



Synthesis of vanadium-based catalysts and their excellent catalytic behaviors on dehydrogenation of C4 hydrocarbons

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Abstract In this paper, vanadium-based catalysts made from commercial γ -alumina (V1 series) and from pseudo-boehmite (V2 series) were, respectively, prepared via impregnation method. The samples were characterized and evaluated by various characterization techniques (e.g. X-ray diffraction, N₂ adsorption–desorption isotherms, ammonia temperature programmed desorption, and hydrogenation temperature programmed reduction) and dehydrogenation reactions, respectively. The results reveal that the most suitable loading amount of the V1 series of vanadium-based catalysts is 12 % and it is superior to the C4 olefin selectivity. On the other hand, the most suitable loading amount of V2 series of vanadium-based catalysts is 15 %, and this optimal catalyst has better dehydrogenation activity. The two series of samples are mainly composed of weak acid sites and V2 series of vanadium-based catalysts have larger specific surface area, larger pore volume, wider pore size, and better active component dispersion.

Keywords Dehydrogenation · Vanadium-based catalysts · γ -Alumina pseudo-boehmite

Introduction

With the rapid growth of oil refinery capacity, the production of C4 hydrocarbons, as by-products from FCC or hydrocracking, also increases. It is reported that the C4 hydrocarbon output of China alone in 2013 was 15.7 million tons [1]. Therefore, increasing attentions is being paid on the consumption of C4 hydrocarbons during refinery and petrochemical processes. However, the consumption of these C4 hydrocarbons is currently focused on butylenes because they can be converted for MTBE manufacturing. But the butanes, the amount of which is nearly equal to the amount of butylenes in the C4 hydrocarbon mixtures [1], can only be burned as uneconomic fuels. On the other hand, with the expansion of C4 olefin derivatives production, demand for butylenes increases gradually. Thus, the development of butane-to-butylene techniques and the enhancement of the C4 hydrocarbons' efficiency by oil refining are of vital importance [2].

Dehydrogenation of butane into butylenes is a feasible method to overcome the aforementioned problem [3]. The dehydrogenation process is not only of great significance for the integrated utilization of C4 hydrocarbons made from oil refining, and broadens the feed resources for manufacturing MTBE, MMA, butadiene, synthetic rubbers, etc. It also can effectively raise the economic benefits by decreasing the amount of butanes which can only be used for uneconomic fuels with low added value.

Hitherto, dehydrogenation processes can be divided into catalytic dehydrogenation [4–6], oxidative dehydrogenation [7–9], and membrane catalytic dehydrogenation [10, 11]. During oxidative dehydrogenation, the product of oxidative dehydrogenation is water rather than hydrogenation, which makes the process not limited by thermodynamic constraints. The existence of oxygenants

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restrains more carbon deposition, so it decreases the operation temperature and increases the life span of catalysts at the same time [12]. However, product distribution during oxidative dehydrogenation method is difficult to be controlled due to the unavoidable generation of by-products. As emerging techniques, membrane catalytic dehydrogenation has many outstanding advantages such as high catalytic activity, selectivity, mechanical strength, and thermal stability [2, 13]. Hydrogen can selectively pass through the membrane and avoid thermodynamic equilibrium limitation. Elimination of hydrogen can also suppress the side reactions such as hydrogenolysis and isomerization, and decrease the chance to form carbon deposition [14]. However, preparing inorganic membranes with high hydrogen flux as well as high selectivity is still under extensive research.

Catalytic dehydrogenation is the only method that has been industrialized [3, 15]. The catalysts used in commercial processes are platinum-based (e.g. Oleflex and STAR) or chromium-based catalysts (e.g. Catofin and Linde). However, despite their dehydrogenation performances and industrial applications, both platinum-based and chromium-based catalysts have their own disadvantages [15]. Platinum-based catalysts and derived processes require dedicated operation conditions and high operation cost due to the consumption of platinum. Chromium-based catalysts are so easy to lose their activity that frequent regeneration is needed. Besides, generation of Cr^{6+} , which is a kind of carcinogen, means that chromium-based processes are not environmentally friendly.

