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Structure and properties of BiCeVMoO mixed metal oxides catalysts for selective oxidation of propane

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Abstract

The structure and catalytic properties of BiCeVMoO catalysts with different composition for selective oxidation of propane have been investigated. It has been shown that bismuth may be substituted by a low amount of cerium while the Scheelite structure of BiVMoO remains unchanging. With the increasing of Ce (Ce/(Ce + Bi) > 0.15), new phases of $CeVO_4$ and $Ce_2(MoO_4)_3$ formed. The cerium which probably entered into the lattice of BiVMoO promotes the forming of acrolein, and the selectivity to acrolein increased to a maximum at Ce/(Ce + Bi) atomic ratio = 0.15 (45 mol% at ∼30 mol% propane conversion). Further increasing Ce content results in further oxidation of propylene and acrolein to CO_x due to the strong oxidative ability of catalysts. The proper amount of introduced cerium, which probably occupied the lattice sites of Bi^{3+} enhanced the oxidative ability of catalysts moderately by increasing the activity and the amount of surface active oxygen species.
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1. Introduction

Direct oxidation of propane to acrolein could be an interesting alternative to propylene oxidation, and it has attracted much attention for a long time world widely. Bi–Mo-based catalysts have been heavily studied for the selective oxidation (ammoxidation) of propylene to acrolein (acrylonitrile). The scheme of the reaction has been established [1–4] and the role of Bi and Mo are proposed [5–7]. It has been revealed that incorporating V into BiMoO enhanced the activity and selectivity of catalyst for direct oxidation of propane [8–11], the promotion effects are investigated and discussed [5,12]. Our previous work have shown that the V in tetrahedral $BiVO_4$ can be substituted by Mo and forming the tetrahedral Mo=O species which has moderate catalytic activity for selective oxidation of propane [13].

Cerium has a strong capability as an oxygen carrier [14], low amount of Cerium can accelerate the circulation of reduction–oxidation of catalyst [15], Sleight concluded that Ce can been incorporated into Sheelite structure of ABO_4 and occupied the A position [12]. It is inferred that catalysts containing cerium might exhibit different catalytic properties for the selective oxidation of propane. In this study, we try to incorporate Ce into BiVMoO ($Bi_{0.85}V_{0.55}Mo_{0.45}O_4$) catalyst in an effort to further improve the performance of catalysts for the partial oxidation of propane and try to elucidate the role of Ce in the reaction.

2. Experimental

2.1. Catalysts preparation

The composite oxides catalysts of BiCeVMoO were prepared by evaporating a complex of desired metal ions

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solution of citric acid and oxalic acid at 60 °C, Ce^{3+} was added into $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ according to the $(Ce + Bi)/V/Mo = 0.85/0.55/0.45$ of molar ratio and Bi^{3+} was substituted by Ce^{3+} step by step. All samples were dried overnight in air at 110 °C and then treated in dry air at 600 °C for 6 h.

2.2. Catalytic activity tests

The catalytic experiments were performed in a fixed bed continuous flow stainless steel tubular reactor (20 mm i.d.) under atmospheric pressure, 0.5 g of catalyst diluted by 2 g 20–40 mesh quartz was packed and tested over a temperature range of 480–500 °C. A gas mixture was feed at a ratio of $V(C_3H_8):V(O_2):V(N_2) = 45:56:10$ with GHSV of $1800 h^{-1}$ (no inner and outer diffusion effects were observed under this condition). Post-reaction gases were analyzed online by GC to determine the propane conversion and product distribution.

2.3. Test of propene oxidation by lattice oxygen

Molecular oxygen oxidation of propylene were conducted at 500 °C with a feed of pure propylene into a U-shape stainless steel tubular reactor (2 mm inner diameter, 30 mg catalyst), pure He (after deoxygenated) flowed at a rate of 40 ml/min and carried the propylene to the reactor via a 6-way valve, before the reaction were carried, the samples were preheated at 500 °C with He flowing for 5 h to remove the possible adsorbed surface oxygen. The pulse amount of propylene was 1.65 μmol and the products were analyzed on-line by GC.

