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Effect of different $VOPO_4$ phase catalysts on oxidative dehydrogenation of cyclohexane to cyclohexene in acetic acid

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Abstract

α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ have been investigated as catalysts for the gas phase oxidative dehydrogenation (ODH) of cyclohexane to cyclohexene with the addition of acetic acid (HOAc) in the feeds in a fixed bed reactor. Different $VOPO_4$ phases showed different acidity and reducibility. β-$VOPO_4$ phase is more active than α_I-$VOPO_4$ and α_{II}-$VOPO_4$ in the ODH without acetic acid addition. In the presence of acetic acid, the acidity of the catalyst may play an important role in the ODH process. Due to higher acidity, α_I-$VOPO_4$ phase catalyst gives better catalytic performances than α_{II}-$VOPO_4$ and β-$VOPO_4$ for the ODH of cyclohexane by adding of acetic acid in the reactants.

Keywords: α_I, α_{II}, β-$VOPO_4$ catalysts; Oxidative dehydrogenation; Cyclohexane; Cyclohexene; Acetic acid

1. Introduction

Catalytic selective oxidative dehydrogenation (ODH) of cycloalkane has been the subject of many studies due to the importance of refining and reforming process in the petroleum industry, but there are very few practical processes for converting alkanes directly to more valuable products [1,2]. As the aimed products transformed from alkanes are usually relatively active than consequent alkanes, therefore, it is hard to control the high conversion of alkanes with high selectivity of alkene simultaneously [3]. Cyclohexene is one of chemicals of considerable industrial importance which is a valuable intermediate for producing cyclohexanol, cyclohexanone, epoxycyclohexane, adipic acid, the precursors for nylon-6,6 and nylon-6 [4–6]. Cyclohexene obtained by oxidative dehydrogenation of cyclohexane has been reported by using vanadate, molybdena and zeolite catalysts [7–10]. However, obtaining a high selectivity of cyclohexene from the oxidative dehydrogenation of cyclohexane is difficult owing to the deep dehydrogenation to benzene which is thermodynamically much more favorable [11]. In previous study, we reported a new route to control the product selectivity in gas phase catalytic oxidative dehydrogenation of cyclohexane and cyclohexene over vanadium phosphorus oxide (VPO) catalyst with the addition of acetic acid (HOAc) in the feed [12].

VPO is an active catalyst well known in the vapor phase oxidation of *n*-butane to maleic anhydride (MA) [13,14]. Vanadium phosphorous oxide catalysts have also been widely investigated for the partial oxidation and oxidative dehydrogenation of others lower hydrocarbons [15–20]. V^{5+} species play an important role in abstracting H-atom from alkanes [21,22]. However, vanadyl phosphate phases ($VOPO_4$ V^{5+}) have been received less attention in the oxidative dehydrogenation of alkanes. Lisi et al. detailed reported the correlation between physical–chemical properties and catalytic activity in the ethane oxidative dehydrogenation to ethene in the use of vanadyl phosphate and vanadyl phosphate supported on oxides (TiO_2, γ-Al_2O_3 and SiO_2) as catalysts [23–26].

Various $VOPO_4$ (V^{5+}) crystalline structures reveal the different reactivity. α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ phases have similar structure with $VOPO_4 \cdot 2H_2O$, each equatorial oxygen of VO_6 sharing a corner of one PO_4, with vanadyl chains

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running in the perpendicular direction, but the oxygen of PO_4 being shared with the VO_6 is different, which lead to the different catalytic activity [14,27].

Here the effect of different $VOPO_4$ (V^{5+}) catalysts (i.e. α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$) on gas phase-oxidative dehydrogenation of cyclohexane to cyclohexene with the addition of acetic acid (HOAc) in the feeds is reported.

2. Experimental

2.1. Catalyst preparation

Different VPO phases were prepared from the two precursors $VOPO_4 \cdot 2H_2O$ and $NH_4(VO_2)_2PO_4 \cdot VOPO_4 \cdot 2H_2O$ was prepared by long-term boiling of V_2O_5 in aqueous phosphoric acids as previously described [28]. $NH_4(VO_2)_2PO_4$ was obtained by adding 85% H_3PO_4 to a solution of NH_4VO_3 according to reference [29].

