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Article

Catalytic oxidative dehydrogenation of *n*-butane over $V_2O_5/MO-Al_2O_3$ ($M = Mg, Ca, Sr, Ba$) catalysts

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ABSTRACT

$V_2O_5/MO-Al_2O_3$ ($M = Mg, Ca, Sr, Ba$) catalysts with different V_2O_5 loading were prepared by impregnation with ammonium metavanadate as the V precursor and characterized and tested for the selectively oxidative dehydrogenation of *n*-butane to butenes. Characterization by BET, XRD, FTIR, H_2 -TPR and Raman spectra showed that the catalysts doped with different alkaline earth metals had different structure and catalytic activity. The catalysts doped with Ca, Sr or Ba had the orthovanadate phase that was difficult to reduce, so their redox cycles could not be established and they exhibited low activity. The catalysts doped with Mg showed high catalytic activity and selectivity. The catalyst with 5% V_2O_5 loading exhibited the highest *n*-butane conversion (30.3%) and total butene selectivity (64.3%) at 600 °C. This was due to the well dispersed VO_x species and the existence of the MgO crystalline phase, which were both present at a V_2O_5 loading of 5%.

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1. Introduction

Dehydrogenation of light alkanes to the corresponding olefins is an alternative route for the production of light olefins [1]. Since light alkanes are widely available, cheap and environment friendly, they are potential raw materials for the future chemical industry. In particular, *n*-butane can be recovered from liquefied petroleum gas (LPG) by distillation [2]. Conversion of *n*-butane to high value added products has caught much attention from researchers. The catalytic dehydrogenation of *n*-butane to 1-butene, 2-butene, and 1,3-butadiene is an alternative route for the production of butenes. Among the butenes, 1,3-butadiene is the most important because of its wide use in the manufacture of butadiene-styrene rubber, synthetic rubbers, and plastics with special mechanical properties [3]. Compared to the direct dehydrogenation, the oxidative dehydro-

genation (ODH) of *n*-butane has three advantages: (1) the reaction is exothermic and therefore does not need external heat input; (2) the oxidative dehydrogenation reaction is not limited by thermodynamic equilibrium; (3) there is no catalyst deactivation induced by coking, so frequent regeneration of the catalyst is not needed [4,5]. However, the low selectivity is still a main issue which blocks the application of the process. Therefore, a high performance catalyst needs to be developed for the catalytic oxidative dehydrogenation of *n*-butane.

For *n*-butane oxidative dehydrogenation, supported vanadium oxide catalysts have been reported as the most active and selective catalysts [6–8]. The variable valence states between V^{4+} and V^{5+} makes V the active component for many catalytic reactions. The catalytic activity of supported vanadium catalysts for *n*-butane oxidative dehydrogenation is related to the structure of the VO_x surface species, redox properties of the VO_x

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surface species and acid-base character of the catalyst and support [9–14]. According to previous works, the oxidative dehydrogenation of *n*-butane to butene and 1,3-butadiene follows the Mars-van Krevelen mechanism [6,15–17]. This indicates that the redox properties of the catalyst play an important role in the oxidative dehydrogenation of *n*-butane [15,18–20]. In addition, the acid-base properties have influences on the activity and selectivity of vanadium catalysts by affecting the adsorption and desorption of the reactants and products [21].

Although MgO is a good support for vanadium catalysts to catalyze *n*-butane oxidative dehydrogenation [21–23], its low mechanical strength and low specific surface area indicate that it is not the ideal support for practical application. γ -Al₂O₃ supported vanadium catalysts have been reported in several studies [1,24,25] because γ -Al₂O₃ with a high specific surface area, suitable pore structure and high mechanical strength is suitable for loading the active components. However, unlike on the alkaline support MgO, it is difficult to get a good dispersion of VO_x on the acidic γ -Al₂O₃ surface, and thus crystalline V₂O₅ is frequently found at high loading.

Here, alkaline earth metal oxide-doped Al₂O₃ was synthesized as the support for vanadium catalysts, and the dehydrogenation of *n*-butane to butenes was conducted to find the relationship between the alkaline earth metal doping and catalyst performance. In addition, catalysts with different amounts of V₂O₅ loading were prepared to study the relationship between V₂O₅ loading and catalytic performance.

2. Experimental

2.1. Catalyst preparation

MO-Al₂O₃ (M = Mg, Ca, Sr, Ba) supports were prepared by a modified sol-gel method. First, an amount of boehmite powder was dispersed in nitric acid solution (0.1 mol/L). The mixed solution was vigorously stirred for 2 h at room temperature to make the boehmite powder particles fully dispersed. After aging at room temperature for 12 h, an AlOOH sol was formed. After this, an alkaline earth metal nitrate solution was added into the AlOOH sol with an M:Al molar ratio of 1:2. Then the mixture was vigorously stirred at 80 °C for 2 h. Finally, the MO-Al₂O₃ (M = Mg, Ca, Sr, Ba) support was obtained after drying and calcining at 70 °C for 12 h and 550 °C for 3 h, respectively.