2.4. Catalytic characterization

XRD patterns were recorded on a Shimadzu-3A diffractometer using a radiation source of nickel-filtered Cu Kα ($\lambda = 0.15418$ nm) operating at 35 kV and 15 mA.

FT-Raman spectra were recorded on a RFS-100 FT-Laser Raman spectrometer (Bruker) with an InGaAs detector cooled by liquid nitrogen, Raman excitation at 1064 nm provided by Nd-YAG laser resource was used for excitation, the laser power applied on samples was 100 mW and the wave number accuracy was $4 cm^{-1}$.

For TPR measurement, 30 mg catalysts samples were charged in a U-shape quartz tubular reactor and were heated linearly at a rate of $10 °C min^{-1}$ under a flowing H_2–Ar mixture (6.0% H_2 by volume) of $35 ml min^{-1}$. The consumption of hydrogen was detected by an on-line GC.

3. Results and discussion

The XRD patterns of catalysts with various Ce fractions are shown in Fig. 1. In the Sheelite type structure of $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ mixed oxides, Bi^{3+} is octa-
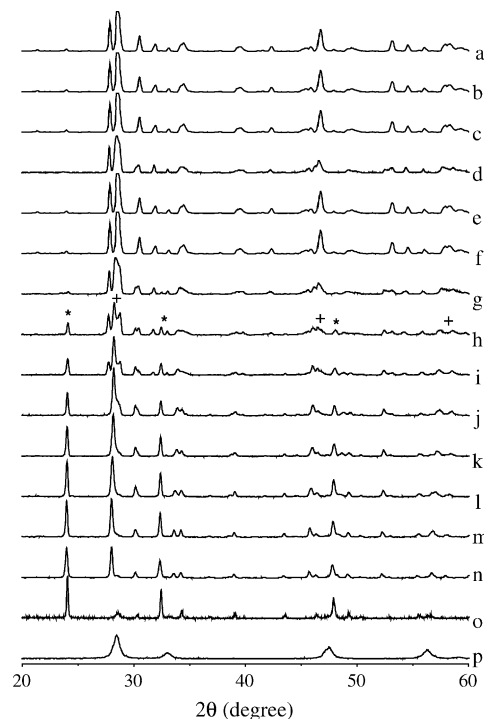

Fig. 1. XRD patterns of Bi–Ce–V–Mo–O composite oxide catalysts with different Ce/(Ce + Bi) molar ratio. (a) Ce/(Ce + Bi) = 0.00; (b) Ce/(Ce + Bi) = 0.05; (c) Ce/(Ce + Bi) = 0.10 (d) Ce/(Ce + Bi) = 0.15; (e) mechanical mixture of CeO_2 and $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ with Ce/(Ce + Bi) = 0.15; (f) mechanical mixture of $CeVO_4$ and $Bi_{0.85}V_{0.55}Mo_{0.45}$ with Ce/(Ce + Bi) = 0.15; (g) Ce/(Ce + Bi) = 0.25; (h) Ce/(Ce + Bi) = 0.35; (i) Ce/(Ce + Bi) = 0.45; (j) Ce/(Ce + Bi) = 0.55; (k) Ce/(Ce + Bi) = 0.65; (l) Ce/(Ce + Bi) = 0.75; (m) Ce/(Ce + Bi) = 0.85; (n) Ce/(Ce + Bi) = 1.00; (o) $CeVO_4$; (p) CeO_2; (*) $CeVO_4$; (+) $Ce_2(MoO_4)_3$.

hedral by oxygen [12] while V^{5+} and Mo^{6+} are tetrahedral [12,13] by four coordinated oxygen atoms. For the samples with Ce/(Ce + Bi) atomic ratio ≤0.15, XRD patterns showed no evident difference from the pattern of $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$, no obvious information associated with Ce were observed under the experiment conditions. For samples with Ce/(Ce + Bi) > 0.25, the profiles showed typical crystallites diffraction peaks of $CeVO_4$ and $Ce_2(MoO_4)_3$, and with the increasing of Ce contents, crystallites peaks intensity of $CeVO_4$ kept increasing. XRD could not detect the crystallites of CeO_2 and $CeVO_4$ in the mechanical mixture of $CeO_2 + Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ and $CeVO4 + Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ with Ce/(Ce + Bi) = 0.15 neither, so more sensitive methods were needed for studying the present state of Ce with low contents in BiCeVMoO.