α_I-$VOPO_4$ was obtained by calcining the precursor, $VOPO_4 \cdot 2H_2O$, at 500 °C for 8 h under air atmosphere and α_{II}-$VOPO_4$ catalyst was prepared as above but calcined at 750 °C for 17 h. β-$VOPO_4$ catalyst was obtained by the decomposition of $NH_4(VO_2)_2PO_4$ in dry air with a heating rate of 1.25 °C min^{-1} and kept temperature at 600 °C for 10 h [29,30].

2.2. Characterization of catalysts

X-ray diffraction patterns (XRD) of the catalysts were obtained with a D/Max-IIB X-ray diffractometer (Rigaku Co.) at room temperature. Ni-filtered, Cu Kα radiation was used.

Temperature programmed desorption of ammonia (NH_3-TPD) and temperature programmed reduction with hydrogen (H_2-TPR) were carried out using a GC102 gas chromatography equipped with TCD as a detector. In TPD experiments the sample (0.1000 g) was saturated with pure ammonia at room temperature for 1 h, after purging with pure He for 3 h, it was heated to 500 °C at constant rate (10 °C min^{-1}) in flowing He (50 $cm^3\,min^{-1}$). Before saturating with pure ammonia the samples were treated in flowing helium (40 $cm^3\,min^{-1}$) at 400 °C for 1 h in order to clean up the adsorbed water. In TPR experiments, the sample (0.0250 g) was reduced with a 5%H_2/N_2 mixture (25 $cm^3\,min^{-1}$) by heating to 650 °C at a rate of 10 °C min^{-1}.

BET surface areas were measured by N_2 adsorption at 77 K with a Micromeritics ASAP 2010 instrument.

2.3. Catalytic procedure

ODH of cyclohexane reactions were preformed in a fixed-bed reactor made of quartz glass tube of 6 mm inner diameter operated isothermally at atmospheric pressure. 0.20 g of the VPO catalysts (40–80 mesh) was adopted in the test and cyclohexane was fed at a flow rate of 9.25×10^{-3} mol h^{-1} by means of a micro-perfusion pump. Acetic acid was also fed at a different flow rate by means of another micro-perfusion pump. The flow rate of air was maintained at 40 $cm^3\,min^{-1}$ by a mass flow controller for all experiments. The system was allowed to stabilize for 60 min before the first product sample was taken for analysis. The product stream at reactor exit was collected in a liquid nitrogen trap. Blank test showed that the reactor was inert with respect to cyclohexane oxidative dehydrogenation in the temperature range investigated. The products were analyzed by gas chromatography employing a β,β′-oxydipropionitrile column for cyclohexane, cyclohexene, cyclohexidene and benzene separation, XE-60 column (13.5 m × 0.25 mm) for maleic anhydride equipped with flame ionization detector and porapak Q column for HOAc with TCD. N_2, O_2, CO_x were separated by β,β′-oxydipropionitrile and 5A molecular-sieve column with TCD. Mole conversion of cyclohexane is defined as $[(M_0 - M_i)/(M_0)] \times 100\%$, where M_0 is the initial number of moles of cyclohexane feeding to the reactor per unit time and M_i is the number of moles of cyclohexane exiting from the reactor. Mole selectivity in terms of products C_6 is calculated by $[(M_{C_6})/(M_0 - M_i)] \times 100\%$, where M_{C_6} is the number of moles of individual C_6 compound in the product (C_6 indicate cyclohexene, cyclohexadiene or benzene). The carbon balance was measured within a ±5% error.

3. Results

3.1. H_2-TPR results

Results of hydrogen temperature programmed reduction (H_2-TPR) experiments carried out on α_1-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ samples are reported in Fig. 1. α_I-$VOPO_4$ sample gives rise to a single, almost symmetric peak with maximum temperature at 615 °C, and a small undistinguishable shoulder peak by the left of the main reduction peak. Both of H_2-TPR of α_{II}-$VOPO_4$ and β-$VOPO_4$ samples show two reduced peaks, at 550 and 622 °C for β-$VOPO_4$, at 571 and 615 °C for α_{II}-$VOPO_4$.

