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Article

Nature of active phase of VO_x catalysts supported on SiBeta for direct dehydrogenation of propane to propylene

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ABSTRACT

The VO_x catalysts supported on dealuminated Beta zeolite (SiBeta) with varying V loadings (from 0.5 to 10 wt%) are prepared and tested for their catalytic activities in the reaction of direct dehydrogenation of propane to propylene (PDH). It is characterized that the VSiBeta catalysts possess different kinds of vanadium species on the SiBeta support, including monomeric or isolated VO_x species at a low V loading, and polynuclear VO_x species in different polymerization degrees at higher V loadings. The 3VSiBeta catalyst (V loading is 3 wt%), containing isolated VO_x species in monolayer, shows around 40% of propane conversion with 90% of propylene selectivity (reaction conditions: 600 °C, 4000 mL g⁻¹ h⁻¹) which are comparable to VSiBeta catalysts with higher V loadings. The catalytic activity exhibits a good linear relationship with the amount of generated acidic sites, which are derived from the interaction sites between VO_x species and SiBeta support, and keeps stable after several regeneration cycles. Thus, as the VO_x species directly contact with SiBeta support via V–O–Si bonds, a reactivity enhancement can be achieved. While, the initial valence state of V does not seem to influence the catalytic performance. Moreover, the aggregation degree of VO_x species determines the propylene selectivity and deactivation rate, both of which increase as raising the V loading amount.

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1. Introduction

Propylene is an important basis of numerous chemical products, such as polymers, resins, solvents and fibers, mainly obtained from the steam cracking of naphtha and fluid catalytic cracking of heavier oil [1–3]. With the increasing demand of propylene and the exploitation of shale gas, direct dehydrogenation of propane to propylene (PDH) as an alternative way has drawn great attention and been widely employed in commercial propylene production, and is a great mean for turning low-value propane into value-added propylene [4–8]. The

commercial PDH catalysts are based on Pt and CrO_x based catalysts, while the high cost of Pt and toxicity of CrO_x greatly hinder their further wide application. Moreover, both of them are easy to be deactivated and need frequently regeneration [9–11]. These issues necessitate the exploration of alternative catalysts that should exhibit advantages in terms of environmental and economic aspects.

Supported VO_x catalysts have been intensively employed in oxidative dehydrogenation of propane to propylene (OPDH) [12–14], while they have received relatively less attention in oxygen-free PDH reaction. Yan's group prepared the VO_x cata-

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lysts on crystallized mesoporous γ - Al_2O_3 , demonstrating that low-polymerized V (IV) species are more active than isolated V species in PDH reaction [15]. David et al. [16,17] reported that MCM-41 as the support of VO_x catalyst employed in PDH reaction would bring about the generation of active Lewis acidic $\text{V}^{3+/4+}$ species. And, the isolated VO_x species showed higher catalytic activity compared to their oligomerized counterparts. Gong's group employed commercial Al_2O_3 as the support of vanadium catalyst, finding that rationally increasing the surface VO_x species density can lead to a higher proportion of V^{3+} species which are more active in PDH [18]. Guo's group reported that V-doped porous silica material showed great catalytic activity for PDH, in which both monomeric and low-polymerized VO_x species in tetrahedral coordination were catalytically active phases in PDH reaction [19]. Sokolov et al. grafted vanadyl acetylacetonate on the Al_2O_3 support mixed with different SiO_2 contents, showing the great effect of support of vanadium catalyst on the catalytic performance of PDH [20]. Given the above, there is not a definite conclusion about the kind of active vanadium species for PDH, in terms of polymerization degree, acidity and oxidation state, because the surface chemistry of VO_x species is deeply affected by support characteristics. Thus, the nature of VO_x species supported on other different materials should be carefully studied, for obtaining a general rule of the active phase of VO_x catalysts in PDH reaction.

