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Effect of Potassium Modification on Structure and Reactivity of V_2O_5/γ-Al_2O_3 for Isobutane Dehydrogenation to Isobutene

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Undoped and K-doped V_2O_5/γ-Al_2O_3 catalysts for the dehydrogenation of isobutane to isobutene were prepared by impregnation and characterized by means of BET, H_2-TPR, NH_3-TPD, XPS and ESR. It is found that potassium addition changes acidic and electric properties of V_2O_5/γ-Al_2O_3 and results in a better spreading of V_2O_5 over γ-Al_2O_3 surface. Small addition of potassium to V_2O_5/γ-Al_2O_3 catalyst (K:V = 0.05), consisting of 12 wt% V_2O_5, increased the activity and selectivity in dehydrogenation of isobutane to isobutene.

Key words: K-doped V_2O_5/γ-Al_2O_3, surface structures, dehydrogenation, isobutane

Supported vanadia-containing catalysts have been widely used because of their high catalytic activity in oxidative dehydrogenation and dehydrogenation of light alkanes to the corresponding alkenes, as well as in many oxidation processes [1–8]. The catalytic properties of vanadia-based catalysts depend on various factors, such as the preparation method, thermal treatment, V_2O_5 loading, the nature of support, and presence of metal additives, *etc* [9–12]. The effects of alkali addition to the supported vanadia catalysts on their acidic properties and surface structures have received much attention because of their basic properties and electropositivity. Various vanadia-based catalysts with alkaline metal addition have been reported [13–15]. Generally, alkali addition results in decreasing the Brønsted acidity. However, Lietti *et al.* reported that both Brønsted and Lewis acid sites were poisoned by the potassium doping on vanadia/titania de-NO_xing catalysts [16]. There are some contrary views on the effect of alkali metal in selective catalytic reduction (SCR) [17–18]. For the oxidative dehydrogenation of olefins on the alkalis doped vanadia catalyst, some authors indicate that the role of alkalis consists in decreasing the catalyst acidity and increasing its basicity. The change of acido-basic properties makes desorption of an olefin easy and prevents combustion reaction or coke formation, thus increasing the selectivity to olefin [1,19,20].

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The purpose of this paper was to examine how potassium oxide affects the surface structure of $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts and their reactivity in isobutane dehydrogenation. Therefore, we have studied such undoped and K-doped catalyst by various techniques and the catalytic activity measurements.

EXPERIMENTAL

Catalysts: The catalysts with 12 wt% V_2O_5 loading were prepared by the impregnation method. The desired amount of KOH and NH_4VO_3 solution was added into $\gamma\text{-}Al_2O_3$ (161 m^2/g, Beijing Research Institute of Chemical Industry), then it was dried upon stirring on water bath at 70°C for 2 h. The samples were further dried at 120°C for 8 h and calcined in air at 550°C for 15 h.

Characterization: Surface areas of the catalysts were measured by the BET method with a mictomeritics Asap model 2010. Temperature programmed reduction (TPR) measurements were performed in a quartz tube with 30 mg catalyst in a dried gas mixture of H_2/N_2 with a ratio 1/10. The tubular furnace was linearly heated from room temperature to 900°C at a heating rate of 15°C/min. The hydrogen consumption was detected by a thermal conductivity detector (TCD). Temperature programmed desorption (TPD) of NH_3 were carried out in quartz tube reactor with a tubular furnace which was heated at a rate of 10°C/min between 100°C to 400°C. A stream of N_2 at a rate of 40 $cm^3\ min^{-1}$ was allowed to pass over the reactor in which 50 mg of catalyst was packed. To prevent physisorption of NH_3, the catalysts were kept at 100°C for sufficiently long time. The desorbed NH_3 was detected by TCD. The ESR spectra of undoped and potassium doped catalysts were recorded on a JES-FE2XG spectrometer with 9.5 GHz (X band) modulation at ambient temperature. XPS spectra were recorded by using a VG-ESCA lab MK II spectrometer working in the constant analyzer energy mode with a pass energy of 50 eV and Mg K_α radiation as the excitation source. The C1s lines were taken as internal references.

