Selective oxidation of propane to acrolein over Ce-doped Ag–Mo–P–O catalysts: influence of Ce promoter

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The selective oxidation of propane to acrolein was performed on Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts. The maximal acrolein yield of 4.4% with 28.7% acrolein selectivity was obtained on $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst. The apparent activation energy of $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts decreased with the addition of Ce. The addition of Ce facilitated the C–H activation of propane and enhanced conversion of intermediate propene to acrolein. The reducibility and the concentration of Mo^{5+} improved as the Ce content increased and was closely related to acrolein selectivity and propane conversion. The role of Ce in these catalysts was proposed: there was formation of the redox cycle "$Ce^{3+} + Mo^{6+} \Leftrightarrow Ce^{4+} + Mo^{5+}$" in Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts, leading to the modification of properties and catalytic performance of these catalysts.

KEY WORDS: propane; selective oxidation; acrolein; Ce promoter.

1. Introduction

The selective oxidation of propane to acrolein is always attractive because it has potential application as a source of cheap raw materials [1,2]. A great deal of research has already been done to develop catalyst systems and understand the catalytic properties [1,2].

Catalysts based on vanadium and/or molybdenum are considered to be effective [1,2]. The redox properties of these catalysts always play important roles in activity and selectivity in selective oxidation of propane, due to the fact that the selective oxidation of propane usually implies a Mars–van Krevelen mechanism [1,2]. It is well known that some promoters modify the redox properties of catalysts, which in turn affect the activity and selectivity in selective oxidation of propane. Moro-oka *et al.* [3–5] found that the addition of Ag promoter into BiMoVO catalysts significantly enhanced acrolein selectivity. The Ag promoter enhanced the diffusion of lattice oxygen and helped Bi sites to accomplish a redox cycle [3–6]. Baerns *et al.* [7] reported that $Ag_{0.01}Bi_{0.85}Mo_{0.54}V_{0.45}O_4/Ca_7Bi_5Mo_{12}O_x$ catalyst showed higher acrolein selectivity than $Ag_{0.01}Bi_{0.85}Mo_{0.54}V_{0.45}O_4/Mg_7Bi_5Mo_{12}O_x$ catalyst, due to more active lattice oxygen species in the former catalyst involved in selective oxidation of propane to acrolein. Teng and Kobayashi [8] observed that the addition of K^+ to Fe/SiO_2 catalysts appreciably increased propane conversion along with high acrolein selectivity. The authors considered that the formation of basic Fe–K sites on the silica surface enhanced the conversion of π-allyl cation and aldol intermediates to acrolein. In view of the above, it is important to understand the role of promoters for devising catalyst that work well for the selective production of acrolein. Therefore, it is necessary to further develop the direct and selective oxidation of propane to acrolein.

In the present work, we report the catalytic performance and properties of Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts for the selective oxidation of propane to acrolein. The catalytic performance and properties of these catalysts were modified with the addition of Ce. The roles of Ce promoter are discussed.

2. Experimental

2.1. Catalyst preparation

$Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ (Ag/Mo/P = 0.3/0.5/0.3, mole ratio) catalysts and Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts with different Ce/Mo mole ratios were prepared by the method of grinding $(NH_4)H_2PO_4$ (Shanghai Chemical Co., AR), MoO_3 (Shanghai Chemical Co., AR), Ag_2O (Shanghai Chemical Co., AR) and CeO_2 powder (Shanghai Yuelong Chemical Co., 99.99%) with a certain amount of deionized water. The samples were dried overnight in air at 383 K. After drying, the samples were calcinated at 623 K for 5 h and then at 823 K for 12 h.

2.2. Catalytic testing

The catalytic tests were carried out at atmospheric pressure in a continuous flow system with a fixed-bed

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quartz tubular reactor (6 mm i.d.). To minimize possible homogeneous reactions, the space of the reactor up and down the catalyst bed (0.5 g, 60–80 mesh) was filled with quartz wool. The exit gases were heated to 393 K to prevent product condensation. The feedstock and products were analyzed with two on-line gas chromatographs operating three columns: a TDX-601 column and Al_2O_3 column impregnated with squalane (102-GC, Shanghai Analysis Instruments Co., TCD) for the separation of C_3H_8, C_3H_6, C_2H_4, C_2H_6, CO and CO_2, and a GDX-103 column (103-GC, Shanghai Analysis Instruments Co., FID) for the separation of acrolein, acetone and propionaldehyde.