For the preparation of V₂O₅/MO-Al₂O₃ catalysts with different V₂O₅ loading (mass ratio), an aqueous solution containing ammonium metavanadate and oxalic acid (molar ratio = 1:2) was added to the MO-Al₂O₃ support by the wet impregnation method. The impregnation was performed at 70 °C with continuous stirring. After drying the slurry at 120 °C for 12 h, the resultant powder was pressed into pellets, and then crushed and sieved to 20–40 mesh.

2.2. Catalyst characterization

The specific surface area of the V₂O₅/MO-Al₂O₃ catalyst and V₂O₅/MgO-Al₂O₃ catalysts with different V₂O₅ loading were

measured on an OMNISORP 100CX fully automatic physical and chemical adsorption device using the nitrogen adsorption-desorption isotherm method (adsorption data obtained in the relative pressure ranges of 10^{−6}–1 bar for nitrogen at −196 °C). Powder X-ray diffraction (XRD) measurements were used to identify the crystallographic structure of the fresh and used catalysts. The XRD diffraction patterns of the catalyst samples were obtained on a Rigaku D/MAX-RB instrument using Cu K α radiation source (40 kV, 100 mA) and a graphite monochromatic between 20°–80° at a scan rate of 5°/min. Infrared spectra were recorded on a Nicolet 6700 Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR, Thermo Scientific Co.) spectrophotometer. Powder samples were placed in contact with an attenuated total reflectance (ATR) multibounce plate of ZnSe crystal at ambient temperature (25 °C). The Raman spectra were recorded at an excitation wavelength of 532 nm and a laser power of 20 mW. H₂ temperature programmed reduction (H₂-TPR) was performed to observe the reducibility of the catalysts. Prior to the analysis, 100 mg of sample was treated in 20% O₂–80% N₂ (30 mL/min) at 300 °C for 30 min. The reactor temperature was raised to 900 °C at a heating rate of 10 °C/min in 5% H₂–95% N₂ (30 mL/min). The H₂ consumption during the reaction was measured by a thermal conductivity detector (TCD).

2.3. Catalytic testing

The catalytic experiments were performed on a fixed bed quartz tubular reactor (10 mm i.d.) under atmospheric pressure. For each catalytic test, 1.0 g catalyst (20–40 mesh, total bed height of 15 mm) was used. The reactor was heated in a furnace and the temperature was controlled by a microprocessor (Model AI-708, Xiamen Yuguang Electronics Technology Research Institute, China) to within ± 1 °C of the set points using a K type thermocouple. The catalysts were calcined under flowing N₂ (100 mL/min) for 5 h at 600 °C in the reactor before the catalytic reaction. The catalytic tests were conducted in the temperature range of 500 to 600 °C. The flow rates of *n*-butane, O₂ and N₂ (*n*-butane:O₂ ratio = 1.2:1, 1.5:1 and 2:1) were controlled by mass flow controllers. The *n*-butane volume fraction in the feed gas was 5%. The products of the reactions were analyzed by an online gas chromatograph equipped with a thermal conductivity detector (TCD). Two columns were used for the separation of the products. One was a 30% sebacic dinitrile/Chromosorb packed 9 m 1/8" column for the separation of all the hydrocarbons, and another was a 3 m 1/8" PQ column for the separation of O₂, N₂ and CO. The conversion of *n*-butane, selectivity to total butenes (including 1-C₄H₈, 2-*t*-C₄H₈, 2-*c*-C₄H₈, 1,3-C₄H₆) and selectivity to 1,3-butadiene were calculated on the basis of the carbon balance. The yield was calculated by multiplying the conversion of *n*-butane and selectivity to butenes products as follows:

$$n\text{-butane conversion, } X_{n\text{-C}_4\text{H}_{10}} (\%) = \frac{\sum Mi \times ni}{4 \times \text{moles of } n\text{-butane feeded}} \times 100$$

$$\text{Selectivity to } C_4 = \text{tot, } S (\%) = \frac{Mi \times ni}{\sum Mi \times ni} \times 100$$

(M_i : the moles of products; n_i : the carbon atoms of the product molecules)

