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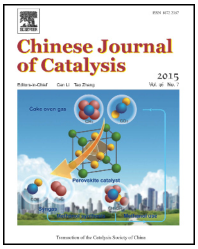

Article

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

Bing Xu [a,b], Xuefeng Zhu [b,*], Zhongwei Cao [a,b], Lina Yang [a,#], Weishen Yang [b]

[a] *School of Petrochemical Engineering, Liaoning Shihua University, Fushun 113001, Liaoning, China*
[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

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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%.

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 dehydrogenation (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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[*] Corresponding author. Tel: +86-411-84379301; Fax: +86-411-84694447; E-mail: zhuxf@dicp.ac.cn
[#] Corresponding author. Tel: +86-024-56865618; Fax: +86-024-56861709; E-mail: lnqdsd@aliyun.com

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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-Al_2O_3 supported vanadium catalysts have been reported in several studies [1,24,25] because γ-Al_2O_3 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-Al_2O_3 surface, and thus crystalline V_2O_5 is frequently found at high loading.

Here, alkaline earth metal oxide-doped Al_2O_3 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 V_2O_5 loading were prepared to study the relationship between V_2O_5 loading and catalytic performance.

2. Experimental

2.1. Catalyst preparation

MO-Al_2O_3 (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-Al_2O_3 (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 V_2O_5/MO-Al_2O_3 catalysts with different V_2O_5 loading (mass ratio), an aqueous solution containing ammonium metavanadate and oxalic acid (molar ratio = 1:2) was added to the MO-Al_2O_3 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 V_2O_5/MO-Al_2O_3 catalyst and V_2O_5/MgO-Al_2O_3 catalysts with different V_2O_5 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. H_2 temperature programmed reduction (H_2-TPR) was performed to observe the reducibility of the catalysts. Prior to the analysis, 100 mg of sample was treated in 20% O_2–80% N_2 (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% H_2–95% N_2 (30 mL/min). The H_2 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 Al-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 N_2 (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, O_2 and N_2 (*n*-butane:O_2 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 O_2, N_2 and CO. The conversion of *n*-butane, selectivity to total butenes (including 1-C_4H_8, 2-*t*-C_4H_8, 2-*c*-C_4H_8, 1,3-C_4H_6) 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:

$$n\text{-butane conversion, } X_{n\text{-C4H10}}\ (\%) = \frac{\sum Mi \times ni}{4 \times \text{moles of } n\text{ - butane feeded}} \times 100$$

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