With the properties of high surface area, well-crystallized structure and high thermal stability, dealuminated Beta zeolites (SiBeta) have been intensively used as an ideal support to attach transition metal species [21–24]. It is reported that SiBeta support can effectively disperse and stabilize the introduced VO_x species due to the existence of vacant T-sites after removing lattice Al atoms [25,26]. The V-loaded SiBeta serving as effective heterogeneous catalysts have been applied in various catalytic reactions, such as methanol oxidation, NO reduction, conversion of carbohydrates into 2,5-diformylfuran and propene epoxidation [27–30]. Noticeably, it is confirmed that the catalytic performance of VSiBeta catalysts in some reactions depends on the type of VO_x species, which is mainly controlled by V loading amount [21,26,31]. Considering of the catalytic activity of VO_x species in OPDH [32], we first propose that the V-loaded SiBeta system may be of great promising to be employed in PDH reaction.

Herein, we prepared VO_x catalyst supported on SiBeta by using a two-step postsynthesis method [33,34], and then treated the as-prepared samples with a high-temperature calcination in air. The obtained xVSiBeta catalysts (x represents the wt% V which is from 0.5 to 10) were tested in PDH reaction. The ideal catalytic performances were simultaneously realized on the 3/7/10VSiBeta catalysts, about 40% of propane conversion and 90% of propylene selectivity. Meanwhile, the catalytic performance of the 3VSiBeta catalyst was completely restored after several regeneration cycles, presenting its great reusability. The physicochemical and structural properties of these xVSiBeta samples were systematically investigated by X-ray diffraction (XRD), N_2 sorption, Diffuse reflectance ultraviolet-visible (DR UV-vis), H_2 temperature programmed reduction (H_2 -TPR), NH_3 -temperature programmed desorption

(NH_3 -TPD), Raman spectra and X-ray photoelectron spectroscopy (XPS) techniques. The characterization and test results drew the conclusions about the states of VO_x species as well as the acidic sites of VSiBeta catalysts, and their roles in the PDH reaction, giving a new insight into the active phase of VO_x catalysts. The correlation between the V loading and catalytic performance of the VSiBeta catalysts in PDH was also discussed.

2. Experimental

2.1. Catalysts preparation

The AlBeta zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is of 60) provided by Tianjin Shenneng, Corp. was treated in a concentrated nitric acid solution (13 mol L^{-1}) at 100°C for 12 h under stirring, and followed by washing the dealuminated AlBeta (noted as SiBeta) several times with distilled water. Subsequently, the as-obtained SiBeta was dried at 100°C in air overnight. Afterwards, the SiBeta solid was excessively impregnated with calculated ammonium metavanadate (1 g of SiBeta in 20 ml of solution), and kept stirring at ambient temperature overnight. After that, the suspension solutions were dried at 80°C overnight, and then calcined at 600°C for 6 h in a muffle furnace (air atmosphere). The final products were denoted xVSiBeta with $x = 0.5, 1, 3, 7$ and $10 \text{ wt\%}$. AlBeta zeolite was used to prepare reference catalyst, and the preparation procedure of 3VAlBeta was similar to that of xVSiBeta.

2.2. Characterization

N_2 adsorption–desorption measurements were tested on a Quantachrome NOVA 2000e sorption analyzer. Before the analysis, the samples were degassed at 200°C for 8 h. The specific surface areas were obtained based on the Brunauer-Emmett-Teller (BET) equation, and the total pore volumes were determined at a relative P/P_0 of 0.98. Powder XRD patterns were carried out on a Bruker D8 Focus diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). DR UV-vis spectra were recorded on a Shimadzu UV2450 by using BaSO_4 as white standards. H_2 -TPR experiments were carried out on a Quantachrome ChemBET 3000 analyzer, which is equipped with a U-shaped tubular micro-reactor fixed inside an electrical furnace. The sample (50 mg) was degassed at 600°C in He for 30 min. After cooling down to ambient temperature, the sample was reduced by 10 vol% H_2/Ar mixed gas (110 mL min^{-1}), from 80 to 700°C at the heating rate of $10^\circ\text{C min}^{-1}$. NH_3 -TPD profiles were similarly obtained from the Quantachrome ChemBET-3000 analyzer. 100 mg of sample was pretreated at 600°C for 1 h in He atmosphere, and then the sample was saturated with NH_3 at 80°C for 30 min. After that, the experiments were conducted in He from 80 to 550°C . Raman spectra of the samples were acquired at ambient temperature by using the DXR Raman spectrophotometer (SR-500I-A, TEO) with a 532 nm excitation source. XPS measurements were recorded on a Thermo Scientific ESCALAB 250Xi spectrometer equipped a monochromatic $\text{Al-K}\alpha$ X-ray source. The reported binding energies have been corrected by referring to C 1s at 284.8 eV. The

thermogravimetric thermal analysis (TGA) were performed on a TA SDT Q600 instrument from ambient temperature to 800 °C with a heating rate of 10 °C min⁻¹ in flowing air.