The FT-Raman spectra of BiCeVMoO catalysts are presented in Fig. 2, $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ sample exhibited two Raman bands at 887 and $820 cm^{-1}$ which could be assigned to the vibration of tetrahedral Mo=O and V=O species, respectively [16,17]. The spectra of BiCeVMoO samples with Ce/(Ce + Bi) ≤ 0.15 showed no obvious difference from the spectrum of $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$, but the spectra of mechanical mixture of $CeO_2 + Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ and $CeVO_4 + Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ with Ce/(Ce + Bi) atomic
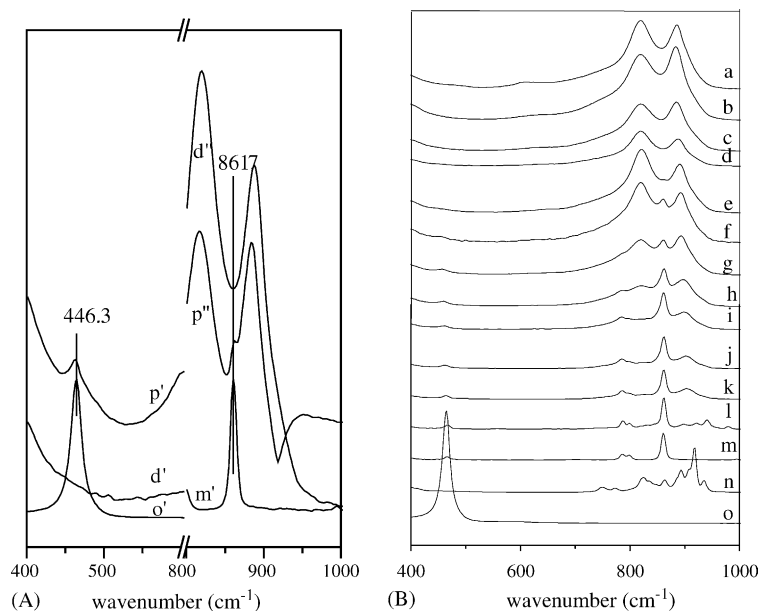
Fig. 2. FT-LRS spectra of Bi–Ce–V–Mo–O composite oxide catalysts with different composition of Ce. (a) Ce/(Ce + Bi) = 0.00; (b) Ce/(Ce + Bi) = 0.05; (c) Ce/(Ce + Bi) = 0.10; (d) Ce/(Ce + Bi) = 0.15; (e) Ce/(Ce + Bi) = 0.25; (f) Ce/(Ce + Bi) = 0.35; (g) Ce/(Ce + Bi) = 0.45; (h) Ce/(Ce + Bi) = 0.55; (i) Ce/(Ce + Bi) = 0.65; (j) Ce/(Ce + Bi) = 0.75; (k) Ce/(Ce + Bi) = 0.85; (l) Ce/(Ce + Bi) = 1.00; (m) $CeVO_4$; (n) $Ce_2 (MoO_4)_3$; (o) CeO_2; (o′) line; (o) ranged in 400–600 cm^{-1}; (m′) line; (m) ranged in 800–1000 cm^{-1}; (d′) line; (d) ranged in 400–600 cm^{-1}; (d″) line; (d) ranged in 800–1000 cm^{-1}; (p′) mechanical mixture of CeO_2 and $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ with Ce/(Ce + Bi) = 0.15 ranged in 400–600 cm^{-1}; (p″) mechanical mixture of $CeVO_4$ and $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ with Ce/(Ce + Bi) = 0.15 ranged in 800–1000 cm^{-1}.