Faced with these problems, vanadium-based dehydrogenation catalysts are one of the most promising alternatives to platinum- and chromium-based dehydrogenation catalysts. It has been reported that types of supports, support surface area, and loading amount of vanadium-based active components are the decisive parameters for the catalytic performance of vanadium-based dehydrogenation catalysts [16]. Thus, many attentions have been paid into the selection of catalyst support. To our best knowledge, Al_2O_3 [17], SiO_2 [17, 18], and SBA-15 [19] have been reported as supports for vanadium-based catalysts. However, different supports lead to different catalytic behaviors on dehydrogenation reactions. Vislovskiy et al. systematically investigated V-Sb-based dehydrogenation catalysts supported on $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, SiO_2 , and MgO. By comparing their dehydrogenation conversions, they found that Al_2O_3 has the highest conversion among these V-Sb-based dehydrogenation catalysts [17]. Thus, we can infer from the conclusion that Al_2O_3 is very suitable as the support for vanadium-based dehydrogenation catalysts. Pseudo-boehmite is widely used as precursor of Al_2O_3 because it can be conveniently converted. Therefore, in this paper, we prepared a series of vanadium-based

dehydrogenation catalysts where pseudo-boehmite served as catalyst supports. Their structure properties and dehydrogenation behaviors were also evaluated and compared with the catalysts where commercial mesoporous Al_2O_3 used as supports.

Experimental section

Catalysts preparation

Vanadium-based dehydrogenation catalysts were prepared via impregnation method. Ammonium vanadate, oxalic acid, commercial mesoporous alumina, and pseudo-boehmite were purchased from Alfa Aesar Co. Ltd, Sinopharm Chemical Reagent Co. Ltd, Zibo Lituo Aluminum Co. Ltd, and Zibo Wanglin Hi-tech Co. Ltd, respectively. In a typical experiment, different amount of ammonium vanadate was dissolved into oxalic acid aqueous solutions, and then was impregnated on commercial mesoporous alumina or pseudo-boehmite. The samples were first dried in a water bath at 343 K, then transferred into an oven at 383 K for 12 h, and subsequently calcined at 823 K for 10 h. Finally, the vanadium-based catalysts were sieved to 40–60 mesh. The catalysts prepared from commercial alumina were denoted as V1– x , while the catalysts prepared from pseudo-boehmite are denoted as V2– x , where x represents the vanadium loading amount on the mesoporous alumina or pseudo-boehmite.

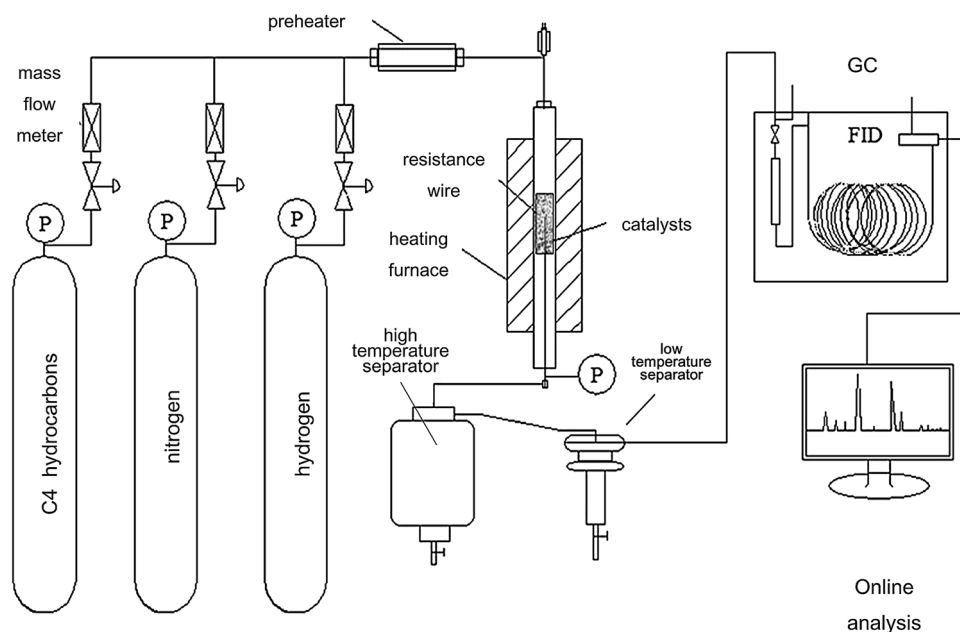
Characterization

Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO MPD X-ray diffractometer with wavelength $\lambda = 0.154$ nm using a Cu $\text{K}\alpha$ radiation source (35 kV, 40 mA). N_2 adsorption–desorption isotherms were obtained at 77 K by a Micromeritics TriStar 3000 analyzer. The surface area was calculated by the Brunauer–Emmett–Teller (BET) equation, the pore volumes were calculated by the N_2 quantity adsorbed at $p/p_0 = 0.95$, and the average pore size were obtained by the Barrett–Joyner–Halenda (BJH) method. Prior to the measurements, all the samples were evacuated at 573 K for 3 h to eliminate moisture in the samples. Both ammonia temperature programmed desorption (NH_3 -TPD) and hydrogen temperature programmed reduction (H_2 -TPR) were characterized by a Quatachrome Instrument CHEMBET-3000 chemical adsorption analyzer.