2.3. Catalytic evaluation in PDH reaction

The PDH reactions were carried out in a quartzose fixed-bed microreactor (6 mm in inner diameter) under atmospheric pressure, packed with 0.2 g of catalyst particles in the isothermal zone of the reactor by using two quartz wool plugs. A thermocouple was fixed in the isothermal zone to measure the reaction temperature. The reaction products were analyzed by an on-line gas chromatograph (SP-6890) with a GDX-01 column and a flame ionization detector (FID). The reaction conditions were established in the activity tests: reaction temperature, 600 °C; the total flow rate of gas reactant, 20 cm³ min⁻¹ (5 vol% propane in nitrogen). The propane conversion (C_{propane}), propylene selectivity ($S_{\text{propylene}}$) and propylene yield ($Y_{\text{propylene}}$) were calculated as follows based on a carbon atom balance method:

$$C_{\text{propane}} = \frac{\text{moles of propane reacted}}{\text{moles of propane fed}} \times 100\%$$

$$S_{\text{propylene}} = \frac{\text{moles of propylene formed}}{\text{moles of propane reacted}} \times 100\%$$

$$Y_{\text{propylene}} = \frac{\text{moles of propylene formed}}{\text{moles of propane fed}} \times 100\%$$

3. Results and discussion

3.1. Materials characterization

The apparent surface V densities calculated by connecting the V loading to the specific surface area of VSiBeta catalysts are listed in Table 1 [30]. With the V loading less than 7 wt%, the isolated VO_x with a monolayer coverage on the support is theoretically possible, due to the theoretical value of 2.5 V nm⁻² for a monolayer of isolated VO_x [35–37]. Nevertheless, it is unavoidable that partial VO_x species interact with each other to form oligomeric VO_x species, attributable to the statistic distribution of vanadium on SiBeta support. The surface V density of 10VSiBeta is 3.4 V nm⁻², higher than 2.5 V nm⁻² but lower than the surface density of 10 V nm⁻² with a two-dimensional polyvanadate layer [12,38]. It can thus be speculated that the polymerization degree of VO_x increases with the increase of V surface density, and a part of highly-polymerized VO_x species and even V₂O₅ crystallite are existent in the 10VSiBeta catalyst.

Partial textural properties of the prepared samples and bare support are concluded in Table 1. As expected, the specific sur-

Table 1

Partial details of the VSiBeta samples.

Samples	A_{BET} (m ² g ⁻¹)	ωV^a (V nm ⁻²)	V_{total} (cm ³ g ⁻¹)
SiBeta	520.35	—	0.982
0.5VSiBeta	505.93	0.075	0.975
1VSiBeta	495.49	0.238	0.976
3VSiBeta	454.88	0.778	0.979
7VSiBeta	413.98	1.996	0.935
10VSiBeta	386.13	3.412	0.886

^a Apparent surface V density.

Fig. 1. XRD patterns of SiBeta and xVSiBeta catalysts.

face area and total pore volume of xVSiBeta catalysts are smaller than that of SiBeta (520 m² g⁻¹, 0.982 cm³ g⁻¹). What's more, the specific surface area and total pore volume of xVSiBeta continuously reduce with the elevated V loading. This decrease is moderated for the V loading up to 7 wt% but slightly drastic for the highest V loading of 10 wt%, may be ascribed to severe blockage of the pores in SiBeta zeolite. The XRD patterns of all VSiBeta catalysts are displayed in Fig. 1. It can be identified that the characteristic structure of SiBeta zeolite preserves well after loading with vanadium. No additional diffraction peaks are observed until the V loading up to 10 wt%, indicating that a fraction of bulk-like V₂O₅ is formed on the 10VSiBeta surface.