3. Results and discussion

3.1. Catalyst characterization results

3.1.1. BET surface area

Table 1 and Table 2 list the BET specific surface areas of the catalysts before and after the reaction. Of all the catalysts, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5/\text{CaO}-\text{Al}_2\text{O}_3$ have the highest and the lowest surface area, respectively. After the reaction at 600 °C for a set time, all the catalysts showed significant decrease in the specific surface areas compared with before the reaction. The decrease in the specific surface area was attributed to the sintering of the nanoparticles during the catalytic reaction [26]. The surface areas of $\text{V}_2\text{O}_5/\text{MO}-\text{Al}_2\text{O}_3$ catalysts with different alkaline earth metal dopants showed irregular changes, but the Mg doped sample had the highest specific surface area among the doped samples. In addition, compared to the undoped sample, the MgO-doped sample has a higher surface area after the reaction, which indicated that doping MgO can inhibit the sintering and stabilize the pore structure of the catalyst support although it gave a slightly lower initial surface area. As shown in Table 2, the specific surface area of the $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$ catalyst before the reaction decreased slightly with the increase of V_2O_5 loading. This can be ascribed to the gradual reduction of the volume fraction of the support. After the reaction, the specific surface areas of the MgO-doped catalysts were still higher than 60 m^2/g .

3.1.2. XRD results

Figure 1 shows the XRD patterns of the $\text{V}_2\text{O}_5/\text{MO}-\text{Al}_2\text{O}_3$ catalysts (before and after the reaction) and $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$ catalysts with different V_2O_5 loading. As shown in Fig. 1(a), orthovanadates and carbonates were formed in the samples doped by Ca, Sr and Ba. The diffraction peaks of the carbonate became stronger after the reaction. Meanwhile the strong orthovanadate diffraction peaks indicated that the Ca, Sr and Ba ortho-

Table 1

BET area of $\text{V}_2\text{O}_5/\text{MO}-\text{Al}_2\text{O}_3$ catalysts with different alkaline earth metal dopants.

Sample	V_2O_5 content (%)	$S_{\text{BET}}/(\text{m}^2/\text{g})$	
		Before reaction	After reaction
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	10	224	40
$\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$	10	148	62
$\text{V}_2\text{O}_5/\text{CaO}-\text{Al}_2\text{O}_3$	10	13	7
$\text{V}_2\text{O}_5/\text{SrO}-\text{Al}_2\text{O}_3$	10	56	28
$\text{V}_2\text{O}_5/\text{BaO}-\text{Al}_2\text{O}_3$	10	42	19

Table 2

BET area of $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$ catalysts with different V_2O_5 loading.

Sample	V_2O_5 content (%)	$S_{\text{BET}}/(\text{m}^2/\text{g})$	
		Before reaction	After reaction
3%- $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$	3	182	124
5%- $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$	5	156	79
10%- $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$	10	148	62
15%- $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$	15	143	65
20%- $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$	20	136	68

Fig. 1. XRD patterns of $\text{V}_2\text{O}_5/\text{MO}-\text{Al}_2\text{O}_3$ catalysts with different alkaline earth metal dopants before (a) and after (b) reaction, (c) $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$ catalysts with different V_2O_5 loading after the reaction. (1) $\text{V}_2\text{O}_5-\text{Al}_2\text{O}_3$; (2) $\text{V}_2\text{O}_5/\text{MgO}-\text{Al}_2\text{O}_3$; (3) $\text{V}_2\text{O}_5/\text{CaO}-\text{Al}_2\text{O}_3$; (4) $\text{V}_2\text{O}_5/\text{SrO}-\text{Al}_2\text{O}_3$; (5) $\text{V}_2\text{O}_5/\text{BaO}-\text{Al}_2\text{O}_3$. •: $\text{M}_3(\text{VO}_4)_2$, ♦: MCO_3 , ▽: MgAl_2O_4 , ◇: MgO , △: Al_2O_3 , □: V_2O_3 , *: Mg_2VO_4 (M: Ca, Sr, Ba).

vanadates were stable under the reaction conditions. However, for the MgO doped catalyst (10%- V_2O_5), no diffraction peaks corresponding to the orthovanadate and carbonate were detected but those for MgAl_2O_4 spinel and MgO were detected. In addition, the diffraction peaks of the V_2O_3 and $(\text{Mg},\text{V})_3\text{O}_4$ phases were detected after the reaction. For the undoped catalyst (10%- $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$) (Fig. 1(c)), the V_2O_3 crystalline phase was also detected by XRD, as shown in Fig. 1(b). On the $\text{MgO}-\text{Al}_2\text{O}_3$

support, the increase in V_2O_5 loading made the diffraction peaks of the V_2O_3 and $(\text{Mg,V})_3\text{O}_4$ phases stronger, while they disappeared when the loading was decreased to 5%. In other words, the VO_x species were well dispersed on the support surface when the V_2O_5 loading was lowered to 5%. The content of the MgO phase decreased with the V_2O_5 loading increasing. When the loading was further decreased to 3%, the diffraction peaks of MgO almost disappeared, and all the strong peaks were due to MgAl_2O_4 spinel.

