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Dehydrogenation of Isobutane to Isobutene over V_2O_5/γ-Al_2O_3 Catalysts: Effects of the Extent of Catalyst Reduction on Catalytic Performance

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V_2O_5/γ-Al_2O_3 catalysts for the dehydrogenation of isobutane to isobutene were prepared by impregnation and characterized by BET, H_2-TPR, ESR and XPS. Based on our studies of the effects of the extent of catalyst reduction on catalytic performance, we conclude that the V_2O_5/γ-Al_2O_3 catalytic activity for the dehydrogenation of isobutane is related to the valence state of vanadium present in the catalyst, in the order of $V^{4+} > V^{3+}$. Furthermore, V^{4+} species are the main active sites of this reaction under the present reaction conditions.

Key words: dehydrogenation, isobutane, reduction, vanadium oxide

Vanadium oxide on different supports have been widely used as catalysts for the partial oxidation of hydrocarbons, the oxidative dehydrogenation and the reduction of NO with NH_3, *etc.* [1–11]. However, the dehydrogenation of alkane, to corresponding alkene using vanadium oxide catalysts, has not been widely reported [12–15]. The structure of the vanadium oxide catalyst has been extensively studied by different techniques [12,13,16–25]. The extent of reduction of vanadium oxide in the catalysts obviously depends on the support. For example, V_2O_5/Al_2O_3 catalysts exhibited an average degree of reduction closely corresponding to that of VO_2, whereas for V_2O_5/SiO_2 catalysts the reduction of V_2O_5 to V_2O_3 was about 70% as reported in [21]. However, Harlin *et al.* observed different results for the reduction of V_2O_5/Al_2O_3 catalyst and reported that the surface vanadium can be reduced to V^{4+} and V^{3+} states. A few reports of the effect of the reduction of vanadium oxide catalysts on the catalytic dehydrogenation of alkanes have been published [12,13].

In this paper, we examine the effects of the oxidation states of vanadium on the activity regarding the dehydrogenation of isobutane. The characterization of the V_2O_5/Al_2O_3 samples was carried out using BET, H_2-TPR, ESR and XPS. A catalyst with the vanadium content of 10wt% on alumina support was chosen for the study, because the vanadium oxide could be well dispersed on the alumina surface [26], and the catalytic activity for the dehydrogenation could be optimized.

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EXPERIMENTAL

Catalysts: Catalysts with 10 wt% V_2O_5 loading were prepared by impregnation. A desired amount of NH_4VO_3 solution was added to γ-Al_2O_3 (176 m^2/g, manufactured by Beijing Research Institute of Chemical Industry). The product was dried upon stirring on water bath at 70°C for 2 h. It was further dried at 120°C for 8 h and calcined in air at 550°C for 15 h.

Characterization: The ESR spectra of the samples were recorded on a JES-FE2XG spectrometer with 9.5 GHz (X band) modulation at ambient temperature. The samples reacted in dehydrogenation of isobutane at different time were put in each quartz tube in nitrogen atmosphere (99.99%) respectively and the quartz tubes were sealed using a plasticine for the ESR measurement. Temperature Programmed Reduction (TPR) measurements were performed in a quartz tube with 30 mg of pre-reduction samples in a dried mixed gas of H_2/N_2 with a ratio 1:10. The quartz tube can be used also to the pre-reduction of the catalyst before the TPR. The tabular furnace was linearly heated from room temperature to 900°C (15°C/min). The hydrogen consumption was detected by Thermal Conductivity Detector (TCD) and recorded by a Shimadzu C-R6A data detector. The oxidation states of vanadium on the surface of pre-reduced catalysts were investigated by X-ray photoelectron spectroscopy (XPS). The pre-reduced samples were transferred into the XPS chamber. XPS spectra were recorded using a VG-ESCA lab MK II spectrometer equipped with a MgK_α X-ray excitation source and hemispherical electron analyser. The C1s lines were taken as internal references. The curves were fitted by the least square method assuming Gaussian-shaped lines. The preparation procedure of the pre-reduced samples for the measurement of TPR and XPS is as follows: Fresh catalysts were heated at 600°C in mixed gas O_2/N_2 (1/10) for a half hour first, and then were pre-reduced by a mixed gas of H_2/N_2 (1/10) at 580℃ for 0, 30 and 1200 minutes respectively. Some of the samples were stored in sample tubes in nitrogen atmosphere (99.99%) for XPS measurement. Surface areas of the samples were measured by BET with micrometrics ASAP 2010.