ratio 0.15 showed Raman bands at 464.3 and 861.7 cm^{-1}, respectively which are characteristic Raman features for crystalline CeO_2 and $CeVO_4$ [18] (p′ and p″ in Fig. 2A). These results suggest that low amount of additive Ce into CeBiVMoO catalysts (with Ce/(Ce + Bi) ≤ 0.15) may be incorporated into the Sheelite structure of BiVMoO and occupied the position of crystal Bi [12]. When the composition of BiCeVMoO catalysts varied to Ce/(Ce + Bi) > 0.25, the spectra exhibited a Raman band at 861.7 cm^{-1}, which is the characteristic Raman band for $CeVO_4$ [18], and the intensity of the peak kept increasing with the increase of Ce content, indicates the crystal $CeVO_4$ formation in BiCeVMoO mixed oxides, this was consistent with the results by XRD.

The catalytic results obtained during the oxidation of propane on BiCeVMoO catalysts are shown in Fig. 3. Under about 30 mol% of propane conversion, the selectivity of cracking products varied not much but the selectivity of propene and acrolein associated closely with the Ce content in catalysts. With the increase of Ce contents, complete oxidation products CO_x (CO and CO_2) changed not much incipiently but propylene selectivity decreased gradually, while acrolein selectivity kept increasing. When the composition of catalyst reached the vicinity of Ce/(Ce + Bi) atomic ratio of 0.15, acrolein selectivity attained maximum (about 45 mol%). After this, with the further elevation of Ce/(Ce + Bi) molar ratios, propylene selectivity kept almost constant but acrolein selectivity decreased gradually while complete oxidation products CO_x increased sharply. Published data showed that propylene is the probable intermediate products during the selective oxidation of propane to

acrolein [8,10], our reactivity studies indicates that proper addition of Ce into BiVMoO mixed oxides catalysts improved the performance of converting propane to acrolein via propylene, but exceeding Ce caused over oxidation of propylene on the catalysts.

For investigating the role of low amount of additive Ce, we studied the oxidative ability of metal cations and the selective propylene oxidation activity of lattice oxygen species in
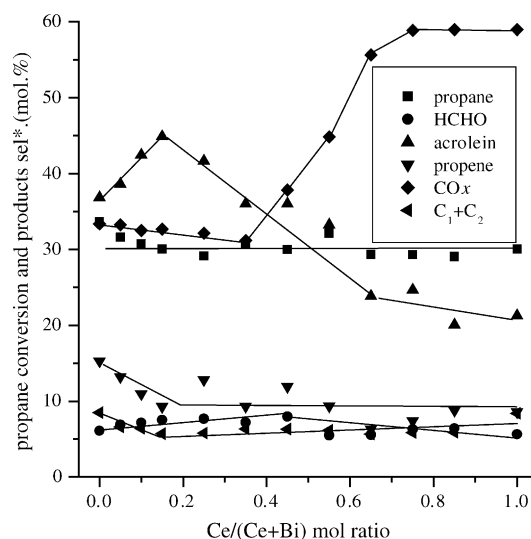

Fig. 3. The catalytic properties of Bi–Ce–V–Mo–O composite oxide catalysts with different Ce/(Ce + Bi) molar ratio for selective oxidation of propane. (*The products selectivity are referred as propane consumption to respect the reaction stoichiometry.)
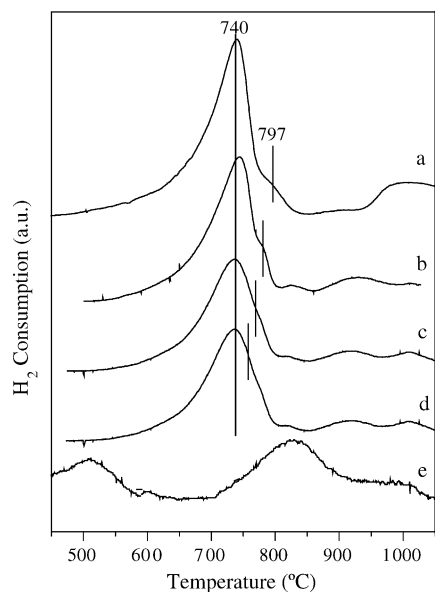
Fig. 4. H_2-TPR profiles of the Bi–Ce–V–Mo–O composite oxide catalysts with Ce/(Ce + Bi) ≤ 0.15. (a) Ce/(Ce + Bi) = 0.00; (b) Ce/(Ce + Bi) = 0.05; (c) Ce/(Ce + Bi) = 0.10; (d) Ce/(Ce + Bi) = 0.15; (e) CeO_2.