3.1.3. FTIR results

Figure 2 shows the FTIR spectra of the $\text{V}_2\text{O}_5/\text{MO-Al}_2\text{O}_3$ catalysts with different alkaline earth metal dopants before the reaction. The samples doped with Ca, Sr, Ba exhibited clearly visible strong absorption bands at 800–900 and 1400 cm^{-1} . The absorption band at 800–900 cm^{-1} is the stretching vibration of VO_4^{3-} [27], while the absorption band at 1400 cm^{-1} is the anti-symmetric stretching vibration of CO_3^{2-} . The characteristic peak width became narrow gradually in the order of Ca, Sr, Ba. This was ascribed to the increase of the ionic radius in the order of Ca, Sr, Ba (Ca^{2+} : 0.099 nm < Sr^{2+} : 0.112 nm < Ba^{2+} : 0.134 nm). The characteristic peaks were located at 1422.4 (CaCO_3), 1480.4 (SrCO_3), 1453.0 cm^{-1} (BaCO_3) [28], respectively. Therefore, the FTIR spectra result agreed with the XRD analysis that the orthovanadate and carbonate were present in the Ca, Sr, Ba doped catalysts but not in the Mg doped and undoped catalysts.

3.1.4. H_2 -TPR results

The redox properties of the catalysts were characterized by H_2 -TPR as shown in Fig. 3. The reduction peaks shifted to high temperature in the order $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ as the catalysts were doped with alkaline earth oxides. In addition, the intensity of reduction peaks was weaker for the catalysts doped with Ca, Sr, Ba than for the catalysts doped with Mg, which indicated that the orthovanadate crystalline phase in the Ca, Sr, Ba doped catalysts were difficult to reduce. This finding is consistent with

Fig. 2. FTIR spectra of the $\text{V}_2\text{O}_5/\text{MO-Al}_2\text{O}_3$ catalysts with different alkaline earth metal dopants before the reaction. (1) $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$, (2) $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$, (3) $\text{V}_2\text{O}_5/\text{CaO-Al}_2\text{O}_3$, (4) $\text{V}_2\text{O}_5/\text{SrO-Al}_2\text{O}_3$, (5) $\text{V}_2\text{O}_5/\text{BaO-Al}_2\text{O}_3$.

Fig. 3. H_2 -TPR profiles of the $\text{V}_2\text{O}_5/\text{MO-Al}_2\text{O}_3$ catalysts with different alkaline earth metal dopants. (1) $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$, (2) $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$, (3) $\text{V}_2\text{O}_5/\text{CaO-Al}_2\text{O}_3$, (4) $\text{V}_2\text{O}_5/\text{SrO-Al}_2\text{O}_3$, (5) $\text{V}_2\text{O}_5/\text{BaO-Al}_2\text{O}_3$.

the XRD results (Fig. 1(b)). Thus, it can be expected that the Ca, Sr, Ba doped catalysts will have lower catalytic activity than the Mg doped and undoped catalysts.

3.1.5. Raman spectroscopy

Figure 4 shows the Raman spectra of the $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$ catalysts with different V_2O_5 loadings after the reaction. The peak intensity at 100–400 and 800–1000 cm^{-1} increased gradually as the V_2O_5 loading increased from 3% to 20%. The stretching vibration peak of $\text{V}=\text{O}$ at 995 cm^{-1} appeared as the V_2O_5 loading was increased to 10%. This means the V_2O_5 crystalline phase was formed in the $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$ catalysts with 10%, 15%, 20%- V_2O_5 loading. Han et al. [29] reported that vanadium species achieve the highest monolayer dispersion when the V_2O_5 loading was 5% for the $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ system, and an additional increase in the V_2O_5 loading led to the appearance of the V_2O_5 crystalline phase. Here, as the V_2O_5 load-

Fig. 4. Raman spectra of the $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$ catalysts with different V_2O_5 loading after the reaction.

ing was decreased to 5%, the stretching vibration peak at 995 cm^{-1} disappeared, which indicated VO_x species were well dispersed on the $\text{MgO-Al}_2\text{O}_3$ support. The peaks at 100–400 cm^{-1} also belonged to the V_2O_5 stretching vibration [30]. The wide band vibration at 800–900 cm^{-1} revealed the polymerization of vanadium oxygen species [31]. The peak strength became gradually stronger with the further increase of vanadium content.