The structures and distributions of supported VO_x species were recorded by DR UV-vis at ambient temperature. As shown in Fig. 2, the band at ca. 240 nm related to the isolated V (monomeric VO_x species) with V–O–Si bridge becomes more significant in the VSiBeta catalysts with V loading from 0.5 to 3 wt%, and its intensity has no evident change as further increasing the V loading up to 10 wt%. The band centered at the range of 240–400 nm corresponds to the tetrahedral V charge

Fig. 2. DR UV-vis spectra of VSiBeta catalysts with different V loadings.

transfer involving terminal (V=O) oxygens [27,39], and cannot be observed until the V loading is up to 3 wt%. In addition to above two bands, no band in the range of 400–600 nm correlated with octahedral V (V–O–V) is discerned in the 10VSiBeta catalyst [27,28,40], probably ascribed to the trace amounts of V_2O_5 crystallites. It is reported that the O→V charge transfer bands within V–O–V bond of VO_x catalysts can be used to judge the coordination environment of vanadium. Herein, the band gap energy (E_g) determined by the wavelength (λ_g , the wavelength is obtained from the intersection of the horizontal and vertical parts of DR UV–vis spectra) is calculated by using the formula of $E_g = 1240/\lambda_g$ [39,40]. The obtained values of E_g are listed in Table S1, and the band gap energy decreases with increased V loading amount, indicating that the ratio of polymerized VO_x to isolated VO_x species rises as elevating the V loading.

The reducibility of V species of VSiBeta catalyst was tested by H_2 -TPR experiments, and the obtained curves are displayed in Fig. 3. Clearly, there is no any reduction peak of the SiBeta support. With the V loading varied from 0.5 wt% to 3 wt%, the H_2 -TPR profiles of these catalysts exhibit an obvious reduction peak accompanied with a weak shoulder peak in the range of 450–550 °C. According to previous reports [36,43], the presence of a sharp peak at ca. 450–550 °C is attributable to the reduction of isolated VO_x species bonded to zeolite framework. While with the further increase of V loading to 7 wt% and 10 wt%, the main reduction peak shifts to higher temperature of ca. 565 °C and the hydrogen consumptions are higher, indicating the progressive formation of less reducible polymerized vanadium species. For the 10VSiBeta catalyst, another reduction peak appearing at ca. 660 °C suggests the formation of highly-polymerized VO_x species or bulk-like V_2O_5 [19], consistent with above XRD result. The TPR results agree with the previous reports that the reducibility of VO_x species decreases with the increasing polymerization degree and follows the order: monomeric single VO_x species > polymerized VO_x species > V_2O_5 clusters [20]. Noticeably, the main reduction peaks of 3VSiBeta and 7VSiBeta have a significant demarcation, indicating that 3 wt% may be the maximum loading for acquiring the VO_x species in monolayer on SiBeta support, and polymerized

Fig. 3. H_2 -TPR profiles of SiBeta and VSiBeta catalysts with different V loadings.

Fig. 4. NH_3 -TPD profiles of SiBeta and VSiBeta catalysts with different V loadings.

VO_x species in multilayers start to appear in 7VSiBeta catalyst [34].

Fig. 4 presents the NH_3 -TPD profiles of x VSiBeta catalysts, which can be used to investigate the influence of V loading on the acidity of catalyst. The quantitative analysis results calculated by the peak area deconvolution method are listed in Table 2. No NH_3 desorption peaks of SiBeta can be seen, further confirming that the acidic sites of Beta zeolite can be completely removed after dealumination. All of the x VSiBeta catalysts display newborn NH_3 desorption peak in the range of 150–250 °C, and the temperature of maximal peak intensity shifts to higher temperature as increasing the V loading. In line with previous reports [44,45], the V loading amount affects the polymerization degree, and therefore the catalyst surface acidity. The peak below 185 °C corresponding to weak acidic sites, are related to monomeric and low-polymerized VO_x species. The peak located at 215–250 °C is attributable to the medium acidic sites, which corresponds to highly-polymerized VO_x species [19]. Therefore, the higher polymerization degree of VO_x species leads to stronger acidity. It has been reported that VO_x supported on silica materials can introduce both the Brönsted acidic sites and Lewis acidic sites (LAS) [27], while the Brönsted acidic sites would disappear after the high-temperature treatment due to the destruction of hydrated VO_x [44]. So the generated weak and medium acidic sites in VSiBeta catalysts are ascribed to

Table 2

Quantitative analysis of H_2 -TPR, NH_3 -TPD measurements and partial activity test results.

