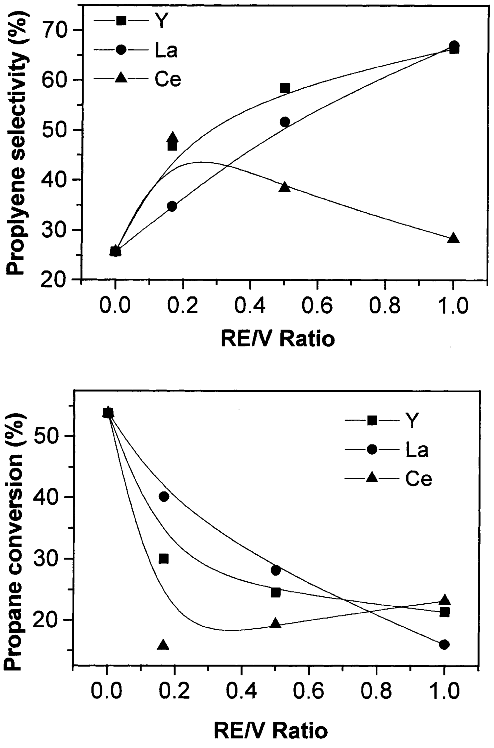

Fig. 6. Variation of the conversion of propane and the selectivity to propylene with the RE/V ratio of catalysts over V-HMS catalysts doped with a rare earth.

catalysts exhibited similar catalytic properties with yttrium catalysts in both conversion and selectivity. But the catalytic properties of cerium promoted catalysts are quite different from those of yttrium and lanthanum promoted samples. At a low doping level of Ce/V = 1/6, the selectivity of propylene is almost the same as that of the corresponding yttrium promoted catalyst. However, with increasing Ce/V, the selectivity toward propylene decreases dramatically due to a substantial deep oxidation of propane.

The increasing in the selectivity to propylene over yttrium and lanthanum promoted catalysts maybe be ascribed to the elevation of reduction temperature of vanadium species [12] and to the appearance of vanadia species which are difficult to be reduced due to the formation of rare earth orthovanadate species on the V-HMS catalysts. Meanwhile, the formation of easily reducible $CeO_2$ phase over the cerium-doped sample can be responsible for the low selectivity to propylene, because of its strong oxygenate properties.

Previous investigations have shown that there is no formation of alkali vanadates on the alkali metals modified V-$SiO_2$ [21] and V-$TiO_2$ [8] catalysts, and the tetrahedral structure of isolated surface vanadia species could be retained. The present results are quite unique in terms of formation of rare earth orthovanadates surface phase over rare earth doped V-HMS catalysts. In order to gain further insights into the role of yttrium addition on vanadia based catalysts, we have prepared various yttrium-doped vanadia based catalysts on different supports. On all samples, the absence of diffraction peaks from $V_2O_5$ suggests the highly dispersed nature of vanadium species on the supports. The diffraction peaks corresponding to $YVO_4$ were clearly identified on the yttrium-doped samples of 2.8V-$SiO_2$ and 2.8V-HMS. However, there is no evidence for $YVO_4$ formation on the 2.8V-$Al_2O_3$, 2.8V-$ZrO_2$ and 2.8V-$TiO_2$ catalysts. The catalytic performances of these catalysts were shown in Fig. 7. It is clear that yttrium exhibited a much higher beneficial

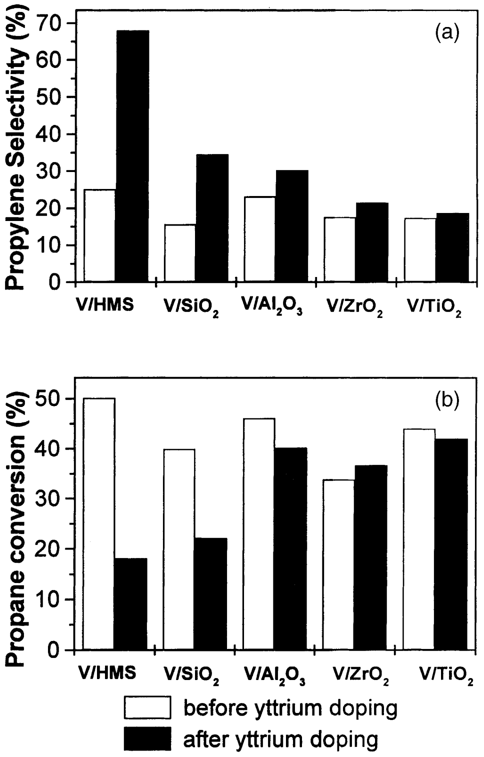

Fig. 7. Propane conversion (a) and the propylene selectivity (b) over vanadia based catalysts.