3.2. Catalytic performance for *n*-butane oxidative dehydrogenation

The catalytic reaction was conducted in the temperature range of 500–600 °C. To account for the gas phase oxidation dehydrogenation and thermal cracking effects, a blank experiment was performed in the empty reactor (without catalyst) with the same feed gas composition. *n*-Butane conversion and butene selectivity in the reactor were 3.36% and 16.6% (9% 1- C_4H_8 , 5.2% 2-*t*- C_4H_8 , 2.4% 2-*c*- C_4H_8 , none 1,3- C_4H_6) at 600 °C, respectively. Based on these results, the influence of the gas phase conversion was insignificant for the evaluation of the active catalysts. The catalytic performance of the various $\text{V}_2\text{O}_5/\text{MO-Al}_2\text{O}_3$ catalysts for *n*-butane oxidative dehydrogenation experiments was measured under different conditions, i.e., reaction temperature, V_2O_5 loading, *n*- $\text{C}_4\text{H}_{10}/\text{O}_2$ ratio, and reaction space velocity. The main carbon-containing products were CO_2 , CO, C_2 , C_3H_6 , *i*- C_4H_{10} , 1- C_4H_8 , 2-*t*- C_4H_8 , 2-*c*- C_4H_8 , 1,3- C_4H_6 .

3.2.1. Effect of different alkaline earth metal dopants

Table 3 shows the *n*-butane conversion and selectivity to

$\text{C}_4^=$,_{tot} and CO_x at a low space velocity (GHSV = 7500 $\text{mL}/(\text{g}\cdot\text{h})$) and at a high space velocity (GHSV = 51000 $\text{mL}/(\text{g}\cdot\text{h})$), respectively. From Table 3, the samples doped with different alkaline earth metals exhibited different activity, resulting in 27.2%, 26.3%, 25%, 25.7% *n*-butane conversion and 61.6%, 36.1%, 59.1%, 57.5% $\text{C}_4^=$,_{tot} selectivity for the Mg, Ca, Sr, Ba doped catalysts at the low space velocity; 26%, 3.8%, 13.4%, 13% *n*-butane conversion and 61.4%, 38.7%, 50.2%, 51.1% $\text{C}_4^=$,_{tot} selectivity were achieved at the high space velocity. The significant decrease in conversion at the higher space velocity revealed that the Ca, Sr, Ba doped catalysts have lower catalytic activity than the Mg doped catalyst. In addition, the Mg doped catalyst was better than the undoped one in terms of both *n*-butane conversion and $\text{C}_4^=$,_{tot} selectivity. Both at the low space velocity and high space velocity, the catalyst doped with Mg exhibited the highest catalytic activity and selectivity among these catalysts. Therefore, the catalytic activity order was: $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3 > \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 > \text{V}_2\text{O}_5/\text{SrO-Al}_2\text{O}_3 \approx \text{V}_2\text{O}_5/\text{BaO-Al}_2\text{O}_3 \gg \text{V}_2\text{O}_5/\text{CaO-Al}_2\text{O}_3$. The low activity and selectivity of the Ca, Sr, Ba doped catalysts were related to their low specific surface areas (Table 1) and the stable orthovanadate (see Fig. 1(a) and (b)) where V^{5+} was difficult to reduce to V^{4+} under the reaction conditions, as shown in Fig. 3. Thus the redox cycle was difficult to establish.

3.2.2. Effect of V_2O_5 loading

The conversion and product selectivity for the *n*-butane ODH reaction are affected by both the vanadium loading and vanadium surface density [32–35]. As shown in Table 4, at the low space velocity, there was no large change in *n*-butane con-

Table 3

Performance of $\text{V}_2\text{O}_5/\text{MO-Al}_2\text{O}_3$ catalysts for *n*-butane ODH ($m(\text{catalyst}) = 1.0 \text{ g}$, $T = 600 \text{ °C}$, *n*-butane/ $\text{O}_2 = 1.5/1$, 10% V_2O_5 loading).

Catalyst	GHSV ($\text{mL}/(\text{g}\cdot\text{h})$)	$X_{n-\text{C}_4\text{H}_{10}}$ (%)	Selectivity (%)					$\text{C}_4^=$, _{tot} yield (%)	STY ^b ($\text{g}/(\text{kg}\cdot\text{h})$)
			$\text{C}_4^=$, _{tot}	1,3- C_4H_6	CO_2	CO	Others ^a		
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	7500	27.5	59.7	11.3	17.1	17.7	5.6	16.4	397
$\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$		27.2	61.6	22.0	20.0	13.0	5.5	16.8	456
$\text{V}_2\text{O}_5/\text{CaO-Al}_2\text{O}_3$		26.3	36.1	6.7	11.5	11.0	41.4	9.5	291
$\text{V}_2\text{O}_5/\text{SrO-Al}_2\text{O}_3$		25.0	59.1	23.4	21.3	13.3	6.3	14.8	542
$\text{V}_2\text{O}_5/\text{BaO-Al}_2\text{O}_3$		25.7	57.5	24.4	21.1	13.7	7.6	14.8	541
$\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	51000	21.6	49.9	16.6	21.6	26.5	2.0	10.8	751
$\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$		26.0	61.4	25.9	19.8	16.8	2.0	16.0	1251
$\text{V}_2\text{O}_5/\text{CaO-Al}_2\text{O}_3$		3.8	38.7	4.1	7.6	9.8	43.8	1.5	130
$\text{V}_2\text{O}_5/\text{SrO-Al}_2\text{O}_3$		13.4	50.2	11.9	16.5	14.3	19.0	6.7	718
$\text{V}_2\text{O}_5/\text{BaO-Al}_2\text{O}_3$		13.0	51.1	13.5	13.7	13.0	22.2	6.7	702

