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Insights into the vanadia catalyzed oxidative dehydrogenation of isobutane with CO₂

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ABSTRACT

Vanadia-based catalysts were prepared using the sol-gel method and were subjected to the oxidative dehydrogenation of isobutane with CO₂. The materials were extensively characterized by using X-ray diffraction, N₂ adsorption-desorption, O₂-temperature programmed oxidation, temperature programmed surface reaction, and in situ Fourier transform infrared techniques. Catalytic results indicate that a high selectivity toward total C₄ olefins over 85% was obtained over all of the catalysts. On the contrary, the highest conversion of isobutane was observed over 12 wt% V₂O₅/Ce_{0.6}Zr_{0.4}O₂ (7 wt%)-Al₂O₃, and a more stable performance was achieved over 6 wt% V₂O₅-Ce_{0.6}Zr_{0.4}O₂ (7 wt%)-Al₂O₃. The catalytic activity for the titled reaction was found to be dependent on the dispersion and crystallinity of the VO_x species over the catalyst, and the deposition of the heavier coke over the catalyst was revealed to be the main reason for the catalyst deactivation. Moreover, the benefit of CO₂ toward the titled reaction was clearly revealed from TPSR results, and the reaction was confirmed to follow the redox mechanism.

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1. Introduction

Light alkanes (C₂–C₄) are important and versatile building blocks for the industrial production of various chemicals and plastics [1–3]. Because the byproducts of steam cracking and fluidized catalytic cracking of naphtha cannot provide sufficient light alkenes for the expanding market, the catalytic dehydrogenation of light alkanes to their respective olefins has received much attention over the last few decades. However, to obtain a reasonably high conversion, the dehydrogenation of light al-

kanes can only be performed at high temperatures because of the endothermic nature of this reaction. As a result, drawbacks such as high energy consumption, low selectivity toward the desired light olefin, and accelerated catalyst deactivation are apparent since thermal cracking reactions are favored at high reaction temperatures [4]. To overcome these obstacles, oxidative dehydrogenation with molecular oxygen has been proposed, and much work has been conducted [5–7]. Its exothermic property makes the oxidative dehydrogenation reaction thermodynamically favorable at low temperatures. However,

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the inherent oxidation property of molecular oxygen makes this process challengeable with regard to olefin selectivity because of the unavoidable oxidation of hydrocarbons to CO₂. Additionally, process control difficulties are encountered because of potential flammability and heat removal difficulties. As an alternative, soft oxidants such as N₂O and CO₂ can replace molecular oxygen and they offer a potentially attractive route for the dehydrogenation of light alkanes to alkenes.

In recent years, the use of CO₂ as a soft oxidant has received much attention, as green chemistry has developed and raised concerns about its greenhouse effect [8,9]. Compared with molecular oxygen, CO₂ is a nonconventional oxidant, and has obvious advantages such as minimizing the deep oxidation of hydrocarbons, enhancing the selectivity of targeted olefins, and alleviating CO₂ emissions [9,10]. As clearly expressed in related papers [11–20], the oxidative dehydrogenation of light alkanes and ethylbenzene with CO₂ is one of the main trends in the catalytic domain.

In principle, the oxide catalysts developed for oxidative dehydrogenation with molecular oxygen are also active when using CO₂ as an oxidant. This has been unambiguously confirmed in the literature. However, analyses of the reported results indicate that much work is still required for the development of a high-performance catalyst for the oxidative dehydrogenation of light alkanes with CO₂ because of its much lower activity. The mechanism for the oxidative dehydrogenation of light alkanes with CO₂ has not been thoroughly explained although different pathways have been proposed, i.e., a one-step process following the Mars-van Krevelen mechanism and the coupled process of the direct dehydrogenation and reverse water-gas-shift reaction [11,17,21]. The redox and acid-base properties of oxides make the differentiation between the two pathways challenging. Therefore, the development of a high-performance catalyst based on a mechanistic understanding is desirable although different oxides such as V₂O₅ [22], CeO₂ [23,24], ZrO₂ [25,26], Gd₂O₃ [27,28], MoO₃ [29,30], La₂O₃ [31] and In₂O₃ [32,33] have been quantitatively investigated for the oxidative dehydrogenation of light alkanes with CO₂.