Catalytic evaluation

Dehydrogenation of C4 hydrocarbon mixture was performed in a fixed bed flow reactor (Tianjin Tiandabei yang

Fig. 1 Schematic diagram of the experimental apparatus



Chemical Equipment Co. Ltd). The schematic diagram of the experimental apparatus is shown in Fig. 1. The C4 hydrocarbon mixture (Dongying Qifa Chemical Co. Ltd) contained 90 % *i*-butane and 5 % *n*-butane. In a typical test process, 0.8 g catalyst sample was filled into the reaction tube (i.d. 10 mm) and reacted under ambient pressure at 863 K. The feed stream was a mixture of hydrogen and C4 hydrocarbons with a molar ratio of one, and the volume flow rate kept at 20 mL/min. The contents of gas products were analyzed with an Agilent 7820A gas chromatography. During the reaction, the product distribution was analyzed every 15 min.

Results and discussion

XRD analysis

Figure 2 illustrates the XRD patterns of V1 and V2 series with different vanadium loadings. From the XRD patterns we can see that all samples show the characteristic peaks of γ -Al₂O₃, which means that the phase of the supports in these two series of catalysts is γ -Al₂O₃. Interestingly, from the marked rectangular shown in Fig. 2, we can see that the peak intensity of V1–12 sample is indeed much higher than that of V2–12 sample. Besides, the peak intensity of V1–15 sample is much higher than that of V2–15 sample. All these show that commercial γ -Al₂O₃ (V1 series) is more stable.

When the amount of vanadium loaded on the γ -Al₂O₃ is small (not more than 15 %), only γ -Al₂O₃ peaks can be seen on both two series of catalysts samples, representing

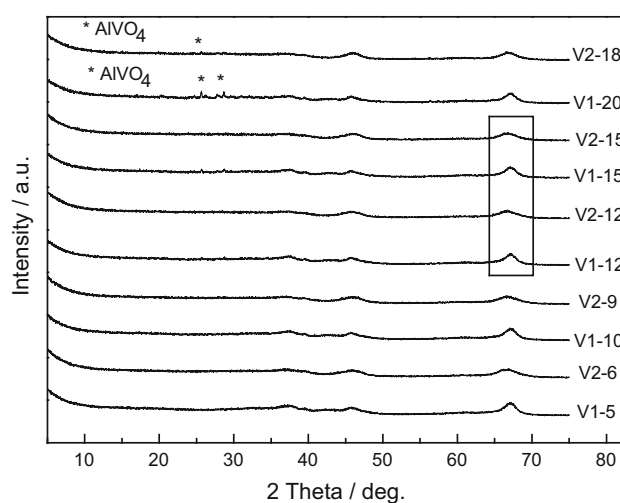


Fig. 2 XRD patterns of different V1 and V2 series samples

that vanadium-based species are well dispersed on the surface of γ -Al₂O₃. With the increase of vanadium loading, some peaks assigned to AlVO₄ appear. This phenomenon infers that if too many active components are loaded, they cannot be effectively dispersed on support and consequently affects the phases and catalytic behaviors of these catalysts.

Textural properties analysis

Tables 1, 2 show textural properties of two series of dehydrogenation catalysts with different vanadium loadings. From these two tables, we can see that V1–0 and V2–0, both of which are free from vanadium-based active

Table 1 Textural properties of different V1 series samples

Sample	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter (nm)
V1-0	200	0.22	3.18
V1-5	180	0.25	3.42
V1-10	176	0.24	3.43
V1-12	165	0.22	3.46
V1-15	149	0.20	3.42
V1-20	137	0.20	3.22