Catalytic test: Catalytic tests were carried out in a conventional fixed bed flow apparatus. The reactor was a stainless steel tube, in which a thermocouple was inserted. 0.5 g of the catalyst was loaded in the reactor. The pre-reduction of the catalyst also was performed *in situ* in the same reactor. The reaction gas was 99.9% isobutane and the space velocity was about 1000 h^{-1}. The reaction temperature was 580°C. The reactant and the products were analyzed by gas chromatography (Shimadzu GC-8A with $AgNO_3$-benzyl column at room temperature and Shimadzu C-R6A data detector). A small amount of by-products such as methane, ethane, propane, butane, propene, 1-butene and 2-butene were detected besides isobutene.

RESULTS AND DISCUSSION

The activities of the dehydrogenation of isobutane to isobutene over V_2O_5/γ-Al_2O_3 catalysts at different temperatures are summarized in Fig. 1. The conversion of isobutane increases with temperature increase. On the other hand, the selectivity of isobutene decreases with the increase of temperature. In addition, we observed an interesting phenomenon illustrated in Fig 1: The isobutane conversion increases with the reaction time at lower reaction temperatures, but at higher temperatures it even decreases. We think that such phenomenon was caused by the reaction of vanadium oxide on the support surface to a certain oxidation state, leading to better dehydrogenation activity. Therefore, we further studied the change of oxidation states, regarding V_2O_5/γ-Al_2O_3 catalysts for the dehydrogenation of isobutane to isobutene at a lower temperature (580°C) using ESR. The conversion of isobutane and the relative intensity of ESR signal of V^{4+} species are summarized in Fig. 2. We found that the relative intensity of V^{4+} ESR signal increases with the increase of reaction time and it reaches a maximum before declining. Furthermore, comparing the conversion of isobutane to the relative intensity change of V^{4+} ESR signal, a similar trend is observed and both reach maximum values at approximately the same reaction time (30 min). These results suggest that the activity of the catalysts is related to the concentration of V^{4+} species and V^{4+} species exhibit the highest activity in the dehydrogenation of isobutane.

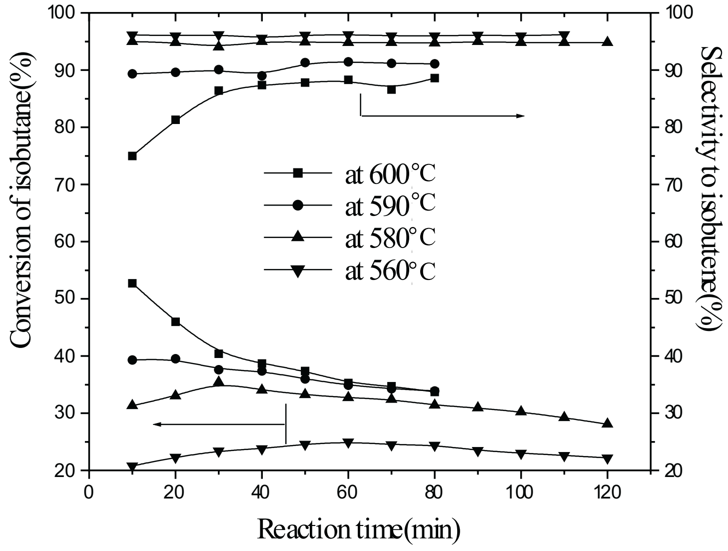

Figure 1. The dehydrogenation of isobutane to isobutene over V_2O_5/γ-Al_2O_3 at different temperature.