In previous works [34,35], we proposed the use of the Ce³⁺–Ce⁴⁺ redox couple to inhibit the deep reduction of V⁵⁺ as a new idea for catalyst design toward the oxidative dehydrogenation of ethylbenzene with CO₂ [35]. A highly active and stable catalyst (V₂O₅/Ce_{0.6}Zr_{0.4}O₂-Al₂O₃) was obtained [34]. In this work, V₂O₅/Ce_{0.6}Zr_{0.4}O₂-Al₂O₃ and V₂O₅-Ce_{0.6}Zr_{0.4}O₂-Al₂O₃ catalysts were comparatively investigated for the oxidative dehydrogenation of isobutane with CO₂ (CO₂-ODB). Reaction results confirmed the validity of our idea for the design of a suitable catalyst for oxidative dehydrogenation reactions with CO₂. The effect of catalyst composition on the conversion of isobutane and the selectivity of butenes was confirmed by characterization results. Moreover, the role of CO₂ in the titled reaction was clear from the results of temperature-programmed surface reaction (TPSR) and in situ Fourier transform infrared spectroscopy (FTIR).

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by a modified sol-gel method using aluminum isopropoxide, cerium nitrate, zirconium nitrate, and ammonium metavanadate as the oxide precursor of Al, Ce, Zr, and V, respectively. The experimental procedure was as follows for the preparation of Ce_{0.6}Zr_{0.4}O₂ (7 wt%)-Al₂O₃ (CZA). A predetermined amount of aluminum isopropoxide was dissolved in a mixture of toluene and ethanol at a volume ratio of 1 for the preparation of 1.5 mol·L⁻¹ aluminum solution (Solution A). After dissolving cerium nitrate and zirconium nitrate at a Ce/Zr molar ratio of 6/4 in 30 mL absolute ethanol, a 0.1 mol·L⁻¹ cation solution was obtained (Solution B). At room temperature, predetermined volumes of solutions A and B were thoroughly mixed, and vigorously stirred for 1 h. The mixture was then refluxed at 85 °C for 3 h, and aged for 12 h. After this, the solvent was evaporated at 50 °C. Finally, CZA was obtained by drying and calcining the solid at 110 °C for 8 h and at 550 °C for 4 h, respectively.

For the V₂O₅-supported catalysts, an aqueous solution of NH₄VO₃ along with oxalic acid was impregnated into CZA via the incipient wetness method. After drying and calcining the solid at 110 °C for 8 h and 550 °C for 4 h, respectively, V₂O₅/CZA with different vanadia loadings was obtained.

Following the same method for the preparation of CZA, the desired amount of NH₄VO₃ was added to the mixture and V₂O₅(*x* wt%)-Ce_{0.6}Zr_{0.4}O₂(7 wt%)-Al₂O₃ with varied vanadia content was obtained after drying and calcining under the same conditions. For brevity, the V₂O₅(*x* wt%)-Ce_{0.6}Zr_{0.4}O₂(7 wt%)-Al₂O₃ catalysts are designated *x*-VCZA, where *x* represents the weight content of V₂O₅.

2.2. Catalyst characterization

N₂ adsorption-desorption isotherms were measured on a Tristar 3000 (Micromeritics) at -196 °C. The BET method was used to calculate the specific surface area of the materials. Before an analysis, the sample was degassed at 300 °C for 6 h to remove any contaminants and physisorbed moisture.

Powder X-ray diffraction (XRD) data were collected on an X-ray diffractometer (Bruker AXS D8) using monochromatic Cu/K_α radiation at 40 kV and 40 mA and a scan rate of 2°·min⁻¹.

Temperature-programmed desorption of carbon dioxide (CO₂-TPD) was performed on a Micromeritics AutoChem II 2920 instrument. A 50.0 mg (40–60 mesh) sample was loaded into a quartz reactor and pretreated at 550 °C for 1 h under an argon flow of 35 mL·min⁻¹. After cooling to 60 °C, CO₂ was pulsed until saturated adsorption was achieved. To remove the physically adsorbed CO₂, the reactor was purged with argon for 1 h. CO₂-TPD was then carried out from 60 to 550 °C at a heating rate of 10 °C·min⁻¹, and the desorbed CO₂ was monitored with a thermal conductivity detector (TCD).