2.3. Characterization

The BET surface area of the catalysts was measured by an ST-03 adsorptionmeter (Beijing Analysis Instruments Co.).

The temperature-programmed reduction (TPR) experiments were carried out using a TPR–mass spectrometer (Omnistar GSD 3000) instrument (TPR-MS). In the TPR experiments, the sample (~100 mg) was exposed to a 20 ml/min 5% H_2/N_2 flow, and heated at a rate of 10 K/min.

Electron paramagnetic resonance (EPR) spectra were obtained using a Brucker 200D-SCR spectrometer at room temperature. The klystron frequency was 9.6 GHz and magnetic field modulation was 100 kHz. Each sample was *ca.* 200 mg.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG ESCLAB MK-II spectrometer with AlKα radiation (1486.6 eV, 10.1 kV). The spectra were referenced with respect to the C 1*s* line at 284.7 eV. The measurement error was ±0.2 eV.

3. Results and discussion

3.1. Selective oxidation of propane and selective oxidation of propene

Table 1 summarizes the catalytic performance of $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts, Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts with various Ce contents and blank reactor in selective oxidation of propane to acrolein. The blank reactor did not show activity in oxidation of propane, indicating that the homogeneous reaction did not make a significant contribution to the heterogeneous oxidation of propane under our experiment conditions. Propene and CO_x were the main products on $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst, and small amounts of oxygenate such as acrolein, acetone and propionaldehyde were also detected. The addition of Ce had great influence on catalytic activity and product distribution of $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts in selective oxidation of propane. As the Ce content increased, the propane conversion monotonically increased, implying that the Ce promoter enhanced the C–H activation of propane. As for the product distribution, the addition of Ce brought about a significant decrease in propene selectivity and a gradual increase in CO_x selectivity. It is interesting to note that acrolein selectivity showed a bell-shape trend with increasing Ce content, and gave the maximum acrolein selectivity of 28.7% on $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$. These results seem to demonstrate that the Ce promoter improved acrolein selectivity.

From the above results, $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalysts showed good performance for acrolein formation in selective oxidation of propane. Thus, the effect of reaction temperature on propane conversion and product distribution of $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst was investigated

Table 1
Catalytic performance of catalysts for selective oxidation of propane to acrolein

Reactant	Catalyst	Temp. (°C)	S_{BET} (m^2/g)	Conv. reactant (%)	Selectivity (%)					Yield ACR (%)
					C_3H_6	ACR	PA + AT	C_2	CO_x	
Propane[a]	Blank	773	–	–	–	–	–	–	–	–
	$Ag_{0.3}Mo_{0.5}P_{0.3}O_x$	773	10.6	10.9	67.9	5.6	4.8	2.8	18.5	0.6
	$Ce_{0.05}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	773	10.7	13.2	43.2	7.0	2.0	20.4	27.4	0.9
	$Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	723	15.7	2.6	67.2	12.4	1.0	10.0	9.3	0.3
		743		9.7	37.5	29.8	1.2	12.4	18.9	2.9
		773		15.3	25.7	28.7	2.0	17.5	26.0	4.4
		823		17.7	18.5	10.2	–	15.8	55.5	1.8
	$Ce_{0.3}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	773	16.3	18.5	26.3	20.6	8.8	1.0	42.6	3.8
	$Ce_{0.5}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	773	18.8	22.0	23.7	14.7	8.0	2.3	50.4	3.2
Propene[b]	$Ag_{0.3}Mo_{0.5}P_{0.3}O_x$	773	10.6	16.6	–	24.9	11.2	31.4	32.5	4.1
	$Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	773	15.7	34.3	–	34.8	3.6	6.2	55.2	11.9

Note: ACR, acrolein; PA + AT, propionaldehyde and acetone; C_2, C_2H_6, C_2H_4 and acetaldehyde; CO_x, CO and CO_2.