Fig. 6. Temperature programmed oxidation profiles of Ce–Bi–V–Mo–O catalysts with varied composition of Ce after reaction with propene: (a) Ce/(Ce + Bi) = 0.00; (b) Ce/(Ce + Bi) = 0.05; (c) Ce/(Ce + Bi) = 0.10; (d) Ce/(Ce + Bi) = 0.15.

catalysts. Shown in Fig. 4 are H_2–TPR profiles of the BiCeV-MoO catalysts with Ce/(Ce + Bi) ≤ 0.15. Two peaks around 740 and 797 °C were observed for sample without Ce (curve a in Fig. 4, Ce/(Ce + Bi) = 0.00), after partial substitution of Ce for Bi, peak around 740 °C kept constant while the peak at higher temperature (peak at 797 °C) shifted obviously to the lower temperature, this indicates that Ce doped catalysts are more easily to be reduced and the lattice oxygen combined with metal cations are more active. For revealing the activity of lattice oxygen in BiCeVMoO catalysts, the catalysts were performed with pulse of propylene. Shown in Fig. 5 are the total acrolein yields by pulse of propylene
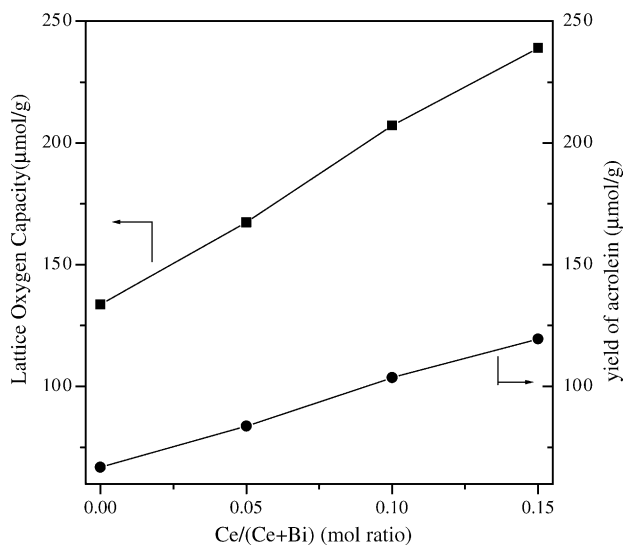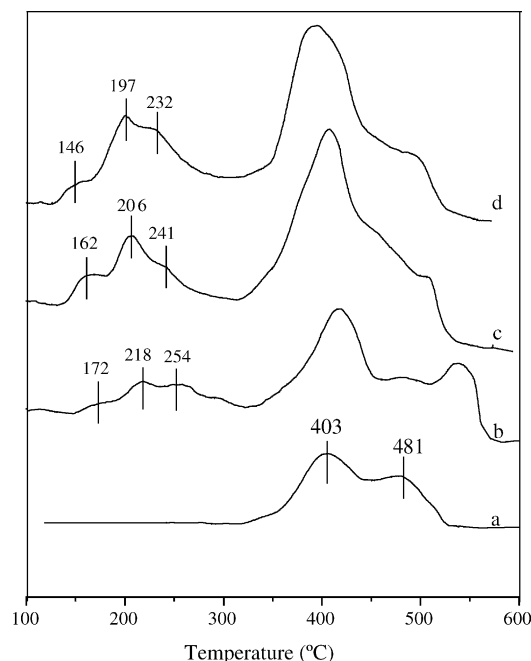

Fig. 5. The reactivity of lattice oxygen in Bi–Ce–V–Mo–O with Ce/(Ce + Bi) ≤ 0.15.

