Catalytic dehydrogenation of isobutane in the presence of carbon dioxide over nickel supported on active carbon

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ABSTRACT

The dehydrogenation of isobutane to isobutene was carried out in the presence of carbon dioxide over the catalyst nickel supported on active carbon (AC). The state and property of nickel species (NiOx) in the catalyst are relevant to its calcination temperature, because NiO may be partially reduced to Ni by AC at high temperature. NiO and Ni species are different in the catalytic behaviors; Ni is only effective for direct dehydrogenation of isobutane, while NiO is also highly active for the coupled dehydrogenation with carbon dioxide. Carbon dioxide can significantly enhance the dehydrogenation of isobutane over NiO/AC through keeping NiO species, in situ eliminating hydrogen produced and suppressing coke formation.

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1. Introduction

Isobutene is widely used in industry to produce polyisobutene, butyl rubber, methyl acrylates, methyl *tert*-butyl ether (MTBE) and other chemicals [1,2]. Although the use of MTBE as octane enhancing additive in gasoline is likely questionable, the use of heavier ethers like ethyl *tert*-butyl ether obtained from isobutene is possible [3,4]. At present, isobutene is mainly obtained from the refinery gas as a by-product of naphtha steam cracking or fluidized catalytic cracking as well as produced by the dehydrogenation of isobutane [5,6]. The increasing demand for isobutene in recent years has drawn considerable attention to the dehydrogenation of isobutane to isobutene.

Because the direct dehydrogenation of isobutane is an endothermic and volume-expanding reaction, it is usually performed at high temperature; hence fast catalyst deactivation due to carbonaceous deposition, poor isobutene selectivity due to numerous side reactions, as well as high energy consumption from the high temperature operation are crucial issues affecting the efficiency of the dehydrogenation process [7]. On the other hand, the oxidative dehydrogenation is an effective way to increase the conversion and/or lower the reaction temperature [8–10]; however, the desirable dehydrogenation product is vulnerable by deep oxidation when using oxygen as oxidant [11].

Many researchers have attempted to employ CO_2 as a mild oxidant in the oxidative dehydrogenation of isobutane [7,12–15], where the dehydrogenation is coupled with reverse water gas shift (RWGS):

$$(CH_3)_3CH = (CH_3)_2CCH_2 + H_2 \qquad (1)$$

$$CO_2 + H_2 = CO + H_2O \qquad (2)$$

In this respect, the yield of isobutene can be enhanced at relatively low temperature by promoting the dehydrogenation and avoiding the deep oxidation of target product with CO_2 in the reaction stream. The catalysts Cr_2O_3 [7], V–Mg–O [12–14] and Fe–O [15] have been used for this reaction. However, the results are still unsatisfactory for practical application. We previously found out that the catalyst nickel supported on active carbon (AC) exhibited excellent performance for the dehydrogenation of isobutane in the presence of CO_2 [16]; the isobutane conversion and isobutene selectivity at 550 °C were 48.0 and 86.8%, respectively. The reaction behavior was largely dependent on the catalyst calcination temperature.

In this work, the dehydrogenation of isobutane to isobutene was carried out in the presence of CO_2 over the AC supported nickel catalyst (NiOx/AC). The variance of active nickel species along with the catalyst calcination and reaction process was investigated. The

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performance of various nickel species and the role of CO_2 in the dehydrogenation of isobutane were clarified.

2. Experimental

2.1. Catalyst preparation

The catalyst NiOx/AC with a Ni loading of 1.0 mmol/g-AC was prepared by incipient wetness impregnation of AC (40–60 mesh, 600 m^2/g) with an aqueous solution of $Ni(NO_3)_2\cdot6H_2O$. The impregnation lasted for 24 h at room temperature, and then the catalyst with Ni precursor was dried at 110 °C in N_2 for 12 h and finally calcined at different temperatures in Ar for 1 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) was performed on a Bruker AXS D8 advanced X-ray diffractometer with Cu Kα radiation (154.06 pm, 40 kV, and 40 mA) in the range of 2θ between 10° and 95°.

Thermogravimetric analyses (TGA) were carried out on the apparatus TGA92 (Setaram Co., France) under Ar (or air) within the temperature range of 20–1000 °C at a heating rate of 10 °C/min.

H_2-TPR was performed in a quartz microreactor (TP-5000, Tianjin-Xianquan, China) and about 50 mg of catalyst sample was used in each measurement. The measurement was conducted from room temperature to 800 °C at a heating rate of 10 °C/min by using a gas flow of 5 vol% H_2 in Ar (30 ml/min). The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD).