Samples	Conv. ^a (%)	Sel. ^a (%)	Yield ^a (%)	Coke ^b (%)	T_{max} ^c (°C)	Acidic sites ^d (mmol NH_3 g ⁻¹)
0.5VSiBeta	20.73	93.67	19.42	5.41	540	0.033
1VSiBeta	31.85	93.45	29.77	8.26	550	0.081
3VSiBeta	37.76	88.35	33.36	12.30	537	0.210
7VSiBeta	39.88	89.78	35.81	13.19	565	0.218
10VSiBeta	38.13	91.65	34.94	13.45	565	0.212

^a Catalytic performance obtained after 10 min of reaction at 600 °C.

^b Coke content obtained after 6 h of reaction at 600 °C.

^c The temperature of maximal reduction peak intensity.

^d Amount of acidic sites calculated from NH_3 -TPD.

Fig. 5. Visible ($\lambda_{\text{excitation}} = 532 \text{ nm}$) Raman spectra of the selected xVSiBeta catalysts.

mono- and polymeric VO_x species, respectively, both of which make contributions to the adsorption and activation of light alkane as LAS [25,46]. According to the quantitative analysis results in Table 2, the total amount of acidic sites of about 0.033, 0.081, 0.210, 0.218 and 0.212 $\text{mmol}_{\text{NH}_3} \text{g}^{-1}$ for 0.5/1/3/7/10VSiBeta catalysts, respectively. Noticeably, the quantitative variation of acidic sites is not obvious as the V loading increases from 3 to 10 wt%, indicating the acidic sites may generate from the interaction sites between VO_x and SiBeta support. For a higher V loading, the amount of acidic sites decreases probably due to the formation of bulk V_2O_5 which results in fewer V atoms directly bond to the support [19].

The Visible Raman spectra of 3/7/10VSiBeta catalysts are shown in Fig. 5. A band at approximately 1020 cm^{-1} related to the terminal $\text{V}=\text{O}$ vibrations is characteristic of isolated monovanadates species in tetrahedral coordination [18,35], which goes down as increasing the V loading from 3 to 10 wt%, as clearly shown in Fig. S1. Also, the band at 918 cm^{-1} corresponding to $\text{V}-\text{O}-\text{Si}$ vibrations, becomes stronger as decreasing the V loading. The results show that isolated and mononuclear VO_x species are present in the VSiBeta catalysts with low V loadings [19]. The bands at 140, 318, 470, 703 and 990 cm^{-1} found under visible laser excitation in the 10VSiBeta catalyst indicate the presence of crystallite V_2O_5 [47], consistent with

Table 3

Results of peak deconvolution of V $2p_{3/2}$ XPS spectra.

Catalyst	V ⁵⁺ (%)	V ⁴⁺ (%)
3VSiBeta	81.4	18.6
7VSiBeta	64.8	35.2
10VSiBeta	79.4	20.6

above XRD and H_2 -TPR results.

XPS measurements were used for obtaining the information about the valence distribution of V element on the surface of VSiBeta catalysts. The XPS spectra of the 3/7/10VSiBeta catalysts in V $2p$ core range are shown in Fig. 6. After the calcination in air, no trivalent V species are formed, in accordance with previous report [15]. As shown in Fig. 6, the peak of V $2p_{3/2}$ can be deconvoluted into two peaks, at about 516.9 and 518.5 eV, assigned to the V^{4+} and V^{5+} species, respectively [48,49]. The binding energies of V are higher than those reported, which is possibly attributed to the strong interaction effect between V species and SiBeta support [15]. The proportion of each oxidation state of V listed in Table 3 was calculated from the normalization of the peak area of V $2p_{3/2}$ signals. The proportion of V^{4+} species reaches the maximum value when the V loading is of 7 wt%. Then the content of V^{4+} decreases as further increasing the V loading up to 10 wt%, indicating the crystalline V_2O_5 gradually forms with the agglomeration of VO_x species. Thus, it is proposed that the proportion of V^{4+} species increases with the increase of V surface density until the domain size is up to polyvanadate monolayer [13,15,29], which may be realized on the 7VSiBeta. The V^{5+} species are less active in PDH compared with the V^{4+} and V^{3+} species (easily obtained from the reduction of V^{4+} species and very active for PDH) [50], while they are easily reduced to V^{3+} under reaction condition. The valence distributions of V in the 3/7/10VSiBeta catalysts are varied, and the roles of them in PDH reaction can be determined according to catalytic performance.