(1.65 μmol/pulse) to almost complete deactivation of catalysts, and estimated amount of lattice oxygen capable of selectively oxidizing propylene to acrolein (represented by LOC). It can be found that with the substitution of Ce for Bi into $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ catalyst, acrolein yield and LOC enhanced gradually, indicating that after the partial substitution of Ce for Bi, the amount of lattice oxygen which can participate in propylene selective oxidation increased, because the lattice oxygen species are the main active species for partial oxidation of propane to acrolein via propylene [13], so this low amount of introduced Ce get rise to the yield of acrolein.

The partial oxidation of propane follows the Mars–van Krevelen mechanism [14], after partial oxidation of propylene to acrolein, the consumed lattice oxygen are compensated by gas-phase oxygen, probably the additive Ce can accelerate the reoxidation process in the reduction–oxidation cycle of catalysts. Shown in Fig. 6 are the temperature programmed re-oxidation profiles of catalysts after oxidation of propylene by lattice oxygen. To the catalyst without Ce, its TPO profile exhibited two oxygen consumption peaks around 403 and 481 °C, respectively, compared to the complementary detecting of CO_2 by mass spectroscopy to the exist gas of TPO of catalyst (shown in Fig. 7), these two peaks could be assigned to the contribution of oxygen consumption by the combustion of carbon deposit on the surface of catalyst. To the samples with additive Ce, TPO profiles showed oxygen consumption peaks in the range <300 °C, and the intensity of the peaks increased remarkably with the increase of Ce contents; this suggests that for the presence of Ce in cata-
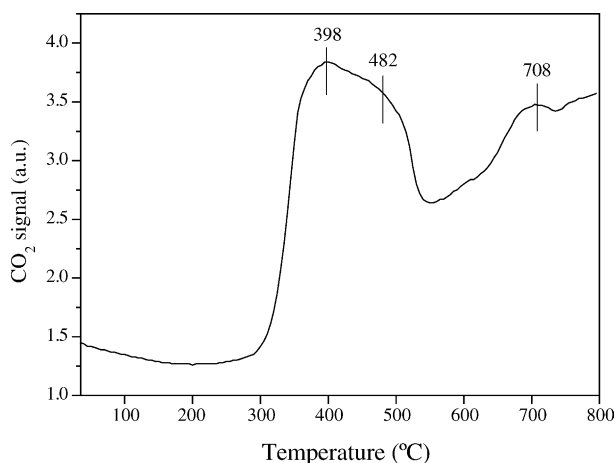
Fig. 7. CO_2 mass spectroscopy of temperature programmed oxidation of Bi–Ce–V–Mo–O with Ce/(Ce + Bi) = 0.15 after reaction with propene.

lysts, the lost lattice oxygen by oxidation of propylene can be regenerated in lower temperature, and simultaneously, the oxygen consumption peaks shifted obviously toward more lower temperature position with the increase of Ce contents, indicating the Ce can promote the regeneration of active lattice oxygen species.

4. Conclusion

In conclusion, it is reasonable to infer that proper amount of Ce may be incorporated into crystal lattice of the Sheelite structure of Bi–V–Mo–O, occupies the crystal lattice position of substituted Bi without obvious changing of the crystal structure of the catalysts. When the Ce content exceed a certain amount, i.e. Ce/(Ce + Bi) > 0.25, the structure of catalyst can not hold and new crystalline $CeVO_4$ as well as $Ce_2(MoO_4)_3$ formed, oxidative ability is strong that the desired product acrolein were easily to be over oxidized to CO_x. Ce doped catalysts has a improved catalytic activity for selective oxidation of propane to acrolein for the proper amount of Ce in the samples. Ce in the crystal structure of BiCeVMoO can promote the selective oxidation activity of the lattice oxygen species in catalysts, enhance the amount of lattice oxygen which can participate in propylene selective oxidation and simultaneously can accelerate the regeneration of active oxygen species.

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