^a Others: $\text{C}_2 + \text{C}_3\text{H}_6 + i\text{-C}_4\text{H}_{10}$. ^b STY: space time yield

Table 4

Performance of $\text{V}_2\text{O}_5/\text{MgO-Al}_2\text{O}_3$ catalysts with different V_2O_5 loading (600 °C, *n*-butane/ O_2 ratio = 1.5/1).

Catalyst	GHSV (mL/(g·h))	$X_{n\text{-C}_4\text{H}_{10}}$ (%)	Selectivity (%)					$\text{C}_4^=$, _{tot} yield (%)	STY (g/(kg·h))
			$\text{C}_4^=$, _{tot}	1,3-C ₄ H ₆	CO ₂	CO	Others		
3%-V ₂ O ₅ /MgO-Al ₂ O ₃	7500	27.3	40.7	11.9	24.2	20.1	15.0	11.1	281
5%-V ₂ O ₅ /MgO-Al ₂ O ₃		27.2	61.3	24.1	18.9	13.1	6.8	16.7	454
10%-V ₂ O ₅ /MgO-Al ₂ O ₃		27.2	61.6	22.0	20.0	13.0	5.5	16.8	456
15%-V ₂ O ₅ /MgO-Al ₂ O ₃		27.4	61.4	15.4	20.5	13.4	4.7	16.8	470
20%-V ₂ O ₅ /MgO-Al ₂ O ₃		29.6	52.5	15.3	20.7	15.1	11.7	15.6	525
3%-V ₂ O ₅ /MgO-Al ₂ O ₃	51000	24.9	42.1	13.7	21.2	22.8	14.0	10.5	796
5%-V ₂ O ₅ /MgO-Al ₂ O ₃		30.3	64.3	32.0	16.8	13.9	5.0	19.5	1530
10%-V ₂ O ₅ /MgO-Al ₂ O ₃		26.0	61.4	25.9	19.8	16.8	2.0	16.0	1251
15%-V ₂ O ₅ /MgO-Al ₂ O ₃		24.1	57.7	21.8	22.3	18.3	1.6	13.9	1118
20%-V ₂ O ₅ /MgO-Al ₂ O ₃		23.6	51.2	17.8	23.4	21.0	4.5	12.1	1176

version and $C_{4^{\text{=}},\text{tot}}$ selectivity for the catalysts with 3%, 5%, 10%, 15% V_2O_5 loadings, but the 1,3- C_4H_6 selectivity gradually decreased with increased V_2O_5 loading after it reached the maximum at 5%. At the high space velocity, n -butane conversion, $C_{4^{\text{=}},\text{tot}}$ selectivity, 1,3- C_4H_6 selectivity and the STY all gradually decreased when the V_2O_5 loading was more than 5%. The high space velocity was more favorable for the ODH reaction compared to the low space velocity in terms of the conversion, butene selectivity and STY. It can be inferred that the monolayer coverage was achieved when the V_2O_5 loading reached 5%. As the V_2O_5 loading was increased to 10%, the V_2O_5 crystalline phase appeared which was reduced to V_2O_3 under the reaction conditions (see Fig. 1(c)). However, as the V_2O_5 loading was decreased to 3%, the MgO crystalline phase disappeared, which was accompanied by a decrease in conversion and selectivity. It has been proved by other researchers that the MgO crystalline phase is necessary to achieve high catalytic activity and selectivity for V-Mg-O catalysts [32]. Therefore, the high performance was dependent on the well dispersed VO_x species and the existence of the MgO crystalline phase, which were both fulfilled at a V_2O_5 loading of 5%.