[a] Reaction conditions: 773 K, $C_3H_8/O_2/N_2 = 3/1/4$, 2400 ml/(g.cat)/h, atmospheric pressure.

[b] Reaction conditions: 773 K, $C_3H_6/O_2/N_2 = 3/1/4$, 2400 ml/(g.cat)/h, atmospheric pressure.

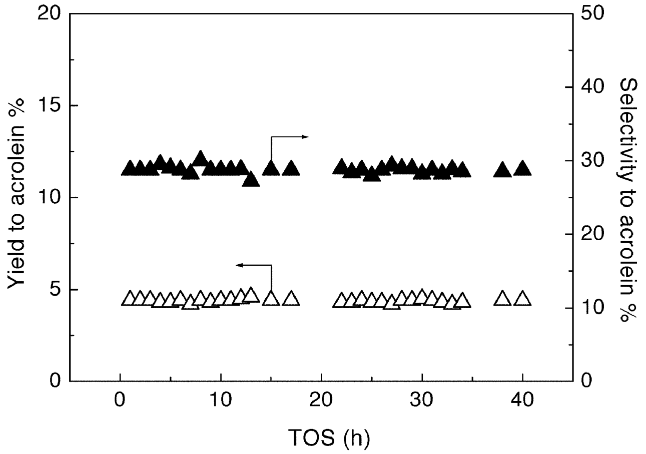

Figure 1. Stability of $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst in selective oxidation of propane to acrolein. Reaction conditions: 773 K, $C_3H_8/O_2/N_2 = 3/1/4$, 2400 ml/(g.cat)/h, atmospheric pressure.

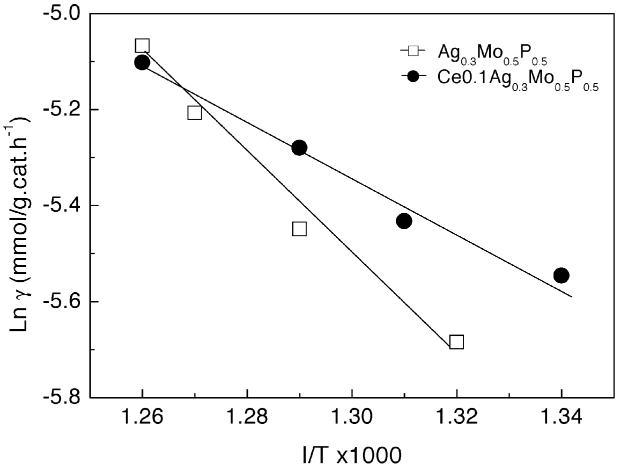

Figure 2. Arrhenius plots of propane conversion on $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst and $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst.

(table 1). With increasing reaction temperature, propane conversion gradually increased. The maximal acrolein selectivity of 29.8% was achieved at 743 K. Propene selectivity monotonically decreased. Deep oxidation products, CO_x, became favorable at the higher temperature. It is well known that primary products have non-zero intercepts while secondary and high-order products have zero intercepts. The data did not distinguish between zero or very low selectivity to acrolein and CO_x; however, it is clear that the dominant primary product was propene because propene selectivity gradually increased with the decrease of propane conversion. Consequently, acrolein formed through sequential oxidation of primary product propene over $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst.

Figure 1 shows the catalytic performance of $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst as a function of TOS (time on stream) at 773 K, $C_3H_8/O_2/N_2 = 3/1/4$, 2400 ml/(g.cat)/h, atmospheric pressure. As can be seen, the selectivity and yield to acrolein appeared to fluctuate slightly under such reaction conditions in 40 h. After about 40 h the catalyst located in the reactor was calcined at 823 K for 12 h in air. Subsequently, the catalysts was exposed to the feed ($C_3H_8/O_2/N_2 = 3/1/4$, 2400 ml/(g.cat)/h) at 773 K and the catalytic performance data were obtained after 1 h. The $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst still showed *ca.* 4.4% yield to acrolein and *ca.* 28.5% selectivity to acrolein. The results indicate that $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst exhibited good stability.