Table 2 Textural properties of different V2 series samples

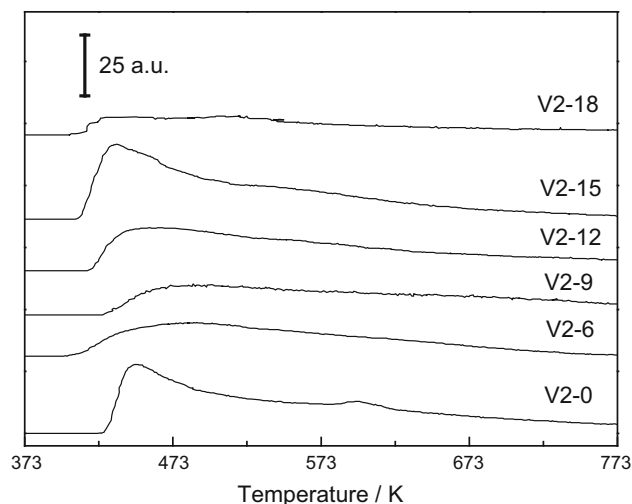
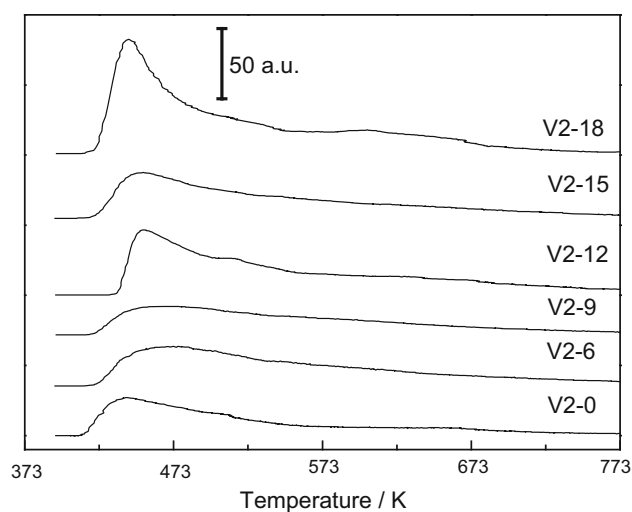
Sample	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter (nm)
V2-0	316	1.05	13.19
V2-6	351	0.84	9.51
V2-9	307	0.77	9.96
V2-12	320	0.83	10.22
V2-15	295	0.70	9.33
V2-18	258	0.61	9.37

components, have superior specific surface area and pore volume. With increasing vanadium loading, the specific surface area and pore volume of both V1 and V2 series of catalysts show a declining trend. This is mainly because the pore structure of V1 and V2 series of catalysts are blocked when increasing vanadium loading. In contrast to specific surface area and pore volume, the mean diameter first increases and then decreases. This may be due to the different blocking consequences of different catalysts with different pore sizes. When the loading amount of vanadium-based species is less than 12 %, narrower pores of the catalysts are choked first, which leads to the increase of mean pore diameter. However, with the continuous increase of vanadium loading, larger pores are consistently occluded, so the mean pore diameter decreases.

Compared with that of V1 series of catalysts, V2 series of catalysts have higher specific surface area, larger pore volume, and larger mean pore diameter. Considering that higher specific surface area and pore volume are in favor of better dispersed active component on the surface of the $\gamma\text{-Al}_2\text{O}_3$ support, vanadium-based active components disperse better on the surface of V2 series samples, which are in consistent with XRD characterization results.

NH₃-TPD analysis

Figures 3, 4 are NH₃-TPD profiles of two series of dehydrogenation catalysts with different vanadium loadings. For V1-0 and V2-0 samples, strong desorption peaks appear at about 443 K meaning that both of these two

**Fig. 3** NH₃-TPD profiles of different V1 series samples**Fig. 4** NH₃-TPD profiles of different V2 series samples

samples mainly possess weak acid site. For V1 series samples, after the addition of vanadium-based active components, the weak peak representing medium strong acid sites disappears, and the position of strong peak does not show apparent changes. Besides, there is another weak peak around 603 K in sample V1-0, representing existence of some medium strong acid sites. While for V2 series samples, desorption peaks shift to higher temperature meaning their increased acidity when vanadium-based active components are added. This phenomenon indicates the interaction between vanadium-based active components and $\gamma\text{-Al}_2\text{O}_3$ support. When the loading amount of vanadium is fixed, the temperatures of desorption peaks of V1 series samples are usually higher than that of V2 series inferring relative strong acid sites comparing to V2 series samples.