3.2. The catalytic performance of xVSiBeta in PDH reaction

Fig. 7 shows the propane conversion and propylene selectivity over xVSiBeta catalysts at 600°C as a function of time on stream. All the catalysts display a concurrent trend in terms of propane conversion, which is a gradual decrement as a function

Fig. 6. V $2p_{3/2}$ XPS spectra of selected xVSiBeta catalysts. (a) 3VSiBeta; (b) 7VSiBeta; (c) 10VSiBeta.

Fig. 7. Propane conversion (a) and propylene selectivity (b) of x VSiBeta catalysts as a function of reaction time.

of time to approach their steady state. The initial propane conversion of VSiBeta catalyst grows along with the V loading amount up to 7 wt% and then goes down on the 10VSiBeta catalyst. The initial propane conversion over the 7VSiBeta reaches the maximal value of about 40%, and then it decreases to around 23% upon 6 h on stream. Although the 3VSiBeta catalyst contains more than two times lower amount of V than the 7VSiBeta, the performance of these two catalysts does not differ significantly. Overall, the propane conversions of 3/7/10VSiBeta catalysts are very similar in spite of the huge difference in the V loadings. The superiority of SiBeta support was proved by the activity test over the 3VAlBeta catalyst (Fig. S2), which shows much lower propane conversion and propylene selectivity compared with the 3VSiBeta catalyst.

The selectivity towards propylene increases with the elevated V loading from 3 wt% to 10 wt%, as shown in Fig. 7(b), suggesting the side reactions are continuously depressed with the aggregation of VO_x species. As for the 0.5VSiBeta and 1VSiBeta catalysts, the high propylene selectivity is due to the very low propane conversion. The analysis of side products produced during the PDH reaction progress was conducted, and the selectivities of three main byproducts including methane, ethane and ethene are depicted in Fig. S3. The selectivi-

ties of all byproducts are much lower in contrast to that of propylene. Generally, the VSiBeta catalysts with higher V loadings tend to produce less byproducts. Among all the VSiBeta catalysts, the 3/7/10VSiBeta catalysts show comparable catalytic performance in terms of overall catalytic performance (Fig. S4). What's more, the catalytic performance of the VSiBeta is above average among that of reported V-based catalysts (Table S2).

The regeneration experiments of the 3VSiBeta catalyst were carried out to investigate its reusability. The regeneration operation was conducted after PDH reaction for 4 h, in which the used catalyst was calcined at 600 °C for 2 h in air to remove the formed coke. As shown in Fig. 8(a), the initial propane conversion of 3VSiBeta is fully restored in the second PDH cycle. This reversible catalytic activity after the first regeneration procedure confirms that the loss of catalytic activity is ascribed to the coke deposition. The catalytic performances in the third and fourth PDH cycles show no evident difference, with a decrease in initial propylene yield of less than 2% and a stable propylene selectivity at about 95%. The catalyst maintains such a good catalytic performance after the four dehydrogenation and regeneration cycles, indicating the structures of VO_x species on the SiBeta support have been rendered stable. The TGA profiles

Fig. 8. (a) Time-on-stream behavior of 3VSiBeta catalyst at 600 °C in four reaction-regeneration cycles; (b) TGA profiles of the used 3/7/10VSiBeta catalysts.

of used 3/7/10VSiBeta catalysts after reaction for 6 h are presented in Fig. 8(b). The amount of deposited coke increases with the increase of V loading amount, probably due to the higher polymerization degree of VO_x species, which is in line with precedent reports [50,51].