effect on 2.8V-HMS and 2.8V-$SiO_2$ catalysts than on the other samples, where the selectivity to propylene over yttrium-doped samples was almost twice that of the their undoped counterparts. In contrast, the promotional effect of yttrium on 2.8V-$Al_2O_3$, 2.8V-$ZrO_2$ and 2.8V-$TiO_2$ appears to be very small. Coupled with the XRD results, the significant increase in reaction selectivity over the yttrium-doped V-HMS catalysts can be attributed to the formation of $YVO_4$. This can become understandable if one takes into account the facts that the $Y_2O_3$ may prefer to react with $V_2O_5$ to form $YVO_4$ and that the isoelectric point (IEP) order for inorganic oxide materials follows $Y_2O_3 > Al_2O_3 > TiO_2 > ZrO_2 > SiO_2 > V_2O_5$ [22]. Therefore, the weaker interaction between the silica support and vanadia species [23] may allow the easy formation of a new active phase of $YVO_4$ in the Y-promoted catalysts, which results in the more significant promotion of the catalytic performance over the HMS silica supported vanadia catalysts.

It would be very interesting to correlate the relationship between the selectivity to propylene and the propane conversion over the Y-promoted vanadia catalysts. Fig. 8 shows the variation of the selectivity to propylene with the propane conversion over the Y-promoted vanadia catalysts with different amounts of vanadium and yttrium contained. The data of yttrium promoted V-HMS catalysts can be plotted as a curve, on which the selectivity to propylene decreases with the increasing of propane conversion. As shown in Fig. 8, Y-V-HMS catalysts exhibited much higher propylene selectivity at low propane conversion as compared to the curve of VMgO plotted by data from the literature [24]. However, similar propylene selectivity was observed at high propane conversion for both catalyst systems. It is particularly noticeable that the selectivity to propylene over V-$SiO_2$ and Y-V-$SiO_2$ is much lower than that over V-HMS and Y-V-HMS at the same propane conversion; such a result cannot be explained in terms of the IEP theory. It is well known that the catalytic behavior of supported vanadium oxide catalysts is affected by the coordination number of active sites, the reducibility of active sites and the distance between active sites [22]. HMS-supported catalysts possess much higher surface areas than those of the commercial amorphous silica-supported catalysts. As a result, much longer distances between the isolated active sites can be

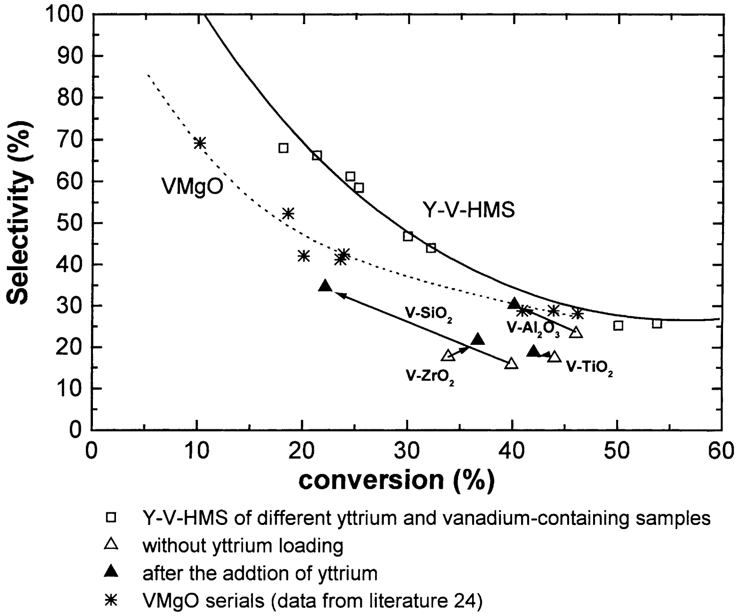

Fig. 8. Propylene selectivity as a function of propane conversion at 500 °C in the presence of rare earth promoted vanadia catalysts supported on various oxides.

obtained over the HMS supported samples, which may inhibit the excess oxidation of propane and propylene. Similar interpretations have been achieved over MCM-41- and MCM-48-supported vanadia catalysts [25].

## 4. Conclusions

We have demonstrated that the addition of La, Y oxides into the V-HMS catalyst allows a significant promotion in the selectivity to propylene, while the Ce oxide shows a reverse effect in the oxidative dehydrogenation of propane. The introduction of yttrium and lanthanum oxides results in a significant modification of the structural properties as well as of the redox and acid properties of the V-HMS catalysts. The formation of new active surface phases of Y- and La-orthovanadates over the modified V-HMS catalysts was considered to be responsible for the improved catalytic performance of the rare earth doped catalysts. Our results clearly show that the rare earth oxides can be promising promoters for the vanadia catalyst system in the oxidative dehydrogenation of propane to propylene.

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