Propene oxidation was also tested over $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ and $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalysts in order to understand the role of Ce promoter on conversion of propene intermediate to acrolein. The oxidation of propene resulted in the production of acrolein, CO_x and C_2 alkane together with a small quantity of acetone and propionaldehyde. No propylene oxide or polymerization of propene were detected in the products. As shown in table 1, the addition of Ce increased propene conversion and acrolein selectivity. These results confirm that the Ce promoter enhanced the propene intermediate to acrolein.

For the sake of illuminating the role of promoter on C–H activation of propane, the apparent activation energy of propane conversion was estimated in terms of Arrhenius plots (figure 2). We hypothesized that the frequency factor of the Arrhenius equation was not much changed by the addition of Ce into $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$. The apparent activation energies were obtained from the slope of the straight lines. The apparent activation energy of $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst was about 152 kJ/mol, while the apparent activation energy of $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst was about 80 kJ/mol. It can be seen from table 1 that $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst showed a lower propane conversion than $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst, which is in agreement with $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst having a higher apparent activation energy of propane. Therefore, the addition of Ce to $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst improving the propane conversion might be due to the decrease in apparent activation energy of propane conversion. The results further indicate that the Ce promoter enhanced the C–H activation of propane.

Moro-oka *et al.* [3–5] achieved 13.1% propane conversion and 63.5% acrolein selectivity over $Ag_{0.01}Bi_{0.85}Mo_{0.54}V_{0.45}O_4$ catalyst at 500 °C. It is worth noting that their results seem to indicate that propene was formed as primary product in the gas phase whereas acrolein was formed through propene oxidation in the second step at the catalyst surface [3–5]. Teng and Kobayashi [8] reported that 10.0% propane conversion and *ca.* 22.0% acrolein selectivity were obtained on $K/Fe/SiO_2$ catalyst at 748 K. Kaddouri *et al.* [9] tested the catalytic performance of Ni–Mo–P–O catalysts in selective oxidation of propane to acrolein: 12.3% propane conversion and 12.7% acrolein selectivity were obtained on Ni–Mo–P–O catalyst at 460 °C. In these

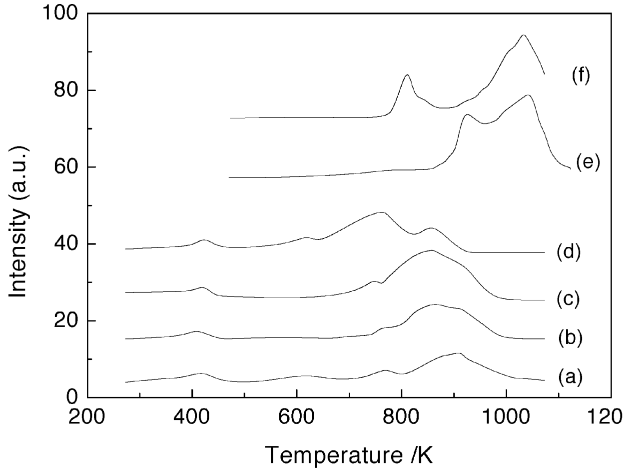

Figure 3. H_2-TPR profiles of the catalysts: (a) $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$, (b) $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$, (c) $Ce_{0.3}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$, (d) $Ce_{0.5}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$, (e) MoO_3, (f) CeO_2.

studies, $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst showed 15.3% propane conversion and 28.7% selectivity to acrolein in selective oxidation of propane, and the homogeneous gas-phase oxidation of propane was almost eliminated under the operating conditions used. Compared with the above well-known catalysts, $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst shows good catalytic performance.

3.2. *Characterization*

The BET surface area of the catalysts is shown in table 1. $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ had the lowest surface area of $10.6\,m^2/g$. The surface area of Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts was higher than the original one, and slightly increased with increasing Ce content.