3.3. Dependence of catalytic performance and deactivation rate on the nature of VO_x species

Considering of the acidic sites created by the interaction sites between V species and SiBeta support, the correlations between the catalytic performance and acidic sites amount are depicted in Fig. 9. The initial propane conversion of VSiBeta catalyst shows a linear increase with the amount of acidic sites (Fig. 9(a)), indicating the catalytic activity is greatly dependent on the created acidic sites. Further increasing V loading cannot improve the catalytic activity is because the largest amount of V–O–Si bridges are existent on the 3VSiBeta. Similar result was reported by our group recently, where the ZnO supported on SiBeta could create acidic Zn–O–Si bonds which are active for catalyzing the PDH reaction [52]. In addition, there is no evident correlation between the propylene selectivity and the number of acidic sites, as seen in Fig. 9(b).

The correlation between the V loading amount and the catalytic activity is plotted in Fig. 10(a). At a low V loading, a large part of the zeolite surface remains uncovered, rendering this sample show less activity to desired products. As the V loading is excess, the formed V_2O_5 crystallites cannot make the reactants accessible to the catalytically active sites. With a V loading higher than 3 wt%, the propane conversion almost levels up. Thus, the non-polymerized VO_x species contacting to SiBeta are responsible for enhanced reactivity. Differently, the propylene selectivity increases as increasing the V loading amount, because it deeply depends on the polymerization degree of VO_x species. The deactivation rate of VSiBeta catalyst as a function of V loading is exhibited in Fig. 10(b). Clearly, the deactivation rate increases with the increase of V loading amount. The mononuclear VO_x prevailing on the surface of 0.5/1VSiBeta catalysts possess strong carbon deposition resistance, and thus, exhibiting little deactivation rate. While the VSiBeta catalysts

with higher polymerization degree of VO_x species show higher deactivation rates, because the contacted VO_x species can make two propylene molecular contact with each other and react to generate coke [53]. The regeneration test and TGA results jointly reveal that the deactivation of VSiBeta catalyst is mainly caused by coke deposition, which directly determines the deactivation rate.

Taking into account the structure characterizations of XRD, N_2 -sorption, DR UV-vis, H_2 -TPR and Raman spectra, the VSiBeta catalysts with V loading less than 3 wt% possess monomeric and isolated VO_x species, while isolated and low-polymerized VO_x species coexist in the 7VSiBeta catalyst with the V surface density of *ca.* 2 V nm^{-2} . Moreover, the V surface density of 10VSiBeta greatly exceeds the monolayer coverage, so both of the polymerized VO_x species and bits of bulk-like V_2O_5 are present. The overall turnover frequency (TOF) value decreases steadily as the increase of V loading (Fig. 10(c)), and it is noteworthy that the observed TOF values of VSiBeta catalysts underestimate the true TOF values due to the high propane conversions. The highest TOF value of around 0.07 s^{-1} is realized on the 0.5/1VSiBeta catalysts, which exclusively possess monomeric VO_x , and then decreases to 0.05 s^{-1} after 6 h on stream. However, the TOF values of 3/7/10VSiBeta catalysts obviously decrease. The increase of V content leads to less accessibility of active sites to the reactants, so the activity per V decreases. It also suggests that the acidic sites are created by forming V–O–Si bonds, because the connected VO_x species reduce the V–O–Si bonds but the V–O–V bonds [54]. Combined with the surface chemistry characterizations of NH_3 -TPD and XPS, the 3VSiBeta catalyst possesses isolated VO_x species in monolayer on the zeolite, generating substantial acidic sites, and thus shows the comparable catalytic activity with the 7/10VSiBeta catalysts. Therefore, the catalytic activity of VSiBeta catalyst is exclusively influenced by the interaction sites between the VO_x species and SiBeta support, and seems not be associated with the initial valance of V because the V^{5+} can be reduced by hydrocarbons during reaction [15]. Moreover, the aggregation degree of VO_x species has effects on the propylene selectivity and deactivation rate, both of which increase as raising the V loading. Still, the exact catalytic mechanism of

Fig. 9. Initial propane conversion (a) and propylene selectivity (b) as a function of the amount of acidic sites.

Fig. 10. Influence of the V loading on catalytic performance (a) and deactivation rate (b). And the initial and final turnover frequency of x VSiBeta for PDH (c).

VSiBeta catalyst in PDH needs further investigations.