3.2. NH_3-TPD results

The surface acidity of the different VPO phase catalysts has been measured by ammonia adsorption. Fig. 2 shows the NH_3-TPD curves of α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts

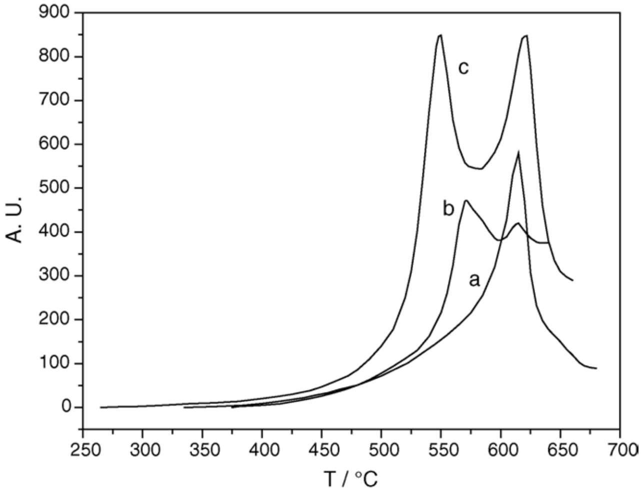

Fig. 1. H_2-TPR curves of fresh VPO catalysts (a, α_I-$VOPO_4$; b, α_{II}-$VOPO_4$; c, β-$VOPO_4$).

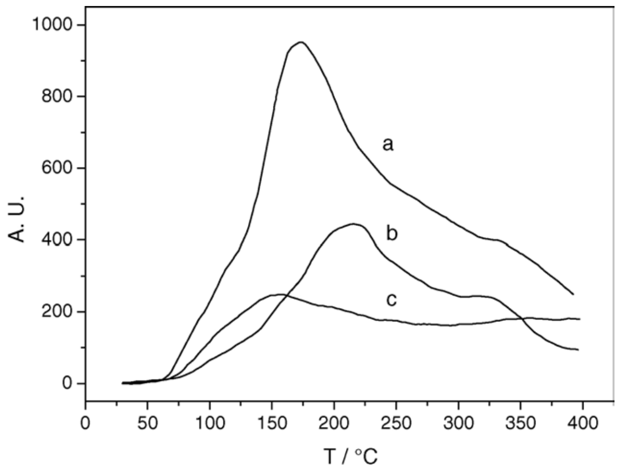

Fig. 2. NH_3-TPD curves of fresh VPO catalysts (a, α_I-$VOPO_4$; b, α_{II}-$VOPO_4$; c, β-$VOPO_4$).

and the relevant amounts of desorbed NH_3. Two peaks are recognizable for the NH_3-TPD curves of every VPO sample. A well-defined peak, with maximum temperature at 172, 216 and 159 °C was arisen from α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$, respectively, and another shoulder peak at about 335 °C for all samples.

3.3. Catalytic test results

Catalytic reaction of cyclohexane with air over α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts only dehydrogenation and/or deeply oxidation products were obtained in the temperature range $400\,°C \leq T \leq 500\,°C$, but no cyclohexanol or cyclohexanone were observed.

The product distribution of oxidation of cyclohexane with air over α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts at 400 °C was shown in Table 1. Benzene is the major product under the reaction conditions. No trace of cyclohexene and cyclohexadiene was detected at 400 °C, although the conversion of cyclohexane is very low for all VPO catalysts (only 6.4% for α_I-$VOPO_4$, 6.9% for α_{II}-$VOPO_4$ and 7.3% for β-$VOPO_4$). β-$VOPO_4$ shows slight higher activity than α_{II}-$VOPO_4$ and α_I-$VOPO_4$ catalysts, but lower selectivity (76.5%). Comparing with α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts, α_I-$VOPO_4$ catalyst is much more favorable to obtain oxidative dehydrogenation products than deep oxidation products. The ODH results of cyclohexane were shown in Tables 2–4 over α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts at 450 °C, respectively. All catalysts show a further increasing in activity towards deep oxidation products, however, the relative sequence in selective benzene formation keeps unchanged. Therefore, the catalytic oxidative activity of cyclohexane over these three catalysts in the absence of HOAc is as follows: α_I-$VOPO_4$ < α_{II}-$VOPO_4$ < β-$VOPO_4$.