2.3. Catalytic tests and analytical procedure

The catalytic tests were performed in a fixed bed tubular reactor (stainless steel tube with an inner diameter of 5.0 mm) at atmospheric pressure. For each test, about 500 mg of catalyst sample was diluted with quartz grain and loaded in the constant temperature zone of the reactor. The temperature of reactor was programmed up to the reaction temperature 550 °C under an Ar flow, and then the Ar flow was switched to the reaction stream (a mixture of isobutane + CO_2/Ar). The mole ratio of CO_2 (or Ar) to isobutane in the feed was 6 when the reaction was conducted in CO_2 (or Ar). The volumetric hourly space velocity (VHSV) of the feed for the dehydrogenation was 1770 h^{-1}. Blank tests were also conducted under the same conditions, by replacing the catalyst with quartz sand of the same particle size.

The effluent was analyzed by using two on-line gas chromatographs: one equipped with C-18 packed column for C_3–C_4 hydrocarbons and another with carbon molecular sieves (80–100 mesh) packed column for CO, CO_2 and CH_4; both using TCD as the detector and H_2 as the carrier gas. The isobutane conversion, isobutene selectivity and CO_2 conversion are denoted as x_{IB}, s_{IB} and x_{CO_2}, respectively.

3. Results and discussion

3.1. Effect of calcination temperature on the state of Ni species

The XRD patterns of the catalysts calcined in Ar for 1 h at different temperatures are shown in Fig. 1. Only NiO phase is observed in the catalysts calcined in Ar at 500 and 550 °C; the scattered peaks suggest a high dispersion of amorphous NiO in the support AC. Ni phase appears in the catalyst calcined at 600 °C or higher temperature. These suggest that NiO can be partially reduced to Ni with AC by calcination at 600 °C. When the catalyst is calcined at higher temperature, more NiO is reduced to Ni and Ni species is agglomerated
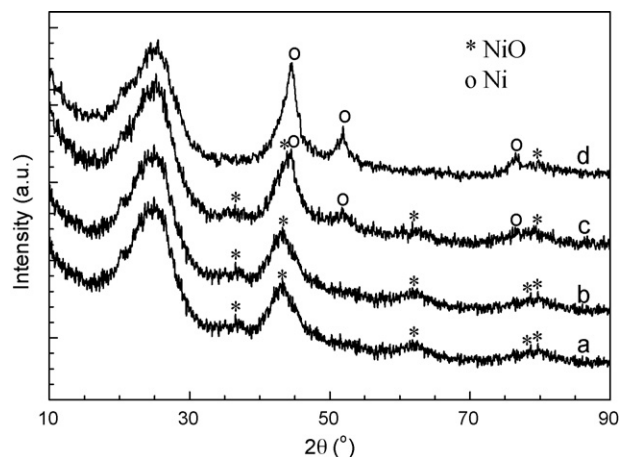

Fig. 1. XRD patterns of the catalysts calcined in Ar for 1 h at different temperatures: (a) 500 °C; (b) 550 °C; (c) 600 °C; and (d) 650 °C.

at high temperature; the peaks of amorphous and well-dispersed NiO species are then immersed in the intense peaks of aggregated Ni species and become indistinct in the XRD patterns.

The TG–DTG profiles of the sample AC loaded with Ni precursor ($Ni(NO_3)_2$/AC) are shown in Fig. 2. Two peaks of weight loss are observed; the first peak around 300 °C is attributed to the decomposition of $Ni(NO_3)_2$ to NiO, and the second around 600 °C is ascribed to the reduction of NiO to Ni by AC. This confirms that the reduction of NiO by AC starts at about 600 °C, as suggest by the XRD results of Fig. 1.

The catalysts calcined at different temperatures are characterized by H_2-TPR. All catalysts exhibit a H_2 consumption peak around 210 °C and the reduction of NiO completed at about 310 °C. The amount of H_2 consumption decreases significantly with the calcination temperature, as shown in Table 1. This supports that more NiO species will be reduced by AC upon calcination at higher temperature. The molar ratio of NiO to Ni species in the catalyst can be estimated by the H_2 consumption; for the catalyst calcined at 700 °C, the molar ratio of Ni to NiO species reaches 0.748. The content of NiO species in the catalyst decreases considerably with the increase of the calcination temperature.