3.2.3. Effect of reaction temperature

The effect of temperature on n -butane ODH reaction was investigated in the temperature range of 500–600 °C. Table 5 lists the conversion and selectivity for the n -butane ODH reaction performed on the 5%- V_2O_5 /MgO- Al_2O_3 catalyst at different temperatures. n -Butane conversion and $C_{4^{\text{=}},\text{tot}}$ selectivity increased with the reaction temperature both at the low and high space velocity. The 1,3- C_4H_6 selectivity increased from 18.7% to 24.1% at the low space velocity and from 23.1% to 32.0% at the high space velocity as the reaction temperature was increased from 500 to 600 °C, which was accompanied by a decrease in CO_x ($CO + CO_2$) selectivity. This result indicated that both high space velocity and high temperature are beneficial to

the formation of 1,3- C_4H_6 . A similar phenomenon was also reported by other researchers on V_2O_5 /MgO catalyst [36,37].

3.2.4. Effects of n -butane/ O_2 ratio

The ODH reactions under different n -butane/ O_2 ratios (i.e. 1.2/1, 1.5/1, 2/1) were conducted to know its effects on the catalytic performance of the 5%- V_2O_5 /MgO- Al_2O_3 catalyst. Table 6 lists the reaction results at 600 °C. The CO_x selectivity decreased with the increase in n -butane/ O_2 ratio. This was due to the decrease in the deep oxidation of n -butane and butenes when the O_2 concentration in the feed gas was decreased. The n -butane conversion decreased as expected, while the selectivity to $C_{4^{\text{=}},\text{tot}}$ increased significantly with the increase in n -butane/ O_2 ratio. As shown in the table, the STY was higher than 1500 g/(kg·h) when the n -butane/ O_2 ratio was higher than 2/1 at the GHSV of 51000 mL/(g·h).

3.2.5. Effect of reaction space velocity

The influence of reaction space velocity is shown in Table 4 to 6 for the V_2O_5 /MgO- Al_2O_3 catalysts. At a fixed n -butane/ O_2 ratio and reaction temperature, the selectivity to 1,3- C_4H_6 and $C_{4^{\text{=}},\text{tot}}$ increased with the space velocity, while that of CO_x decreased. This was attributed to that the reaction contact time was shortened from ~0.48 to ~0.07 s when the space velocity was increased from 7500 to 51000 mL/(g·h). As a result, deep oxidation was inhibited. Since the ODH reaction was conducted at a higher n -butane/ O_2 ratio of 1.5/1, which is much higher than that used in the combustion reaction (n -butane/ O_2 ratio of 1/6.5) and that used by other researchers (n -butane/ O_2 ratio of 1/2) [22], the oxygen conversion was 100% for all the experiments. More oxygen was consumed by the combustion reaction than the selective oxidation reactions, thus the increase of space velocity not only improved the selectivity of 1,3- C_4H_6 and $C_{4^{\text{=}},\text{tot}}$ but also increased the n -butane conversion, as shown in Table 6.

Table 5

Activity of 5%- V_2O_5 /MgO- Al_2O_3 catalyst for n -butane ODH at different reaction temperatures (n -butane/ O_2 ratio = 1.5/1).

GHSV (mL/(g·h))	T (°C)	$X_{n-C_4H_{10}}$ (%)	Selectivity (%)					$C_{4^{\text{=}},\text{tot}}$ yield (%)	STY (g/(kg·h))
			$C_{4^{\text{=}},\text{tot}}$	1,3- C_4H_6	CO_2	CO	Others		
7500	500	20.9	55.7	18.7	25.3	17.7	1.27	11.6	317
	540	22.6	60.0	21.4	22.7	15.0	2.27	13.6	370
	580	25.3	61.7	23.4	20.3	13.7	4.35	15.6	426
	600	27.2	61.3	24.1	18.9	13.1	6.76	16.7	454
51000	500	21.4	61.6	23.1	19.0	14.3	5.13	13.2	1103
	540	26.4	61.9	26.2	18.9	14.6	4.59	16.4	1366
	580	27.6	61.5	26.9	19.2	15.0	4.37	17.0	1418
	600	30.3	64.3	32.0	16.8	13.9	4.97	19.5	1530

Table 6

Performance of 5% V_2O_5 /MgO- Al_2O_3 catalyst for the n -butane ODH ($T = 600$ °C).

GHSV (mL/(g·h))	$n-C_4H_{10}/O_2$ ratio	$X_{n-C_4H_{10}}$ (%)	Selectivity (%)					$C_{4^{\text{=}},\text{tot}}$ yield (%)	STY (g/(kg·h))
			$C_{4^{\text{=}},\text{tot}}$	1,3- C_4H_6	CO_2	CO	Others		
7500	1.2/1	32.7	59.7	27.9	22.7	13.1	4.55	19.5	533
	1.5/1	27.2	61.3	24.1	18.9	13.1	6.76	16.7	454
	2/1	24.3	64.2	24.9	18.0	11.5	3.37	15.6	424
51000	1.2/1	35.5	61.7	33.4	18.7	14.3	5.25	21.9	1736
	1.5/1	30.3	64.3	32.0	16.8	13.9	4.97	19.5	1530
	2/1	24.1	68.8	30.6	15.3	12.4	3.60	16.6	1298

Table 7Comparison with literature results at a similar *n*-butane conversion.