Temperature-programmed oxidation of oxygen (O₂-TPO) was carried out on a TL 5000-II instrument (Xianquan Industry and Trade Development Co., Ltd., China) equipped with a mass spectroscope (Omni Star 200). The catalyst sample (50.0 mg) was pretreated under argon at 200 °C for 1 h. After cooling to 30 °C, 5% O₂ in Ar at a flow rate of 30 mL·min⁻¹ was applied and O₂-TPO was carried out from 30 to 900 °C at a ramp up

rate of 5 °C·min⁻¹. The produced CO₂ was monitored using a mass spectrometer.

The amount of coke deposited on the used catalysts was determined using a thermogravimetric analyzer (Thermo Plus EVO, Rigaku). The sample was heated under an air atmosphere from 30 to 800 °C at a ramp up rate of 10 °C·min⁻¹.

TPSR was performed in a fixed bed reactor connected to a mass spectroscope (Omni Star 200). The catalyst was pre-treated at 200 °C for 1 h under nitrogen flow. After cooling to 30 °C, a 30 mL·min⁻¹ flow of CO₂ (or N₂)/C₄H₁₀ at a molar ratio of 5 was used, and the sample was heated to 700 °C at a ramp up rate of 5 °C per minute.

In situ FTIR spectra were obtained on a Bruker TENSOR 27 spectrometer equipped with a MCT detector. Before a measurement, the sample (30.0 mg) was pressed into a thin disk with a diameter of 13 mm and was treated at 200 °C under high-vacuum conditions ($5\text{--}8 \times 10^{-2}$ Pa) to remove the adsorbed water and the volatile organics. After cooling to 30 °C, CO₂ and isobutane were introduced for 30 min. Finally, the sample was heated to different temperatures and IR spectra with a resolution of 2 cm⁻¹ were collected by accumulating 64 scans.

2.3. Reaction procedure

The catalytic experiments were performed in a stainless steel fixed bed reactor (i. d. = 6 mm). Typically, 200 mg catalyst (40–60 mesh) was loaded into the reactor, and it was heated to 600 °C under a flow of N₂. A flow of CO₂ (or N₂) and isobutane that was separately calibrated using mass flow controllers was then applied and the reaction began under the following conditions at 600 °C, and the CO₂(N₂)/C₄H₁₀ (molar ratio) was 5. The gas hourly space velocity (GHSV) with respect to isobutane was 1500 mL·g⁻¹·h⁻¹. The effluent products were analyzed using an on-line gas chromatograph (Shimadzu GC-14C) equipped with a FID and an alumina packed column.

3. Results and discussion

3.1. CO₂-ODB over different catalysts

Under the reaction conditions used, the blank experiment showed an isobutane conversion of less than 2%, indicating negligible thermal reactions. The results for the CO₂-ODB using different oxides are shown in Fig. 1. During the initial reaction stage, the conversion of isobutane decreased as follows: V₂O₅ >> CeO₂ > ZrO₂ > Al₂O₃. This indicates that bulk V₂O₅ is more active than CeO₂ or ZrO₂ for the CO₂-ODB. However, after a time-on-stream (TOS) of about 3 h, a very similar conversion of isobutane was observed for all the oxides, indicating very fast deactivation of the bulk V₂O₅ during the titled reaction. As far as the products are concerned, the steady selectivity of the total C₄ olefins (mainly isobutene) over V₂O₅ (86%) and ZrO₂ (81%) was very similar and was much higher than that over CeO₂ (33%) and Al₂O₃ (60%).

The TOS results of the ODB over the 6 wt% V₂O₅-supported catalysts are given in Fig. 2. By comparison with the results of

Fig. 1. Time-on-stream iso-C₄H₁₀ conversion and selectivity toward total C₄ olefins over different oxides.

bulk V₂O₅ (Fig. 1), a significant increase in the initial conversion of isobutane was observed over the V₂O₅-supported catalysts. Moreover, a compositional effect of the support materials on the initial isobutane conversion was clear, i.e., 19.6%, 17.2%, and 16.5% at a TOS of 0.33 h for 6 wt% V₂O₅/CZA, 6 wt% V₂O₅/ZrO₂(7 wt%)-Al₂O₃, and 6 wt% V₂O₅/CeO₂(7 wt%)-Al₂O₃, respectively. Compared with the reported results of experiments carried out under similar conditions, the 6 wt% V₂O₅/CZA showed higher catalytic activity toward the titled reaction. However, increasing the TOS to 7 h resulted in all of the catalysts a quick decrease in isobutane conversion, and a relatively more stable performance was obtained over the 6 wt% V₂O₅/CZA. As far as product compositions are concerned, all the catalysts gave a similar high selectivity towards the desired olefin. Moreover, the selectivity toward total C₄ olefins increased slightly from ~86% to ~91% with an increase in the TOS from 0.33 to 7 h.