Catalytic test: The catalytic tests were carried out in a conventional fixed bed flow apparatus of a stainless steel tube, in which a thermocouple was inserted. 0.5 g of a catalyst was loaded in the reactor. The reaction gas was 99.9% isobutane and the space velocity was about 1000 h^{-1}. The reactant and the products were analyzed using a Shimadzu GC-8A gas chromatography with column of $AgNO_3$– benzyl at room temperature and Shimadzu C-R6A data-detector.

RESULTS AND DISCUSSION

The activity of isobutane dehydrogenation over bare and K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts and their specific surface area are listed in Table 1. The selectivity to isobutene increases with the increase of potassium content, while the conversion of isobutane reaches a maximum value when the potassium content is K/V = 0.05. Furthermore, the effect of the smaller potassium content (K/V = 0.02) is obscure. It can be found from Table 1 that specific surface area of the catalysts increases to a certain extent after the doping with potassium.

Temperature programmed reduction (TPR) profiles of undoped and K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts with various potassium content are shown in Fig. 1. The reduction of $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts obviously depends on the potassium content. The reduction temperature increased with the increase of potassium content. The increase of the reduction temperature for K-doped catalysts is ascribed to strong electropositivity of potassium. The reduction temperature of K-$V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.02) is similar to the undoped $V_2O_5/\gamma\text{-}Al_2O_3$, indicating that such small amount of potassium does not affect the vanadia species on the catalyst surface and its activity (see Table 1). Similar TPR results have been observed in the case of V_2O_5/ZrO_2 catalysts [21].

Table 1. Catalytic performance of catalysts with different K content for isobutane dehydrogenation to isobutene and hydrogen.

Catalysts (K/V)	K/V = 0	K/V = 0.02	K/V = 0.05	K/V = 0.1
Conversion (%)	38.6	38.1	43.2	40.4
Selectivity (%)	89.0	90.9	91.4	92.3
Specific surface area (m^2/g)	137	140.5	148.4	142.7

*at 590°C, GHSV = 1000 h^{-1}, reaction time 30 min.

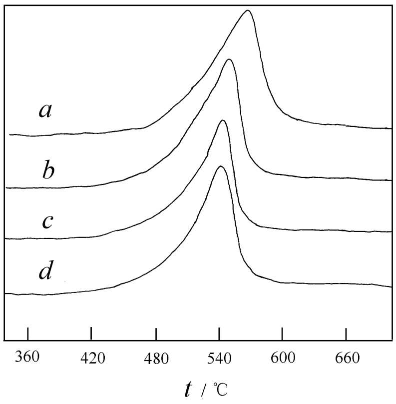

Figure 1. The TPR profiles of undoped and K-doped V_2O_5/γ-Al_2O_3 catalysts: *a*. V_2O_5/γ-Al_2O_3 (K/V = 0.1); *b*. V_2O_5/γ-Al_2O_3 (K/V = 0.05); *c*. V_2O_5/γ-Al_2O_3 (K/V = 0.02); *d*. V_2O_5/γ-Al_2O_3 (K/V = 0).

Fig. 2 shows the NH_3-TPD curves for V_2O_5/γ-Al_2O_3 and K-doped V_2O_5/γ-Al_2O_3 catalysts with various potassium contents. One strong NH_3 desorption peak at ≈130°C appears in all catalysts, which was ascribed to the desorption of coordinately held NH_3 from the Lewis acid sites. Furthermore, the other peak at ≈170–250°C is attributed to the desorption of NH_3 from Brønsted acid sites of vanadium oxide adsorbed on alumina [22]. This NH_3-TPD profile shows that doping with potassium strongly affects the amount of Brønsted acid sites and less affects the amount of Lewis acid sites, suggesting that strong interaction occurs between potassium and vanadium oxide as an interacting additives.

In order to understand better the effect of potassium on the Brønsted acid sites, we have assembled the TPD profiles of catalysts with various potassium contents in Fig. 3, which clearly shows that the decrease of the Brønsted acid amount and the increase of NH_3 desorption temperature are related to the increasing of potassium content, which indicates that the potassium introduced into the catalysts first replaces the weaker Brønsted acid sites on the catalysts surface. The change of the acid amount is accompanied by the change of the isobutene selectivity.