The TPR profiles of Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts, $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts, MoO_3 and CeO_2 are compared in figure 3. The TPR profile of MoO_3 showed two reduction peaks at 926 and 1042 K, corresponding to the stepwise reduction of $Mo^{6+} \Rightarrow Mo^{4+}$ and $Mo^{4+} \Rightarrow Mo^0$, respectively [10,11]. CeO_2 showed two reduction peaks at *ca.* 811 and 1035 K with respect to the reduction of $Ce^{4+} \Rightarrow Ce^{3+} \Rightarrow Ce^0$ [12]. Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts and $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts exhibited low-temperature reduction peaks (<500 K) and high-temperature reduction peaks (>700 K). The low-temperature reduction peak appearing near 420 K may be due to the reduction of $Ag^+ \Rightarrow Ag^0$ [13]. The high-temperature reduction peaks could be assigned to the contribution of the molybdenum oxide reduction and the cerium oxide reduction. The high-temperature reduction peaks (>700 K) monotonically shifted to lower temperature with increasing Ce content, revealing that there was an interaction between Ce and Mo ions. The area of the TPR profile was integrated to estimate the H_2 consumption. The area of TPR profile increased with increasing Ce content (table 2). The results suggest that the Ce promoter improved the reducibility of $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts.

Table 2
Area of TPR peaks (*A*) of the catalysts

Catalyst	*A* (a.u.)
$Ag_{0.3}Mo_{0.5}P_{0.3}O_x$	1434
$Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	1549
$Ce_{0.3}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	2223
$Ce_{0.5}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	2387

EPR and XPS were used to investigate the presence and changes of Mo^{5+} and Ce^{3+} in $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ and Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts. The EPR spectra of these catalysts exhibited signals at $g_1 = 1.94$ and $g_2 = 1.89$ which were attributed to Mo^{5+} [14,15] (figure 4(A)). The EPR signal at $g_3 = 1.98$ with respect to Ce^{3+} was also found in Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts [16,17]. The formula $[I_i(\Delta H_{pp})_i^2]/[I(\Delta H_{pp})^2]_{\text{standard sample}}$ could be used to calculate the relative concentration of Mo^{5+} in these catalysts, in which I_i is the intensity of peaks and ΔH_{pp} is the line width at peak to peak maximum. The relative concentration of Mo^{5+} increased following the increase of Ce content (see figure 5).

Figure 4(B) shows the EPR spectra of $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst treated under different conditions. Compared with the fresh catalyst, the EPR spectrum of the used catalyst showed a broader and stronger peak. After the catalyst was treated in O_2 flow at 773 K for 15 min and then sealed in a glass tube, the EPR signal of Mo^{5+} and Ce^{3+} remarkably weakened. The results suggest that Mo^{5+}/Mo^{6+} and Ce^{3+}/Ce^{4+} were involved in both the activation of molecular oxygen and oxidation of propane.

The binding energy (BE) of Mo $3d_{5/2}$ on MoO_3 was 233.5 eV, which was used as a reference to identify the possible changes of Mo (table 3). The BE of Mo $3d_{5/2}$ on $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ was about 233.1 eV. It can be seen that Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts had a slightly lower BE of Mo $3d_{5/2}$ than $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst. The BE of Mo $3d_{5/2}$ on Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts decreased with increasing Ce content, suggesting that the unsaturated coordination of Mo increased on the surface. In addition, shoulder peak of Mo $3d_{5/2}$ at 234.5 eV was observed. Table 3 also gives the BE of Ce $3d$ on Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts. The peaks near 915.6 and 910.5 eV were assigned to Ce^{4+} [18,19]. The appearance of peak at 885.0 eV was due to Ce^{3+} [18,19]. With increasing Ce content, the BE of Ce slightly decreased.

From the above results, the addition of Ce promoter in the $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts improved the reducibility and increased the concentration of Mo^{5+}, which in turn determined the catalytic performance in selective oxidation of propane to acrolein. The variation of such properties of Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts could