The impact of vanadia loading over V₂O₅/CZA on the performance of CO₂-ODB is shown in Fig. 3. All the vanadia-loaded catalysts showed very similar selectivity toward total C₄ olefins (~90%), which is much higher than that without vanadia

Fig. 2. Time-on-stream iso-C₄H₁₀ conversion and selectivity toward total C₄ olefins over different catalysts.

Fig. 3. Effect of vanadia loading over $\text{V}_2\text{O}_5/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2(7 \text{ wt}\%)\text{-Al}_2\text{O}_3$ on the time-on-stream iso- C_4H_{10} conversion and selectivity toward total C_4 olefins.

(~60%). This clearly indicates the negligible influence of vanadia loading toward targeted product selectivity, which confirms the benefits of CO_2 as a soft oxidant [8,9]. With an increase in vanadia loading from 0 to 9 wt%, the conversion of isobutane during the initial reaction stage of 0.33 h increased significantly. This indicated that the vanadium species are active sites for the titled reaction. Moreover, a further increase in vanadia loading to 12 wt% led to a slight increase in isobutane conversion. A slight decrease in isobutane conversion was obtained when the vanadia loading was 18 wt%. Irrespective of the vanadia loading, almost the same conversion of isobutane (~13%–14%) was obtained at a TOS of 3 h and a limited decrease was evident until the end of the tests. This may be caused by fast coke deposition over the catalysts, which will be discussed later with the characterization results of the used catalysts.

To determine the effect of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2\text{-Al}_2\text{O}_3$ composition on catalytic performance, the 6 wt% V_2O_5 -supported $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (5 wt%)- Al_2O_3 , $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (7 wt%)- Al_2O_3 , and $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (9 wt%)- Al_2O_3 catalysts were subjected to the CO_2 -ODB and the TOS results are given in Fig. 4. As expected, a higher than 90% selectivity of total C_4 olefins was obtained over all of the catalysts, indicating the negligible effect of the amount of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$. However, the 6 wt% $\text{V}_2\text{O}_5/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2(7 \text{ wt}\%)\text{-Al}_2\text{O}_3$ showed slightly higher activity and stability toward CO_2 -ODB than the remaining catalysts.

The TOS results for the CO_2 -ODB over VCZA are shown in Fig. 5. For catalysts with the same composition (Figs. 3 and 5), the difference in selectivity toward total C_4 olefins was negligible. However, a significant impact on the activity and stability was found by using different vanadia loading methods. As indicated in Figs. 3 and 5, VCZA gave a clearly lower initial conversion of isobutane than $\text{V}_2\text{O}_5/\text{CZA}$ with the same vanadia loading. On the contrary, more stable performance was observed over VCZA than over $\text{V}_2\text{O}_5/\text{CZA}$, and 9-VCZA gave the highest performance throughout the test.

From these catalytic results, it is obvious that vanadium species are the active sites for CO_2 -ODB, and the activity and

Fig. 4. Effect of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ content on the time-on-stream iso- C_4H_{10} conversion and selectivity toward total C_4 olefins over 6 wt% $\text{V}_2\text{O}_5/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2\text{-Al}_2\text{O}_3$.

stability of the vanadia-based catalysts are promoted by the method of V_2O_5 introduction and the addition of CeO_2 , ZrO_2 , and $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$, the extent of which is obviously dependent on their content. Moreover, all of the vanadia-loaded catalysts showed relatively fast deactivation from the start of the reaction to a TOS of ~3 h, and this leveled off until the end of the test. On the contrary, all of the catalysts showed high selectivity toward total C_4 olefins (~90%), which matches the benefits of the CO_2 -ODB well. In the next section, the activity and stability results of the CO_2 -ODB over the vanadia-based catalysts will be related to the characterization results of the materials.