3.2. Catalytic behaviors of different Ni species

To understand the catalytic behaviors of different Ni species (NiO and Ni) in the dehydrogenation of isobutane, a series of
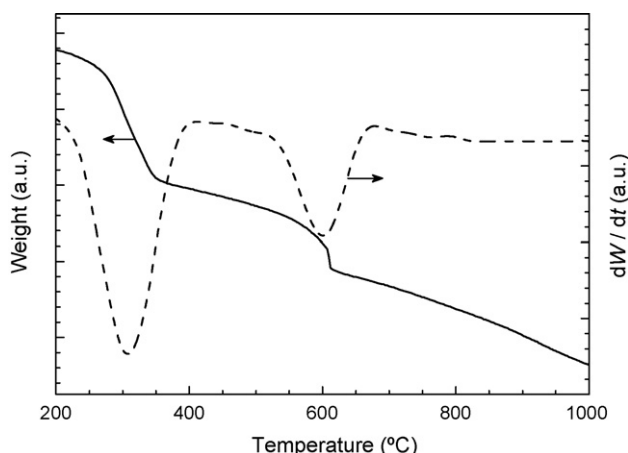

Fig. 2. TG–DTG profiles of $Ni(NO_3)_2$/AC in Ar.

Table 1
H_2 consumption in H_2-TPR measurement and the Ni/NiO molar ratio estimated for the NiO/AC catalysts calcined at different temperatures.

Calcination temperature (°C)	H_2-TPR intensity (a.u.)	H_2 consumption (mmol/g)	Ni/NiO molar ratio
550	832	0.902	0
600	637	0.691	0.306
650	516	0.560	0.612
700	476	0.516	0.748

catalysts are prepared. The catalyst with NiO species (NiO/AC) is obtained by calcining $Ni(NO_3)_2$/AC in Ar at 550 °C for 1 h to prevent NiO from reduction by AC; while the catalyst with Ni species (Ni/AC) is prepared by reducing NiO/AC with H_2 (10%) in Ar at 400 °C for 4 h. A comparison of isobutane dehydrogenation over different catalysts as well as in different atmospheres (CO_2 or Ar) was then conducted at 550 °C; the results are illustrated in Fig. 3.

In the blank tests with quartz sands loaded in the reactor, the isobutane conversion x_{IB} is about 3.8% with the isobutene selectivity s_{IB} of about 87.5%, regardless of the reaction atmosphere (Ar or CO_2); this suggests that thermal non-catalytic dehydrogenation of isobutane may occur at 550 °C, but the isobutane conversion is very low and independent on the reaction atmosphere.

Over the catalyst Ni/AC, the isobutane conversion is largely increased. The reaction behavior over Ni/AC in the presence of CO_2 is actually identical with that in the Ar atmosphere. At 550 °C

Fig. 3. Dehydrogenation of isobutane over NiO/AC, Ni/AC and inert quartz sand in the atmospheres of CO_2 and Ar: (a) isobutane conversion; (b) isobutene selectivity; and (c) CO_2 conversion for the reaction in CO_2. Reaction conditions: 550 °C; VHSV of 1770 h^{-1}; the mole ratio of CO_2 (or Ar) to isobutane in the feed was 6 when the reaction was conducted in CO_2 (or Ar).

with the time on stream of 1 h, the isobutane conversion x_{IB} and isobutene selectivity s_{IB} are 37.6 and 86.0%, respectively; with the increase of reaction time, the isobutane conversion decreases, while the isobutene selectivity increases gradually. The results here suggest that Ni/AC is catalytically active for the direct dehydrogenation of isobutane (in an inert atmosphere). Over Ni/AC, CO_2 cannot bring on any promoting effect on the isobutane dehydrogenation. Actually, the conversion of CO_2 is also not observed here for the reaction over Ni/AC in CO_2.

Over NiO/AC, the dehydrogenation of isobutane is further promoted. At 550 °C in Ar with the time on stream of 1 h, the isobutane conversion x_{IB} and isobutene selectivity s_{IB} are 40.7 and 86.1%, respectively. In contrast with the reactions over Ni/AC, the presence of CO_2 in the reaction stream here can significantly enhance the isobutane conversion for the dehydrogenation over NiO/AC; at 550 °C in CO_2 with the time on stream of 1 h, x_{IB} and s_{IB} reach 48.0 and 86.8%, respectively; the decrease of isobutane conversion with the time on stream is also much milder. Moreover, a significant conversion of CO_2 ($x_{CO_2} \approx 6.0\%$) is observed for the isobutane dehydrogenation over NiO/AC in CO_2. This then strongly suggests that NiO species present in the catalyst is effective for the promotion of isobutane dehydrogenation with CO_2.