In order to reduce deep oxidation of cyclohexane, HOAc is added into reaction system as a reaction controlling agent. A new route to control product selectivity in cyclohexane oxidative dehydrogenation process has been put forward [12]. Tables 2–4 show the effect of HOAc on the oxidative dehydrogenation of cyclohexane over different VPO catalysts. After adding a certain amount of HOAc (the mole ratio of HOAc to cyclohexane is 2.4:1), the conversion of cyclohexane decreases and the products distribution is changed for all catalysts. It is noteworthy that the conversion of cyclohexane reduced significantly over α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts and more selective to benzene than that of α_I-$VOPO_4$ catalyst. Selectivity to cyclohexene increases and other products decrease with the increase of HOAc. Furthermore, a low level of unstable intermediates, 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD), were simultaneously observed at the mole ratio of HOAc/cyclohexane about 5.3:1. Here, the selectivity of 1,3-cyclohexadiene and 1,4-cyclohexadiene in Tables 2–4 as a whole denoted by cyclohexadienes. For α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ catalysts, almost 100% selectivity to cyclohexene was

Table 1
Cyclohexane oxidation over different VPO catalysts at 400 °C without acetic acid addition

Catalyst	Conversion (%)	Selectivity (%)				
		Cyclohexene	Cyclohexadiene	Benzene	MA	CO_x
α_I-$VOPO_4$	6.4	0	0	95.0	3.2	1.8
α_{II}-$VOPO_4$	6.9	0	0	86.8	6.7	6.5
β-$VOPO_4$	7.3	0	0	76.5	8.9	14.6

Table 2
ODH of cyclohexane over α_I-$VOPO_4$ at 450 °C in the adding of different quantity of HOAc

HOAc/cyclohexane (molar ratio)	Conversion (%)	Selectivity (%)				
		Cyclohexene	Cyclohexadiene	Benzene	MA	CO_x
0	24.7	0	0	63.0	15.6	21.4
2.4	16.9	0.50	0	68.1	17.5	13.9
5.3	14.5	50.0	8.1	23.7	5.8	12.4
7.7	11.8	83.4	2.0	14.6	0	0
10.3	7.5	95.5	0.5	4.0	0	0
12.9	6.9	100	0	0	0	0

Table 3
ODH of cyclohexane over α_{II}-$VOPO_4$ at 450 °C in the adding of different quantity of HOAc

HOAc/cyclohexane (molar ratio)	Conversion (%)	Selectivity (%)				
		Cyclohexene	Cyclohexadiene	Benzene	MA	CO_x
0	26.6	0	0	50.0	18.4	31.6
2.4	8.2	2.0	0	98	0	0
5.3	5.5	25.9	11.3	52.8	0	0
7.7	3.8	48.8	34.4	16.8	0	0
10.3	1.8	100	0	0	0	0

Table 4
ODH of cyclohexane over β-$VOPO_4$ at 450 °C in the adding of different quantity of HOAc

HOAc/cyclohexane (molar ratio)	Conversion (%)	Selectivity (%)				
		Cyclohexene	Cyclohexadiene	Benzene	MA	CO_x
0	34.6	0		48.5	13.5	38.0
2.4	12.1	0.7	0	99.3	0	0
5.3	4.0	45.6	14.7	39.7	0	0
7.7	<1.0	100	0	0	0	0

obtained when the mole ratio of HOAc to cyclohexane was 12.9:1, 10.3:1 and 7.7:1, respectively, at 450 °C, correspondingly, conversion of cyclohexane was 6.9, 1.8 and 1.0%. These results indicate that the catalytic activity of ODH of cyclohexane on these three catalysts in the presence of HOAc is as follows: α_I-$VOPO_4$ > α_{II}-$VOPO_4$ > β-$VOPO_4$.