3.2. Insights into the catalytic behaviour of the vanadia-based catalysts

It is commonly known that crystalline V_2O_5 is less active in oxidative dehydrogenation reactions as a result of its platelet morphology and its inactive basal planes [36,37]. As a result, vanadia is generally dispersed over oxides such as alumina to inhibit the formation of well-crystallized V_2O_5 . Thus, highly

Fig. 5. Effect of V_2O_5 loading on the performance of $\text{V}_2\text{O}_5\text{-Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2(7 \text{ wt}\%)\text{-Al}_2\text{O}_3$ for CO_2 -ODB.

dispersed vanadium species that have not formed crystalline V_2O_5 are responsible for the CO_2 -ODB activity of the V_2O_5 -supported catalysts. To give a insight into the varied performance of V_2O_5 -based catalysts for the CO_2 -ODB, the materials were characterized by N_2 adsorption-desorption at $-196^\circ C$ and XRD.

The BET surface areas of typical materials are listed in Table 1. It was shown that the BET surface area of V_2O_5 synthesized by the sol-gel method was very low, which may be due to the high degree of crystallization. In the case of alumina, a very high BET surface area ($> 400\text{ m}^2\cdot\text{g}^{-1}$) was obtained. Compared with Al_2O_3 , the BET surface area of the 6 wt% V_2O_5 -supported catalysts was significantly lower and this is slightly dependent on the presence of ceria and zirconia, or their solid solution. When the BET surface areas of the catalysts were related to the conversion of isobutane, no simple relationship was evident. This indicates its relevant insignificance in determining the activity of the catalysts in the titled reaction.

The XRD patterns of the materials are given in Fig. 6. For all of the samples, the peak intensity of the XRD diffractions was very low, indicating a low extent of crystallization for all the phases in the samples. Specifically, in the case of the alumina synthesized by the sol-gel method, low crystalline $\gamma\text{-}Al_2O_3$ was evident from the clear (440) diffraction at a 2θ of about 66° and the very broad (400) diffraction. In the case of CZA, the addition of 7 wt% $Ce_{0.6}Zr_{0.4}O_2$ to Al_2O_3 resulted in very limited changes to the XRD pattern, indicating the high dispersion and low crystallinity of $Ce_{0.6}Zr_{0.4}O_2$. Moreover, a weak diffraction assigned to cubic ceria was observed for the 6 wt% V_2O_5/CeO_2 (7 wt%)- Al_2O_3 . For all of the V_2O_5 -loaded samples up to 18 wt% V_2O_5 , no vanadium species were detectable by XRD, indicating its highly dispersed state. When the XRD patterns of V_2O_5/CZA were compared with those of VCZA, no difference was found except for a slight decrease in the peak intensity of the (440) diffraction of $\gamma\text{-}Al_2O_3$. Thus, irrespective of the vanadia content over all of the catalysts, the formation of crystalline V_2O_5 was not evident. This can be used to explain the high activity of the vanadia-based catalysts in the CO_2 -ODB. Moreover, the catalytic activity varied with vanadia loading and the effect of method of introduction can be well explained by the dispersion of the monomeric and/or polymeric VO_x species, and this has been

Fig. 6. XRD patterns of Al_2O_3 (1), CZA (2), 6 wt% V_2O_5/CeO_2 (7 wt%)- Al_2O_3 (3), 6 wt% V_2O_5/ZrO_2 (7 wt%)- Al_2O_3 (4), 6 wt% V_2O_5/CZA (5), 9 wt% V_2O_5/CZA (6), 12 wt% V_2O_5/CZA (7), 18 wt% V_2O_5/CZA (8), 6-VCZA (9), 9-VCZA (10), 12-VCZA (11).

clearly revealed in our previous work [34,35].

It is commonly observed that coke deposition is a severe issue during the dehydrogenation of hydrocarbons with CO_2 , and coking plays an important role in determining the stability of the catalyst. Thus, the used catalysts were subjected to TG analyses, and the amount of coke deposited over different catalysts is given in Table 1. It revealed that coke deposition was very severe over all of the catalysts, which agrees with previous results [38,39]. Specifically, 6 wt% vanadia supported catalysts

Table 1

BET surface area of the fresh oxides, the amount of coke deposited, and the deactivation rate of the different catalysts.