H₂-TPR analysis

Figures 5, 6 are H₂-TPR profiles of V1 and V2 series of vanadium-based dehydrogenation catalysts samples of with different vanadium loadings. When the loading amount is lower than 12 %, there is only one hydrogen consumption peak around 823–873 K. This means the existence of strong interaction between vanadium-based active components and alumina support. The active components have been well dispersed on alumina support, which is consistent with the NH₃-TPD profiles. When the loading amount of vanadium is higher than 12 %, there are two desorption peaks in the range of 823–873 and 923–973 K, respectively. Harlin et al. [20] pointed out that the active species of VO_x/Al₂O₃ dehydrogenation catalyst are V³⁺ and V⁴⁺ species. This result indicates that V⁵⁺ species does not prefer to C4 dehydrogenation reactions. However, when the loading amount of active component is rather high (such as V1–20 sample), V⁵⁺ species (AlVO₄) appears considerably, which is well consistent with XRD pattern.

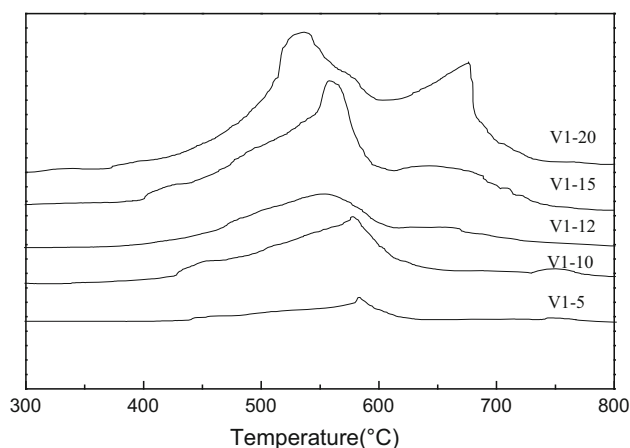


Fig. 5 H₂-TPR patterns of different V1 series samples

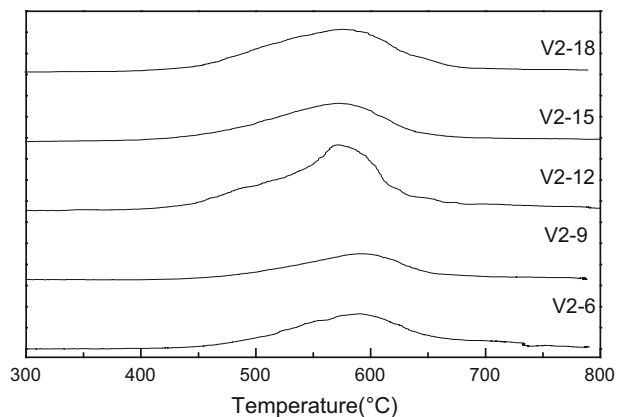


Fig. 6 H₂-TPR patterns of different V2 series samples

The appearance of these inactive V⁵⁺ species will lead to the decrease of reducibility of dehydrogenation catalysts. Besides, these V⁵⁺-contained species can also block the channels of supports and thus further diminish the number of active sites.

Dehydrogenation performance

As has shown in the previous discussions, dispersion of vanadium-based species on the surface of alumina supports are closely related to the loading amount of vanadium and can affect the dehydrogenation behavior of prepared vanadium-based catalysts. Suitable loading amount of vanadium can make vanadium-based active components uniformly loaded on the surface of alumina support.

From Figs. 7, 8, it can be seen that pure alumina support (i.e. V1–0 and V2–0) show very poor dehydrogenation performances. The conversions of C4 alkanes on V1–0 and V2–0 are only 12.11 and 11.25 %, respectively. Furthermore, their selectivities for propylene, rather than, butylenes, are very high, meaning that most conversion of C4