4. Discussion

It is well known that the performance of various vanadium phosphorus oxide catalysts is dependent on the following factors: surface area, redox-capability and surface acidity. In the present study, α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ samples have similar specific surface area: 6.42 $m^2\ g^{-1}$ for α_I-$VOPO_4$, 5.75 $m^2\ g^{-1}$ for α_{II}-$VOPO_4$ and 6.64 $m^2\ g^{-1}$ for β-$VOPO_4$. The difference of catalytic performance among all $VOPO_4$ catalysts cannot be attributed to the surface area. Redox properties of the catalysts play a key role in alkane oxidation over vanadium-based catalysts; the simultaneous presence of V^{4+} and V^{5+} species on the surface has been proved to be essential for the selective oxidation of butane over VPO catalyst [31]. In fact, $VOPO_4$ compounds have the capability of reversible transition from one oxidation state to the others in the reaction process [32]. In general, starting from V^{5+} precursors, the layered α_I-$VOPO_4$ and α_{II}-$VOPO_4$ are more stable as compared to β-$VOPO_4$ and their reduction leads to the formation of $(VO)_2P_2O_7$ phase [27]. In other words, β-$VOPO_4$ should have higher activity than α-$VOPO_4$. The H_2-TPR peaks of α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ samples shown in Fig. 1 can be recognized for reduction of crystal lattice oxygen species of $VOPO_4$ catalysts. Both of α_{II}-$VOPO_4$ and β-$VOPO_4$ H_2-TPR curves show two reduced peaks that indicate α_{II}-$VOPO_4$ and β-$VOPO_4$ each possesses two different kinds of reducible crystal lattice oxygen species. The first peak of β-$VOPO_4$ denotes the reducing crystal lattice oxygen species of +5 oxidation state of vanadium to +4 oxidation state (in $(VO)_2P_2O_7$) that is confirmed by XRD after the TPR experiment at 580 °C, the second peak can be assigned to the formation of +3 oxidation state crystal lattice oxygen species of vanadium as reference described [23]. Compared with α_{II}-$VOPO_4$ and β-$VOPO_4$ samples, the H_2-TPR profile of α_I-$VOPO_4$ shows a much more intense high-temperature peak, which denotes the existence of mainly more difficult reducible crystal lattice oxygen species. As shown in Fig. 1, the TPR curves of all $VOPO_4$ samples indicate that the capability of reversible redox cycle between V^{5+} and V^{4+} for β-$VOPO_4$ is easier than that of α_{II}-$VOPO_4$ and α_I-$VOPO_4$. This suggests that the catalytic activity should be in the order of: β-$VOPO_4$ > α_{II}-$VOPO_4$ > α_I-$VOPO_4$. In the case of no HOAc addition, the activity of β-$VOPO_4$ at reaction temperature 450 °C is conformed to this agreement (Tables 2–4). At low temperature (400 °C), the performance of the samples is also consistent with the relation between catalytic activity and redox property of the catalysts, although the conversion of cyclohexane is similar and low. However, in the presence of HOAc, the activity dramatically decreases with the amount of HOAc as in the order of: β-$VOPO_4$, α_{II}-$VOPO_4$, α_I-$VOPO_4$. It is suggested that the redox ability of the catalysts has been changed by the addition of HOAc. It seems that original redox ability of the catalysts is not determinant factor for the ODH of cyclohexane in the presence of acetic acid.

A basic factor determining the different catalytic performance of α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ samples seems to be changed into the surface acidity, which plays an important role in the presence of acetic acid. In our previous study indicated that acetic acid should be competitively adsorbed on the active sites of VPO catalyst, so that adjacent active sites for the deep oxidation are eliminated obviously. Thus, there are almost no adjacent active sites for the deep oxidation of reactants [12]. In other words, acetic acid competitively adsorbs on the unselective sites of VPO catalyst. The lower the acidity of $VOPO_4$ compounds, the stronger the ability of active sites interacting with HO Ac will be. The results of the surface acidity show all VPO samples possess weak acid site. As known, NH_3-TPD measurements do not give the information of acid type, but from literature data the low temperature peaks could be assigned to Lewis acid sites for VPO catalysts [33,34]. The amount of acid sites, very high for α_I-$VOPO_4$, and their order is as follows: α_I-$VOPO_4 \gg \alpha_{II}$-$VOPO_4 > \beta$-$VOPO_4$. As a result, the activity of β-$VOPO_4$ and α_{II}-$VOPO_4$ catalyst dramatically decreases by adding small amount of HOAc. The better catalytic activity of α_I-$VOPO_4$ to cyclohexane oxidative dehydrogenation by adding HOAc in the feeds can be assigned to the presence of higher surface acidity which was evidenced by ammonia TPD measurements.

5. Conclusions

Adding of acetic acid in the feed is a reliable method to control the activity of catalysts; therefore, high cyclohexene selectivity from ODH of cyclohexane over VPO catalysts can be realized. Different $VOPO_4$ phases inherent different acidity and reducibility. β-$VOPO_4$ phase is more active than α_I-$VOPO_4$, α_{II}-$VOPO_4$ in the absence of acetic acid addition. In the presence of acetic acid, the oxidation-reducibility of catalyst is changed; as a result that α_I-$VOPO_4$ phase catalyst gives better catalytic performances than α_{II}-$VOPO_4$ and β-$VOPO_4$ due to its higher acidity. The higher the acidity of $VOPO_4$ compounds, the weaker the ability of active sites interacting with HOAc, which is one of the reason why the acidity of the catalyst plays an important role in the process.

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