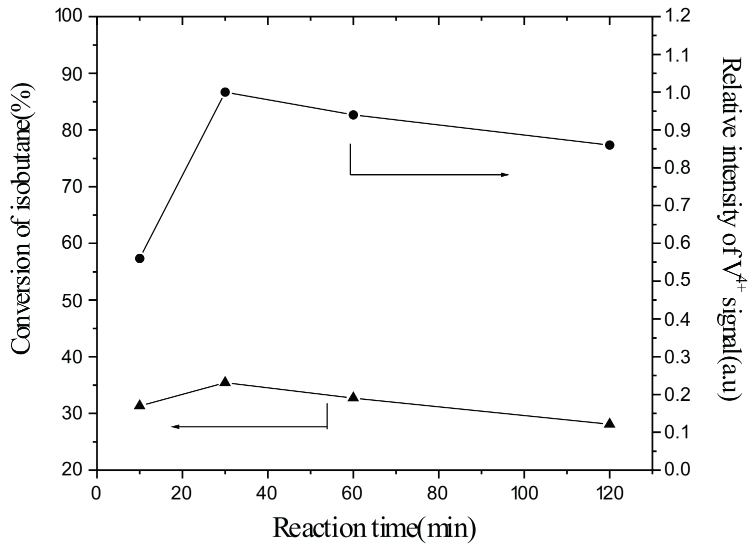

Figure 2. Conversion of isobutane and relative intensity of ESR signal.

Based on the above results, we propose that the extent of reduction of V_2O_5/γ-Al_2O_3 catalyst will affect its catalytic activity. Therefore, we studied the reduction of the catalysts by using V_2O_5/γ-Al_2O_3 pre-reduced by hydrogen at 580°C for 0, 30 and 1200 minutes, respectively. Their catalytic activities for the isobutane dehydrogenation are shown in Fig. 3. For these three samples, the difference in isobutane conversion is apparent, whereas their selectivities to isobutene are similar. The sample pre-reduced for 30 minutes shows a higher catalytic activity than the other two, and the activity rapidly decreases as reaction time increases. Moreover, the catalyst pre-reduced for 1200 minutes exhibits a lower catalytic activity and the activity changes less drastically with regard to reaction time, when compared with the other two samples.

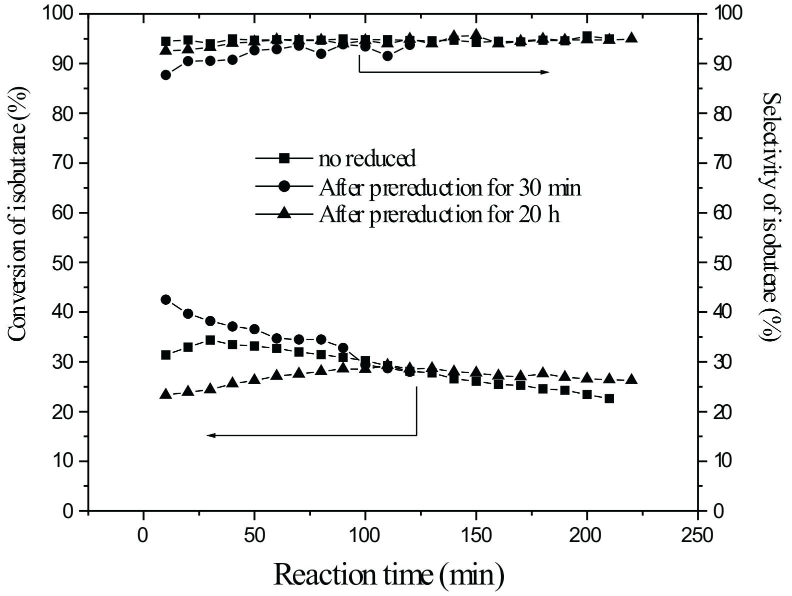

Figure 3. The catalytic performance of unreduced and prereduced catalysts.