Catalyst	$X_{n-C_4H_{10}}$ (%)	Selectivity (%)		[Ref.]
		$C_4^{\pm, tot}$	1,3- C_4H_6	
5%-V ₂ O ₅ /MgO-Al ₂ O ₃	30.3	64.3	32.0	This work
V ₂ O ₅ /MgO-ZrO ₂	32.9	43.1	33.2	[15]
CoMoO ₄	27.4	37.9	15.3	[25]
V ₂ O ₅ /MgO	29.5	52.0	27.0	[32]
NiO-V ₂ O ₅ /MgO	25.8	42.8	14.9	[37]
V ₂ O ₅ /MgO	31.8	55.8	—	[38]
MoO ₃ -V ₂ O ₅ /MgO	24.2	68.5	39.8	[39]
V ₂ O ₅ /SiO ₂	36.0	60.0	21.0	[40]

Table 7 gives a comparison of the catalytic performance of the 5%-V₂O₅/MgO-Al₂O₃ catalyst in this study compared with those reported in the literature at similar *n*-butane conversion. It can be found that the catalyst developed in this study has both higher 1,3- C_4H_6 and $C_4^{\pm, tot}$ selectivity than most of the reported catalysts [38–40]. The high performance was related to that the well dispersed VO_x species and the existence of MgO crystalline phase, which were both fulfilled at 5% V₂O₅ loading.

4. Conclusions

V₂O₅/MO-Al₂O₃ (M = Mg, Ca, Sr, Ba) catalysts were synthesized by wet impregnation. Their catalytic performance was tested with the *n*-butane ODH reaction. For the catalysts doped with Ca, Sr or Ba, the orthovanadate phase was difficult to reduce under the reaction conditions, so the redox cycle of the catalysts was difficult to be established. The catalyst doped with Mg that showed high catalytic activity was easier to reduce than those with the other alkaline earth dopants. The higher specific surface area of the Mg modified support gave

high dispersion of VO_x species, while 5% V₂O₅ loading allowed the existence of the MgO crystalline phase. Therefore, the 5%-V₂O₅/MgO-Al₂O₃ catalyst exhibited high catalytic activity and butene selectivity. Under the optimal operation conditions, a *n*-butane conversion of 30.3%, $C_4^{\pm, tot}$ selectivity of 64.3%, and STY of 1530 g/(kg·h) were achieved at 600 °C.

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Graphical Abstract

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Catalytic oxidative dehydrogenation of *n*-butane over V₂O₅/MO-Al₂O₃ (M = Mg, Ca, Sr, Ba) catalysts

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V₂O₅/MgO-Al₂O₃ catalysts prepared by a modified sol-gel and wet impregnation method showed high catalytic activity and selectivity for the oxidative dehydrogenation of *n*-butane. The high dispersion of VO_x species and the existence of the MgO crystalline phase were important for the good catalytic performance.

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V₂O₅/MO-Al₂O₃ (M = Mg, Ca, Sr, Ba) 催化剂用于正丁烷催化氧化脱氢反应

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摘要: 采用浸渍法制备了不同V₂O₅负载量的V₂O₅/MO-Al₂O₃ (M = Mg, Ca, Sr, Ba) 催化剂, 钒物种的前驱体为偏钒酸铵. 对制备的催化剂进行了一系列表征, 并对催化剂上正丁烷选择性氧化脱氢制取丁烯进行了反应研究. 表征结果(包括比表面积、X射线衍射、傅里叶红外光谱、氢气程序升温还原和拉曼光谱)显示, 不同碱土金属元素掺杂的催化剂显示不同的钒价态信息和催化性能. 其中掺杂Ca, Sr, Ba的催化剂, 正钒酸盐相很难被还原, 因此催化剂的氧化还原循环难以建立, 导致以上三种催化剂在正丁烷氧化脱氢反应中活性较低. 然而, Mg掺杂的催化剂却显示出较高的催化活性和选择性. 实验结果表明: 在Mg掺杂的载体上负载5% V₂O₅的催化剂上600 °C时可获得高达30.3%的正丁烷转化率和64.3%的烯烃总选择性. 这与V₂O₅负载量为5%时, 在获得高度分散的钒氧化物物种时可使MgO晶相稳定存在密切相关.

关键词: 氧化脱氢; 正丁烷; 丁烯; 氧化镁; 氧化铝; 钒基催化剂

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