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The role of active phase in Ce modified BiMo catalysts for oxidative dehydrogenation of 1-butene

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ABSTRACT

$BiMoCe_x$ catalysts ($x = 0–0.4$) were prepared by co-precipitation method and tested in the oxidative dehydrogenation (ODH) of 1-butenes to 1,3-butadiene. The results indicate that the cerium content has significant effects on the performance of catalyst. $BiMoCe_{0.2}$ exhibits the superior activity and stability during the 100 h test. X-ray photoelectron spectroscopy (XPS), temperature-programmed re-oxidation (TPRO), 1-Butene temperature-programmed desorption (TPD) and pulse O_2 adsorption characterization reveal that the oxygen mobility and the adsorption ability of 1-butene of catalysts are two crucial factors determining catalytic performance in ODH reaction. The active phases on $BiMoCe_x$ play different roles in the reaction.

1. Introduction

1,3-Butadiene (BD) is an important raw material for manufacturing a large number of chemical products such as styrene butadiene rubber, acrylonitrile–butadiene–styrene resin, and polybutadiene rubber [1,2]. Many kinds of technologies for producing BD have been investigated extensively. Among these, oxidative dehydrogenation (ODH) of 1-butene to BD has gained much attention for its significant advantages over other processes [3–6]. Firstly, this process can be operated as a single unit and is independent of the naphtha cracking unit in producing 1,3-butadiene. Secondly, no additional by-product like ethylene and propylene are produced in the ODH of n-butene [7,8]. In addition, 1-butene, abundant but inexpensive in industry, is the main by-product of methanol to olefins (MTO) process. With the rapid development of the coal chemical industry, there are a large number of by-products of 1-butene. Consequently, ODH of n-butene has been regarded as a promising process for BD production. The design of a suitable catalyst with excellent activity and stability is one of the key challenges facing this kind of reaction.

Bismuth molybdate has been extensively studied in ODH of n-butene to BD and the Mars–van Krevelen mechanism is believed to take place in the reaction [1,6–13]. That is, n-butene adsorbs on bismuth molybdate and reacts with lattice oxygen in the catalyst to form BD, and in turn, oxygen in the gas phase makes up the oxygen vacancy and complete the redox recycle. This implies that oxygen mobility is one of the crucial factors determining catalytic performance of bismuth molybdate in ODH of n-butene. According to this mechanism, much effort has been devoted to develop more efficient catalysts, which may be categorized into two aspects. One is to identify the active phases in bismuth molybdate and understand their roles in ODH reaction. For example, there are three phases such as α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6 in bismuth molybdate. β-$Bi_2Mo_2O_9$ was reported to be thermally unstable and decomposed into α-$Bi_2Mo_3O_{12}$ and γ-Bi_2MoO_6 in the reaction temperature. γ-Bi_2MoO_6 had a higher capacity of oxygen mobility than that of α-$Bi_2Mo_3O_{12}$, while α-$Bi_2Mo_3O_{12}$ catalyst contained much more adsorption sites for n-butene than γ-Bi_2MoO_6 [14,15].

Another one is to introduce some promoters into bismuth molybdate and enhance its oxygen mobility further and catalytic activity subsequently. Some transit metal like Fe, Co, and Ni has been employed [16–21]. V, Zr, La were also used as promoters in our previous works due to their effective capacity in the oxygen storage and release [22–24]. Our results reveal that the addition of V, Zr and La can improve the activity and stability of BiMo catalyst greatly. We ascribed the enhancements to the formation of some new crystalline including $BiVO_4$, $Zr(MoO_4)_2$ and $La_2(MoO_4)_3$ phase, which may improve the oxygen mobility of BiMo [22–24]. However, the role of active phases in these developed catalysts is not fully elucidated, especially that of the new ones.

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In this work, aiming at further clarifying the function of the promoter in the reaction, the metal with excellent redox property, Cerium, has been employed and is expect to modify the oxygen mobility of the catalysts effectively. Ce is a key component in the catalyst formulations for many industrially important reactions, such as three-way-catalysts for automobile exhaust treatment [25], CO oxidation [26], CO_2 activation [27], low temperature water-gas shift reaction [28] and ODH of ethane [29]. A series of multi-component bismuth molybdate catalysts ($BiMoCe_x$) with different cerium contents ($x = 0–0.4$) were prepared by a co-precipitation method, and were applied in the oxidative dehydrogenation of 1-butene to 1,3-butadiene. $BiMoCe_x$ catalysts were characterized by using N_2 adsorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed re-oxidation (TPRO), 1-butene temperature-programmed desorption (TPD), and pulse O_2 adsorption experiments. The relationship between the catalytic activity and cerium content in the catalysts will be studied, oxygen mobility as well. Furthermore, the roles of active phases of $BiMoCe_x$ in the ODH reaction are discussed and a mechanism will be proposed.

2. Experimental

2.1. Preparation of catalysts

$BiMoCe_x$ catalysts ($x = 0–0.4$) were prepared by conventional co-precipitation. The desired amount of cerium nitrate solution ($Ce(NO_3)_3·6H_2O$, Aladdin, AR) was dissolved in deionized water at 70 °C and added dropwise into ammonium molybdate solution ($(NH_4)_6Mo_7O_{24}·4H_2O$, Sinopharnm Chemical Reagent Co., Ltd, 99%) under vigorously stirring at 70 °C. Afterwards, bismuth nitrate solution ($Bi(NO_3)_3·5H_2O$, Sinopharnm Chemical Reagent Co., Ltd, AR) acidified with 10% nitric acid was added dropwise into the above-mentioned mixture under vigorously stirring at 70 °C for 30 min. The mixture was adjusted to pH 5 by aqueous 27 wt% NH_4OH and aged at room temperature for 2 h. The mixture was stirred to viscous solid at the water bath to remove the excess water and dried at 80 °C overnight. The resulting solid was calcined at 550 °C for 4 h in an air flow and then pressed, crushed and sieved to 40–60 meshes before reaction test. The catalysts were designated by $BiMoCe_x$ ($x = 0–0.4$), where x is the molar ratio of cerium in the catalyst.