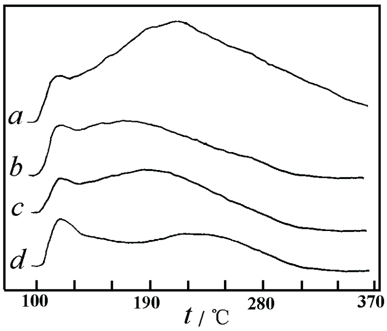

Figure 2. The TPD profiles of undoped and K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts: *a*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0); *b*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.02); *c*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.05); *d*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.1).

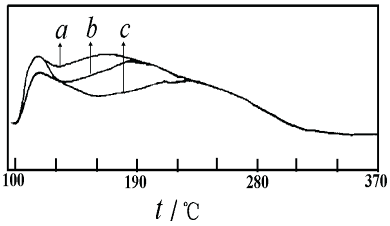

Figure 3. The superposition of the TPD profiles for K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts: *a*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.02); *b*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.05); *c*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.1).

Furthermore, the XPS measurements of undoped and K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ have been carried out. As shown in Figure 4, the $V2p_{3/2}$ binding energies of undoped $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst is higher than that of K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts, moreover, the $V2p_{3/2}$ binding energies shift to lower values with the increase of potassium content. The XPS experiment indicates that a strong electronic interaction occurs between K and V oxides at the surface of the support. This interaction leads to a lower reducibility of the K-doped sample with respect to the corresponding undoped ones (as shown Fig. 1).

In Figure 5 the ESR spectrum of the undoped $V_2O_5/\gamma\text{-}Al_2O_3$ is compared to the one of K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.1). The resolved hyperfine structure, characteristic of isolated V^{4+} species can be observed in undoped and potassium-containing samples. Furthermore, a better resolved hyperfine structure and a stronger ESR signal have been observed in the potassium-containing sample than in the undoped catalyst. The ESR spectra suggest that vanadium oxides are dispersed more on the surface of K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst than on the undoped catalyst [21]. Thus, the potassium additive plays an important role in improving the dispersion of the vanadium oxide surface. The dispersion of vanadium species correlates with the conversion of isobutane (Table 1). K-doping promotes the dispersion of vanadia and increases the conversion of isobutane. The better dispersion of vanadia phase in the presence of po-

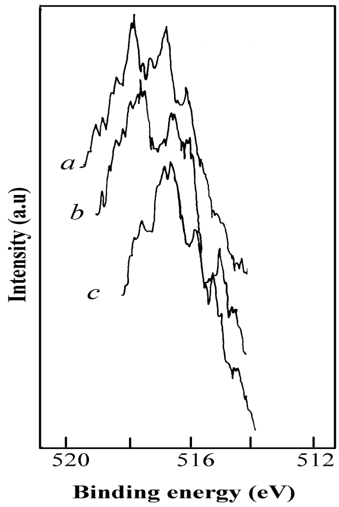

Figure 4. The XPS spectra of undoped and K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts: *a*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0); *b*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.05); *c*. $V_2O_5/\gamma\text{-}Al_2O_3$ (K/V = 0.1).

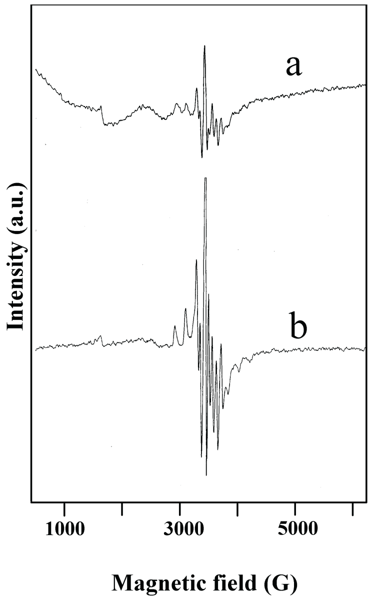

Figure 5. The ESR spectra of undoped and K-doped $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts: *a*. undoped $V_2O_5/\gamma\text{-}Al_2O_3$; *b*. K-doped $V_2O_5/\gamma\text{-}Al_2O_3$.

tassium in supported vanadia catalysts has been directly observed by TEM studies [23]. However, higher amounts of K lead to the formation of potassium vanadates [24–25] and to the decrease of isobutane conversion.

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