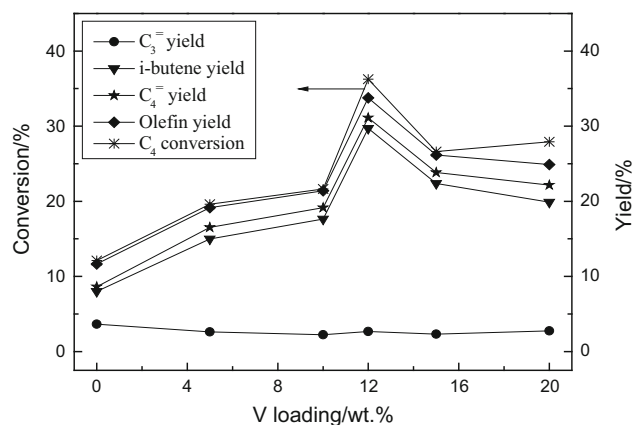


Fig. 7 Influence of V loading on products yield of V1 series catalysts

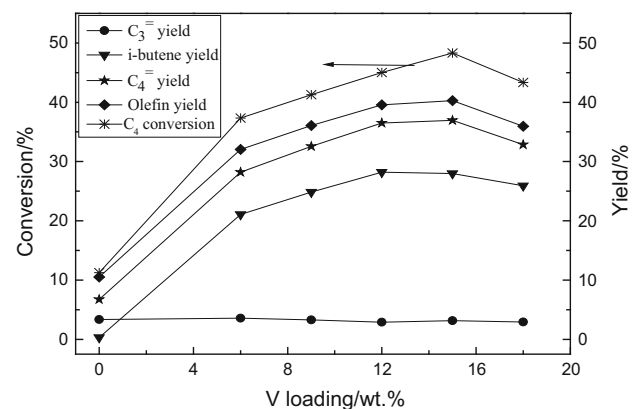


Fig. 8 Influence of V loading on products yield of V2 series catalysts

alkane should be attributed to their pyrolysis rather than dehydrogenation. When a small amount of vanadium is introduced (loading amount = 5–6 %), both the conversions of C4 alkanes and the selectivities of C4 alkenes increase. With the increasing amount of vanadium loadings, the conversion of dehydrogenation reaction increases then decreases. For V1 series samples, dehydrogenation conversion reaches to highest peak (36.25 %) when amount of vanadium loading equals to 12 %. Similarly, the optimum loading amount of V2 series samples is 15 %. Compared with the conversion of V1–12 sample, the conversion of V2–15 sample increases to 48.33 %. When the loading amount of V1 series and V2 series are, respectively, lower than 12 and 18 %, vanadium oxides are mainly existed as isolated tetrahedrons. Alumina support cannot thoroughly be covered by vanadium-based active components. Therefore, the amount of vanadium-based active sites increases with the increase of vanadium-base species loading amount and dehydrogenation conversion increases consistently. After the loading amount of V1 and V2 series samples, respectively, surpluses 12 and 18 %, surface of alumina support is completely covered by V⁵⁺-contained species. The number of dehydrogenation active sites does not continue to increase with the addition of vanadium-based components. Instead, the conversion decreases due to the pore blocking and the formation of V⁵⁺-contained species such as AlVO₄. So the conversion of C4 alkanes decreases with the increase of loading amount. When loading amount of vanadium-based species is fixed, V2 series of catalysts have higher specific surface area, and can make vanadium oxides dispersed better than V1 series of catalysts. Therefore, V2 series catalysts have superior dehydrogenation activity. With the increase of vanadium oxide loading amount, C4 olefin selectivity of both two series of vanadium-based dehydrogenation catalysts increases and then decreases. If comparing with that of V2 series catalysts, C4 olefin selectivity of V1 series catalysts is a bit higher. It indicates that the appearance of AlVO₄ species has adverse effect on the improvement of olefin selectivity. Besides, considering much narrower porosity of V1 series of vanadium-based catalysts, it infers that narrower porosity is more beneficial to the enhancement of C4 olefin selectivity.

From Figs. 7, 8, we can also see that when the content of vanadium-based species on the surface of both two series of dehydrogenation catalysts increases, isobutene yield and total olefins yield increase then decrease consistently. For V1 series of catalysts, when the loading amount of vanadium-based species is 12 %, C4 olefin yield and total olefin yield have maximum values (29.77 % for C4 olefin selectivity and 32.44 % for total olefin selectivity). While for V2 series of catalysts, when the vanadium load amount is 15 %, C4 olefin yield and total olefin yield can reach to

37.41 and 40.76 %, respectively. However, in these two series of vanadium-based catalyst, there is no obvious change for the yield of propylene.

By combining with results gathered by several characterization techniques mentioned above, we can see that the conversion and product distributions of C4 dehydrogenation are strongly influenced by the interaction between vanadium-based active components and alumina support, the textural properties of the vanadium-based catalysts, as well as the reduction ability of the active components. In terms of alkane conversion and C4 olefin yield, V2 series of vanadium-based catalysts are superior to V1 series.

Conclusions

Two series of vanadium-based dehydrogenation catalysts, in which commercial γ -Al₂O₃ (V1 series) and pseudo-boehmite (V2 series) were, respectively, served as supports, were synthesized based on precipitation method. C4 hydrocarbon catalytic dehydrogenation performance shows V1 series are more selective to olefin while V2 series are active to the dehydrogenation conversion of C4 hydrocarbons. The reasons why two kinds of catalysts show their own strengths during the dehydrogenation reactions can be related to the dispersion of active components, the interaction between active components and their supports, the textural properties of catalysts, and reducibility.

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