The TPR profiles of the catalysts after pre-reduction are shown in Fig. 4. The pre-reduced catalyst for 30 minutes exhibits a comparable hydrogen consumption to that of a fresh catalyst, whereas the catalyst pre-reduced for 1200 minutes does not exhibit any hydrogen consumption. We further obtained the average oxidation states of vanadium oxide after pre-reduction with hydrogen using TPR. The results are summarized in Table 1. The vanadium oxide was reduced from V^{5+} to $V^{3.8+}$ and $V^{3.1+}$ for catalysts pre-reduced for 30 and 1200 minutes, respectively. These pre-reduced catalysts were also studied by XPS. The results are also summarized in Table 1 and the peak fitting is shown in Fig. 5. It is found that the $V2p_{3/2}$ binding energies apparently shifted to lower values with the increase of pre-reduction time. Each of the original profiles was fitted into two peaks (Fig. 5a and Fig. 5b) and one peak (Fig. 5c). The average oxidation state, calculated from XPS for the fresh catalyst and catalysts pre-reduced for 30 and 1200 minutes, are approximately 4.8+, 3.7+ and 3.0+, respectively.

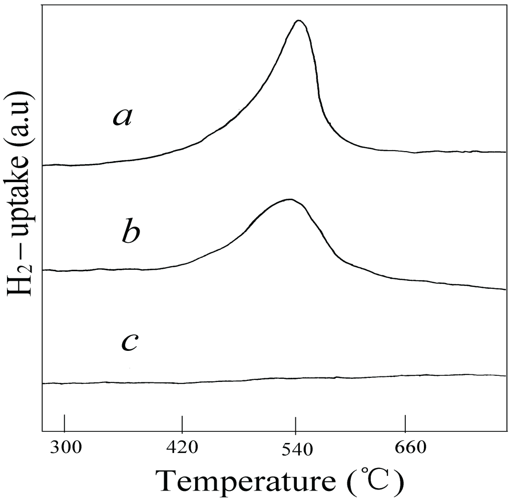

Figure 4. The H_2-TPR profiles of unreduced and prereduced catalysts: a. unreduced, b. prereduced for 30 min, c. prereduced for 1200 min.

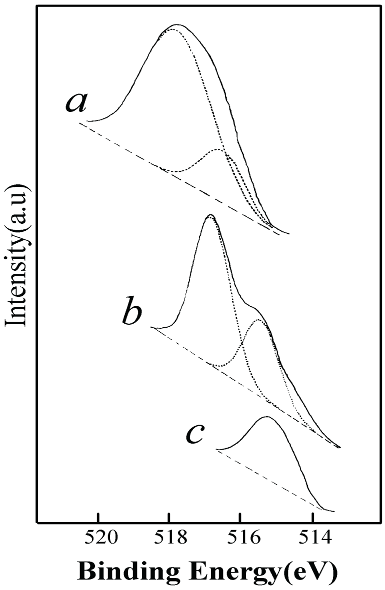

Figure 5. The XPS spectra of unreduced and prereduced catalysts: a. unreduced, b. prereduced for 30 min, c. prereduced for 1200 min.

Table 1. The XPS parameter, average oxidation state of V and specific surface area of catalysts after hydrogen prereduction.

Treatment	XPS parameter			Average oxidation state of V		Specific surface area (m^2/g)
	V^{5+}	V^{4+}	V^{3+}	XPS	H_2-TPR	
Calcination	80% 517.6 eV	20% 516.5 eV		4.8		137
Prereduced for 30 min		70% 516.6 eV	30% 515.3 eV	3.7	3.8	160
Prereduced for 20 h			100% 515.2 eV	3.0	3.1	142

Based on our studies of the effects of the extent of catalyst reduction on catalytic performance, we conclude that the V_2O_5/γ-Al_2O_3 catalytic activity for the dehydrogenation of isobutane to isobutene is related to the valence state of vanadium present in the catalyst. Their activity is in the order of $V^{4+} > V^{3+}$. Furthermore, V^{4+} species are the main active sites of the dehydrogenation of isobutane under the present reaction condition.

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