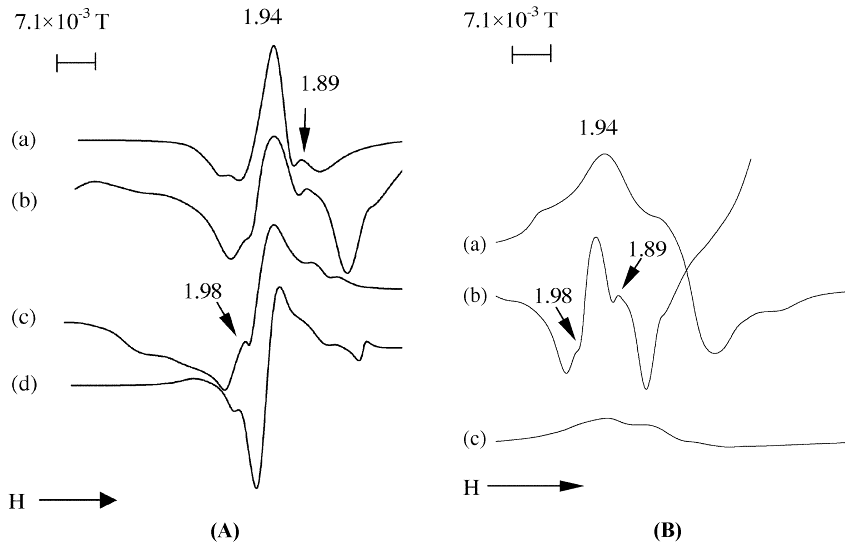

Figure 4. (A) EPR spectra of the catalysts: (a) $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$, (b) $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$, (c) $Ce_{0.3}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$, (d) $Ce_{0.5}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$. (B) EPR spectra of $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst treated under different conditions: (a) the used catalysts, (b) the fresh catalysts, (c) the catalysts treated by O_2 flow at 773 K for 15 min and then cooled at room temperature in N_2 flow.

be due to the interaction between Mo and Ce in these catalysts. Both Mo^{5+} and Ce^{3+} were detected on Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts. Considering the redox potential, Mo^{6+}/Mo^{5+} is *ca.* 0.3 eV and Ce^{4+}/Ce^{3+} is *ca.* −1.61 eV. Furthermore, both Ce and Mo are able to activate/store oxygen and transfer/release oxygen species [18,19]. Hence, the redox cycle "$Ce^{3+} + Mo^{6+} \Leftrightarrow Ce^{4+} + Mo^{5+}$" can form, improving the transfer of electron and oxygen species. As a result, the reducibility of these catalysts was enhanced by addition of Ce promoter. On the other hand, the formation of "$Ce^{3+} + Mo^{6+} \Leftrightarrow Ce^{4+} + Mo^{5+}$" redox cycle made Mo^{5+} and Ce^{3+} stable on the catalysts, so the increase of Mo^{5+} was distinctly observed with Ce content.

In order to elucidate such changes to be responsible for the catalytic performance of Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts, several means have been employed. The catalytic performance has been identified in terms of specific activity (specific activity = mol CH_4 converted/m^2/s) and specific selectivity (specific selectivity = mol acrolein or CO_x obtained/m^2/s). Figure 5 shows the variation of catalytic performance and relative concentration of Mo^{5+} as a function of Ce content in these catalysts. The relative concentration of Mo^{5+} increased with increasing Ce content. Likewise, specific activity also slightly increased with Ce content, indicating that the concentration of Mo^{5+} was closely correlated with propane conversion. It is worth noting that the acrolein specific selectivity showed a volcano-shaped curve with increasing Ce content, and displayed the maximal acrolein specific selectivity on $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst. The results imply that an appropriate concentration of Mo^{5+} enhanced the formation of acrolein in selective oxidation of propane. CO_x specific selectivity gradually increased with Ce content.

Many studies showed that lattice oxygen anions play an important role in the selective oxidation process [20–23]. The mobility of these ions was mainly demonstrated by $^{18}O_2$ and ^{2}D tracer techniques [20–23]. By this means, Ueda *et al.* [23] studied the effect of promoters such as Ca, Sr and Ba on scheelite-structure BiMoO in the selective oxidation process. They observed that these