Sample	BET surface area ($\text{m}^2\text{ g}^{-1}$)	Coke ^a		Deactivation ^b (%)
		(wt%)	mg mol^{-1}	
Al_2O_3	441	—	—	—
CeO_2	49	—	—	—
ZrO_2	17	—	—	—
V_2O_5	4	—	—	—
6 wt% V_2O_5/CeO_2 (7 wt%)- Al_2O_3	210	18.1	3.47	50.9
6 wt% V_2O_5/ZrO_2 (7 wt%)- Al_2O_3	279	21.2	3.63	43.6
6 wt% V_2O_5/CZA	221	21.6	3.18	36.2
6-VCZA	—	22.6	3.20	15.0
9-VCZA	—	21.8	3.97	33.5

^a The coke deposited over the catalysts used was determined by TG analyses, and was expressed as weight percentage over the catalyst (wt%) and as the weight of the deposited coke required to convert 1 mol of isobutane (mg mol^{-1}).

^b Deactivation of the catalyst for CO_2 -ODB = $\frac{(\text{Con}_{C_4H_{10}})_i - (\text{Con}_{C_4H_{10}})_f}{(\text{Con}_{C_4H_{10}})_i} \times 100\%$.

produced a lower amount of coke while 6-VCZA gave the highest amount of coke (22.6 wt%), indicating the significant effect of catalyst preparation method on its coking behavior during the CO₂-ODB. To quantitatively compare the deactivation of the different catalysts in the titled reaction, the deactivation rate was calculated and the results are shown in Table 1. When the amount of coke deposited was correlated to the deactivation rate of the catalysts no simple relationship was found. Moreover, the coke deposited by the conversion of 1 mol isobutane over the catalyst could not be related to the deactivation rate of the catalyst. Thus, the amount of coke was not the main reason for the deactivation of the catalyst although severe coking occurred over all of the catalysts. To determine the reason, O₂-TPO was carried out on selected catalysts after the reaction and the results are given in Fig. 7. From Table 1 and Fig. 7, the amount of coke deposited over the used 6-VCZA and 9-VCZA was similar, and the peak temperature of the O₂-TPO profiles was almost the same (500 °C). However, the O₂-TPO profile of 9-VCZA spanned a much wider range of temperatures than that of 6-VCZA, i.e., a clearly higher starting temperature (~50 °C) and a much higher end temperature (100 °C). As a result, the coke deposited over 9-VCZA was much heavier (lower H/C ratio) than that over 6-VCZA, leading to an enhanced deactivation for the titled reaction. Thus, the quantity of heavier coke deposited is responsible for the deactivation of the catalyst in the CO₂-ODB.

3.3. Mechanistic aspects of the CO₂-ODB

The advantages of CO₂-ODB are clearly related to the catalyst as explained previously by two different proposed pathways [11]. To determine the reaction mechanism, the transient kinetic behavior of isobutane dehydrogenation in the presence of N₂ and CO₂ was comparatively investigated over the vanadia-based catalysts, and TPSR results of the molecular ions at m/z of 43 [M-15]⁺, 56 [M]⁺, 44 [M]⁺, and 28 [M]⁺ are given in Fig. 8.

In the case of 6-VCZA (Fig. 8a), the starting temperature for the consumption of isobutane under a CO₂ atmosphere (~460 °C) was significantly lower than that under a N₂ atmosphere

Fig. 7. Mass spectra of CO₂ during the O₂-TPO using 6-VCZA (1) and 9-VCZA (2).

Fig. 8. Mass spectra of the TPSR results for the dehydrogenation of isobutane under an atmosphere of N₂ and CO₂ over 6-VCZA (a) and 9-VCZA (b).

(~560 °C). The formation of isobutene was clearly observed in both cases. However, with an increase in temperature, the changing pattern indicating the consumption of isobutane and the formation of isobutene in the presence of CO₂ was quite different from those in the presence of N₂. In the presence of CO₂, the consumption of isobutane and the formation of isobutene were more pronounced than that in the presence of N₂. Moreover, a significant peak at about 670 °C was observed under a CO₂ atmosphere. On the contrary, a slight but continuous increase in the content of isobutene was obtained under a N₂ atmosphere. As far as the results for 9-VCZA are concerned, the mentioned observations were still valid. Thus, irrespective of the catalyst the benefits of dehydrogenation over vanadia-based catalysts in the presence of CO₂ are obvious compared with direct dehydrogenation under an inert atmosphere such as N₂.