We can then infer that NiO and Ni species are different in the catalytic behaviors; Ni is only effective for direct dehydrogenation of isobutane, while NiO is also highly active for the coupled dehydrogenation with CO_2 through the RWGS reaction besides the direct dehydrogenation. Moreover, it seems that NiO is also some more active for the direct isobutane dehydrogenation in inert atmosphere than Ni. The dehydrogenation of isobutane over NiO/AC can then be significantly enhanced with CO_2 in the reaction stream.

3.3. Effect of the calcination temperature on the catalytic performance of NiO/AC

The catalytic tests are then performed over the catalysts NiO_x/AC calcined at different temperatures, both in CO_2 and Ar atmospheres. As listed in Table 2, with the increase of calcination temperature, the conversion of isobutane (x_{IB}) decreases considerably, accompanied with an appreciable decrease of the selectivity to isobutene (s_{IB}) (either in CO_2 or Ar). For the reactions in CO_2, the conversion of CO_2 (x_{CO_2}) also decreases obviously with the increase of calcination temperature.

As shown in Table 1, the mole ratio of Ni/NiO in the catalyst increases with its calcination temperature. Namely, with the increase of calcination temperature, the fraction of Ni phase in the catalyst is raised, while the fraction of NiO phase is decreased. As mentioned above, NiO phase is active both for the direct dehydrogenation of isobutane in Ar and for the coupled dehydrogenation in CO_2, while Ni phase is only active for the direct dehydrogenation; even for the direct dehydrogenation, NiO phase is also more active than Ni phase under the same reaction conditions. Moreover, Ni species may be agglomerated at high temperature, which can also decrease its catalytic activity. All these contribute to that the performance of NiO/AC catalyst for isobutane dehydrogenation (especially in CO_2) deteriorates with the increase of its calcination temperature.
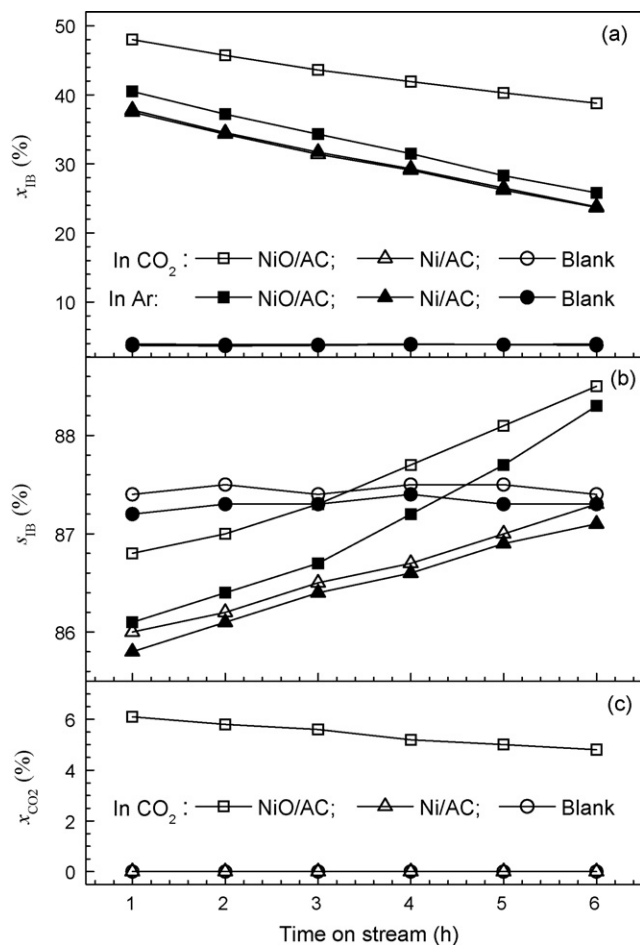
Table 2
Catalytic performance of the NiO/AC catalysts calcined at different temperatures for isobutane dehydrogenation.

Calcination temperature (°C)	in CO_2			in Ar	
	x_{IB} (%)	s_{IB} (%)	x_{CO_2} (%)	x_{IB} (%)	s_{IB} (%)
550	48.0	86.8	6.1	40.5	86.1
600	43.5	86.3	4.8	35.3	85.7
650	37.6	85.9	3.2	29.5	85.3
700	36.3	85.7	2.7	28.7	85.0

Reaction conditions: 550 °C; VHSV of 1770 h^{-1}; the mole ratio of CO_2 (or Ar) to isobutane in the feed was 6 when the reaction was conducted in CO_2 (or Ar). The data were acquired at 1 h on stream.