4. Conclusions

The VSiBeta catalyst reported here is of great potential to be used in PDH reaction. According to the structure characterizations, the polymerization degree of VO_x species of VSiBeta increases as increasing the V loading amount. Herein, the 3VSiBeta catalyst mainly possessing monovanadate shows high catalytic activity comparable to the 7/10VSiBeta catalysts with much higher V loadings, and exhibits restorable performance after several regeneration cycles. The catalytic activity of VO_x catalyst is determined by the amounts of acidic sites, which are related to the V–O–Si bridges and very stable, and achieves its maximum value as entirely monomeric VO_x are existent on SiBeta support. Moreover, the original valance state of V has a negligible impact on the catalytic performance. It is also confirmed that both of propylene selectivity and the deactivation rate caused by coke deposition increase with the increasing polymerization degree of VO_x species. Therefore, the new insight into the active sites of VO_x catalysts in PDH reaction is put forward in this work, and we expect the promising VSiBeta catalyst can open an avenue for rationally designing other transition metal-based catalysts.

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Graphical Abstract

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Nature of active phase of VO_x catalysts supported on SiBeta for direct dehydrogenation of propane to propylene

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The acidic sites of VO_x catalyst supported on SiBeta zeolite are the catalytically active phase, derived from the interaction sites, which shows high activity and great reusability in direct dehydrogenation of propane to propylene.

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SiBeta负载的VO_x催化剂在丙烷直接脱氢制丙烯中的活性位

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摘要: 丙烯是一种非常重要的化工基础原料, 主要用来生产高价值的化学品, 如丙烯腈, 异丙醇和甘油等. 丙烯的传统来源主要是石油的催化裂化反应, 以及石脑油和轻柴油的裂解过程. 随着石油资源的减少, 丙烷直接脱氢制丙烯技术逐渐成为

一条重要的丙烯生产渠道。V基催化剂在丙烷氧化脱氢反应中被广泛研究, 但被用于丙烷直接脱氢反应的报道还较少, 且V基催化剂在丙烷直接脱氢制丙烯中的活性位目前还没有统一论, 可能是由于V的活性物种与载体性质密切相关, 因此研究V基催化剂在不同载体上的活性位具有重要意义。Beta沸石分子筛具有规则微孔结构, 高的比表面积以及可调节的酸性, 是一种理想的金属催化剂载体。本文采用脱铝后的Beta分子筛作为V催化剂载体, 通过调节V的负载量探究丙烷直接脱氢活性和VO_x结构的关系, 以及催化剂的酸性对性能的影响。

活性测试结果显示, V负载量分别为3 wt%, 7 wt%和10 wt%时(催化剂分别命名为3VSiBeta, 7VSiBeta和10VSiBeta), 三者的催化活性十分接近, 此外, 这些催化剂还具有较好的循环利用性, 但碳沉积, 丙烯选择性以及失活率都是随着V负载量的升高而增加。XRD和N₂吸附结果揭示, VO_x在SiBeta上呈高度分散状态, 并且当V负载量从3 wt%升至10 wt%时, 表面V密度发生明显变化, VO_x物种在3VSiBeta中可基本实现孤立的单分散状态。同时, DR UV-vis, H₂-TPR以及Raman测试结果表明, VO_x物种的聚合程度随V负载量的升高逐渐增加。NH₃-TPD结果表明, Beta载体在脱铝后本身的酸性位完全消除, 但是负载V后引入了新的酸性位, 并且3VSiBeta, 7VSiBeta和10VSiBeta三者的酸量基本相当。尽管XPS结果显示, 不同VSiBeta催化剂上的V价态分布有差异, 但是相似的催化活性说明VSiBeta催化剂的活性位与形成的酸性位数目密切相关, 而受V初始价态的影响不大。本文指出, 酸性位可能是与V–O–Si键直接相关, V负载量从3 wt%增加到10 wt%, 会逐渐形成无催化活性的V–O–V键, 导致活性不能进一步提升。因此, 3VSiBeta催化剂中可实现孤立的VO_x物种单层分散在SiBeta载体上, 形成了大量的酸性V–O–Si键, 从而显示出和高负载量的VSiBeta催化剂相当的活性以及较高的脱氢稳定性。

关键词: 丙烷脱氢; 丙烯; VO_x物种; SiBeta载体; 活性位

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