To determine the mechanism of the CO₂-ODB upon catalysis by vanadia-based catalysts, in situ FTIR was performed at different temperatures and the results are given in Fig. 9. The vibrational peaks (Fig. 9(b)) at about 2966, 2953, and 2917 cm⁻¹ are clearly visible at room temperature, and they can be assigned to the stretching vibrations of saturated –C–H bonds (ν (–C–H)) in C₄H₁₀. With an increase in temperature to 450 °C those peaks decreased by a different extent. Furthermore, when the temperature was increased to 400 °C, a stretching vibration absorption of unsaturated =C–H bonds (ν (=C–H)) at about 3017 cm⁻¹ appeared and increased with an increase in

Fig. 9. In situ FTIR spectra upon the CO₂-ODB at different temperatures over 6-VCZA from 4000–1200 cm⁻¹ (a) and 3050–2850 cm⁻¹ (b).

temperature. The production of butene under these reaction conditions is clear. A further increase in the temperature to 450 °C led to the disappearance of the asymmetric stretching vibration absorption of CO₂ ($\nu_{as}(\text{CO}_2)$) located at about 2349 cm⁻¹. The adsorption of CO₂ onto the surface of the catalysts was also affected by the temperature. More importantly, when the temperature was higher than 350 °C, two peaks at about 3700 and 1270 cm⁻¹ appeared, and these can be assigned to stretching vibrations of the –O–H bonds ($\nu(\text{–O–H})$) [40] and the C–O bonds ($\nu(\text{C–O})$) [41], respectively. This demonstrates that isobutane reacted with CO₂ to form intermediates at those temperatures, and this is significantly different from the coupled mechanisms of direct dehydrogenation and reverse water-gas-shift reactions. Therefore, it is reasonable to propose that the CO₂-ODB over the vanadia-based catalysts follows the Mars–van Krevelen redox mechanism.

4. Conclusions

In summary, vanadia-based catalysts were successfully synthesized by using the sol-gel method, and found to be highly active for the CO₂-ODB. All of the catalysts showed over 85% selectivity toward total C₄ olefins. The highly dispersed and low crystallinity VO_x species were found to be the active sites for the titled reaction. Thus, the catalytic activity was significantly influenced by the composition of the catalysts and the intro-

ducing method of V₂O₅, and the highest initial conversion of isobutane was obtained over 12 wt% V₂O₅/CZA. The deactivation of the catalyst was mainly caused by the deposition of the heavier coke, and the titled reaction followed the Mars–van Krevelen redox mechanism.

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Graphical Abstract

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Insights into the vanadia catalyzed oxidative dehydrogenation of isobutane with CO₂

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The oxidative hydrogenation of isobutane with CO₂ over vanadia-based catalysts was confirmed to follow the redox mechanism, and the catalyst deactivation was mainly originated from the deposition of heavier coke.

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钒氧化物催化CO₂氧化异丁烷脱氢的研究

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摘要: 采用溶胶-凝胶法制备了一系列钒氧化物催化剂, 并用于CO₂氧化异丁烷脱氢反应。采用X射线衍射、低温N₂吸附-脱附、O₂程序升温氧化、程序升温表面反应和原位傅里叶变换红外光谱等方法研究了催化剂的性质。反应结果表明, 尽管所有钒氧化物催化剂的丁烯选择性都大于85%, 但随着催化剂组成和制备方法的改变, 催化活性和稳定性差异显著。其中, 12 wt% V₂O₅/Ce_{0.6}Zr_{0.4}O₂(7 wt%)-Al₂O₃的催化活性最高, 而6 wt% V₂O₅-Ce_{0.6}Zr_{0.4}O₂(7 wt%)-Al₂O₃的稳定性最佳。关联分析催化反应结果与催化剂表征表明, 钒氧化物的催化活性取决于VO_x物种的结晶度和分散度, 而催化剂表面所积重质焦炭的特性是决定催化剂稳定性的关键。非稳态反应和原位光谱结果确认, CO₂氧化异丁烷脱氢遵循Mars-van Krevelen氧化还原机理。

关键词: 异丁烷; 氧化脱氢反应; 二氧化碳; 五氧化二钒; 三氧化二铝

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