In order to elucidate the roles of active phases in $BiMoCe_x$ catalysts, $Ce(MoO_4)_2$ catalysts were independently prepared by co-precipitation method. Then it was mixed with BiMo oxide by using ultrasonic waves in hexane as solvent. The mole ratio of BiMo oxide and $Ce(MoO_4)_2$ was 4:1. After that, the hexane was removed by using a rotary evaporator and dried at 100 °C for 12 h.

2.2. Catalysts characterization

Atomic ratios of the prepared catalysts were determined by ICP-AES (Thermo iCAP6300) analyses. The BET surface area and pore volume of the catalysts were measured using N_2 as a sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP2020). The phase identification of $BiMoCe_x$ catalysts was carried out by powder X-ray diffraction (XRD) on XRD 6000(Shimadzu) equipped with Cu Kα radiation at 40 kV and 30 mA. Data were collected in the 2θ range of 5–80° with a scan rate of $1° min^{-1}$.

The relationship between catalytic activity and cerium content was assessed through X-ray photoelectron spectroscopy (XPS) and the temperature-programmed reduction of 1-butene and subsequent oxidation (TPRO) recorded on fixed-bed attached to a Hiden QIC-20 quadruple mass spectrometer. Pulse O_2 adsorption experiments and 1-Butene TPD was carried out on the same apparatus. X-ray photoelectron spectroscopy (XPS) spectra for $BiMoCe_x$ catalysts were conducted by using an Escalab 250Xi XPS system. An Mg $K\alpha$ anode was used as the X-ray source. The binding energy of the electron, correcting charge effects, was calibrated with respect to the signal of the adventitious carbon (binding energy: 284.6 eV). Spectrum deconvolution was carried out using the spectra of X-ray satellite peak subtraction and background correction. For TPRO, 0.2 g catalyst was pretreated at 440 °C for 2 h in flowing 1-butene ($20 cm^3·min^{-1}$), held for1 h at that temperature and then cooled to room temperature in flowing He ($30 cm^3 min^{-1}$). Subsequent temperature programmed oxidation was performed in flowing 2%O_2/He ($30 cm^3·min^{-1}$) from room temperature to 500 °C at $10 °C min^{-1}$.

For 1-Butene TPD, 0.2 g catalyst was pretreated at 200 °C for 2 h in flowing He ($20 cm^3 min^{-1}$), held for 1 h at that temperature and then cooled to 50 °C in flowing He ($30 cm^3 min^{-1}$). 1-Butene was adsorbed at 50 °C and purged under flowing He ($30 cm^3 min^{-1}$) for 0.5 h before TPD from 50 to 800 °C at $10 °C min^{-1}$. Mass signals of $m/z = 54$ ($^\bullet C_4H_6$) was detected.

Pulse O_2 adsorption experiments were performed at 440 °C. 0.1 g catalyst was placed in the U-shape quartz reactor with densely packed quartz wool. All catalysts were pretreated at 440 °C for 1 h under flowing 10% H_2/Ar ($50 cm^3 min^{-1}$) and subsequently purged for 0.5 h under flowing He ($50 cm^3 min^{-1}$). After that, pulse O_2 adsorption experiments were carried out by contacting fixed amounts of reactant gases with He as the carrier gas. The amount of O_2 in each pulse, which was introduced using a volumetric sample loop of $1 cm^3$ (35.5 μmol) and the pulse was repeated ten times with 10 min interval. The mass signal of $m/z = 32$ ($\bullet O_2$) was detected.

Table 1
Atomic ratio, BET surface area, total pore volume of the $BiMoCe_x$ catalysts.

Catalyst	Atomic ratio[a]			S_{BET} ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)
	Bi	Mo	Ce		
BiMo	1	0.98	0	1.2	0.011
$BiMoCe_{0.1}$	1	0.99	0.09	2.3	0.018
$BiMoCe_{0.2}$	1	0.99	0.21	6.6	0.035
$BiMoCe_{0.3}$	1	1.00	0.28	4.3	0.028
$BiMoCe_{0.4}$	1	1.01	0.42	4.6	0.024

[a] Determined by ICP-AES.

2.3. ODH of 1-butene

Catalytic testing was performed in a tubular fixed bed flow micro-reactor (i.d. = 8 mm) with 1.5 g catalyst under atmospheric pressure, gaseous hourly space velocity (GHSV) = 300 mL $(g\,cat)^{-1} h^{-1}$ on the basis of 1-butene, and 1-butene/air/steam = 1:4:10. Prior to the reaction, each catalyst was routinely activated with flowing air stream ($50 cm^3 min^{-1}$) at 440 °C for 2 h. The water feed was continuously vaporized by passing through a pre-heating zone at 120 °C and fed into the reactor together with 1-butene and air. The reactants and products were analyzed by two on-line gas chromatography detectors with two columns. A KB–Al_2O_3/Na_2SO_4 column of 50 m length and 0.32 mm diameter with a flame ionization detector (FID) were used to analyze hydrocarbons. A TDX-01 column of 0.5 m length and 3 mm diameter with a thermal conductivity detector (TCD) was used for the separation of CO and CO_2.

3. Results and discussion

3.1. Formation and characterization of $BiMoCe_x$ catalysts

The data of N_2 adsorption and elemental analysis of the $BiMoCe_x$ catalysts are summarized in Table 1. The BET surface areas of all