Table 3
Binding energy of Mo 3*d* and Ce 3*d* on the catalyst surface

Catalyst	Mo 3*d* (eV)			Ce 3*d* (eV)			Atom ratio		
	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Mo^{5+} $3d_{3/2}$	Ce^{4+} $3d_{5/2}$	Ce^{4+} $3d_{3/2}$	Ce^{3+} $3d_{3/2}$	Ag/Mo	Ce/Mo	P/Mo
MoO_3	233.5	236.7	–	–	–	–	–	–	–
CeO_2	–	–	–	910.8	915.9		–	–	–
$Ag_{0.3}Mo_{0.5}P_{0.3}O_x$	233.1	236.3	234.5	–	–	–	0.36	–	0.33
$Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	232.8	236.0	234.4	910.5	915.6	885.6	0.42	0.33	0.34
$Ce_{0.3}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	232.7	235.9	234.4	910.3	915.4	885.3	0.44	0.45	0.36
$Ce_{0.5}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$	232.4	235.6	234.3	910.2	915.3	885.0	0.50	0.55	0.36

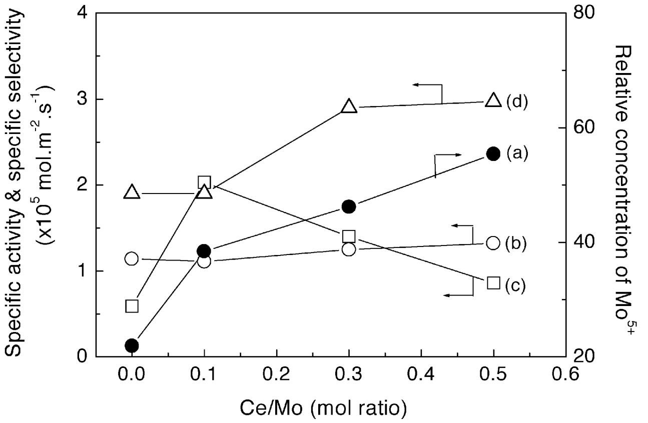

Figure 5. Variation of (a) relative concentration of Mo^{5+}, (b) specific activity, (c) acrolein specific selectivity and (d) CO_x specific selectivity as a function of Ce content in the catalysts.

promoters enhanced the mobility of lattice oxygen so that a high acrolein selectivity could be obtained. Keulks *et al.* [24] found that propene oxidation on BiMoO catalyst obeyed the Mars and Van Krevelen mechanism and was controlled by the reduction step of the catalysts at higher temperature and by the reoxidation step at low temperature. The control of the mobility of lattice oxygen can improve acrolein selectivity in selective oxidation of propane and selective oxidation of propene.

In selective oxidation of propane to acrolein on Ce-doped $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalysts, the oxygen-deficient site around unsaturated-coordination Mo^{5+} reacted with molecular oxygen to form lattice oxygen species for propane activation and the unsaturated-coordination Mo^{5+} was oxidized to Mo^{6+} (Mars–van Krevelen mechanism). Therefore, the increase of the concentration of Mo^{5+} and the enhancement of reducible properties of these catalysts can improve the activation of propane.

On the other hand, propene might be an intermediate for the formation of acrolein in selective oxidation of propane. The transformation of propene to acrolein will be mostly determined by the interaction of propene with the catalyst surface. The appropriate addition of Ce in the catalysts could increase the concentration of Mo^{5+} and improve reducibility of the catalysts, leading to an enhanced transformation of propene to acrolein by reacting with lattice oxygen species. Therefore, higher acrolein specific selectivity was obtained on $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst. However, the lattice oxygen species could also result in the deep oxidation of intermediate propene and product acrolein. Hence, the much more Mo^{5+} and the much more rapid diffusion of lattice oxygen species led to deep oxidation of propene and acrolein, decreasing acrolein selectivity and increasing CO_x selectivity.

4. Conclusion

The addition of Ce promoter into $Ag_{0.3}Mo_{0.5}P_{0.3}O_x$ catalyst modified the reducibility and the concentration of Mo^{5+}, which in turn determined the catalytic performance in selective oxidation of propane to acrolein. The maximal acrolein yield of 4.4% with 28.7% acrolein selectivity was obtained on $Ce_{0.1}Ag_{0.3}Mo_{0.5}P_{0.3}O_y$ catalyst. The addition of Ce facilitated the C–H activation of propane and enhanced conversion of intermediate propene to acrolein. The formation of the redox cycle "$Ce^{3+} + Mo^{6+} \Leftrightarrow Ce^{4+} + Mo^{5+}$" was a way of accounting for the changes of properties and catalytic performance of the catalysts.

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