3.4. About the effect of CO_2 on the isobutane dehydrogenation

As shown in Fig. 3, the conversion of isobutane and the selectivity to isobutene in CO_2 are always higher than those in Ar for isobutane dehydrogenation over NiO/AC. The presence of CO_2 enhances the efficiency of isobutane dehydrogenation significantly, which is generally attributed to that CO_2 as a weak oxidant can eliminate hydrogen produced during the dehydrogenation through the RWGS reaction (Eq. (2)) [7]. This is supported by the formation of CO and H_2O, as detected in the effluents.

Moreover, the decrease of isobutane conversion with the reaction time in CO_2 is also much milder than that in Ar; in CO_2 the conversion of isobutane descends from 48.0 to 38.8% in 6 h, while in Ar it descends from 40.5 to 25.8%. The TGA tests also illustrate that for the isobutane dehydrogenation over NiO/AC, the carbonaceous deposition in CO_2 is much less than that in Ar under the same reaction conditions. This suggests that CO_2 can also alleviate the catalyst deactivation, which may be partially attributed to that CO_2 can suppress the carbonaceous deposition by reaction with coke to form CO [7,15–18].

On the other hand, the catalytic activity of NiO_x/AC is dependent on the valence state of active Ni species, as mentioned above (Fig. 3). H_2-TPR profiles of the fresh and used catalysts after reaction for 6 h in different atmospheres are shown in Fig. 4. The consumption of H_2, which is relevant to the NiO content in the catalyst, decreases considerably after the reaction. However, as listed in Table 3, H_2 consumption for the reduction of the used catalyst after reaction in CO_2 is much higher than that in Ar. It is estimated that about 80.0% NiO species in the catalyst is retained after reaction in CO_2, while about 50.0% NiO species is reduced to Ni after the reaction in Ar. These clearly indicate that CO_2 can help to keep the NiO active species during the coupled dehydrogenation of isobutane, which
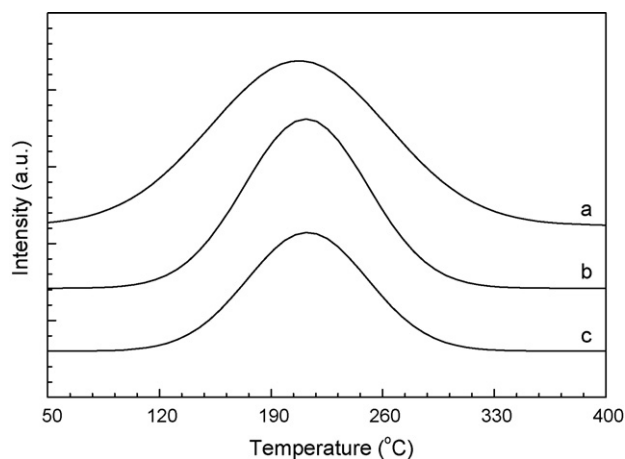
Table 3
H_2 consumption in H_2-TPR measurement and the Ni/NiO molar ratio estimated for the fresh NiO/AC catalyst and used catalysts after reaction for 6 h in different atmospheres (CO_2 or Ar).

Catalyst	H_2-TPR intensity (a.u.)	H_2 consumption (mmol/g)	Ni/NiO molar ratio
Fresh	832	0.902	0
Used after reaction in CO_2	666	0.722	0.249
Used after reaction in Ar	416	0.451	1.000

may also contribute to the higher activity and better stability of NiO/AC catalyst for the reaction in CO_2.

4. Conclusions

The state and property of nickel species in the catalyst NiO/AC are relevant to its calcination temperature, because NiO may be partially reduced to Ni by AC at a temperature higher than 600 °C. For the dehydrogenation of isobutane to isobutene in the presence of CO_2 over the catalyst NiO/AC, NiO and Ni species are different in the catalytic behaviors; Ni is only effective for direct dehydrogenation of isobutane, while NiO is also highly active for the coupled dehydrogenation with CO_2 besides the direct dehydrogenation. Because the NiO content in the catalyst decreases with the increase of the calcination temperature, the catalytic activity of NiO/AC deteriorates at high calcination temperature.

The dehydrogenation of isobutane over the catalyst NiO/AC in the presence of CO_2 exhibits significant superiority over that in the inert atmosphere. This may be attributed to the facts that CO_2 as a weak oxidant can eliminate hydrogen produced from the dehydrogenation, retain the highly active species NiO in the catalyst and suppress the carbonaceous deposition during the reaction.

Acknowledgments

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Fig. 4. TPR profiles of the fresh catalyst NiO/AC (a), the catalyst used after carrying out the isobutane dehydrogenation for 6 h in CO_2 (b), and the used catalyst after the reaction in Ar (c).

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