



Effect of Carbon Modification on the Performance of NiO/ γ -Al₂O₃ Catalyst for Isobutane Dehydrogenation

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The catalyst NiO/ γ -Al₂O₃ was modified with deposited carbon by impregnation of alumina with aqueous solution of Ni(H₂NCH₂CH₂NH₂)_x(NO₃)₂ and used in dehydrogenation of isobutane to isobutene in presence of carbon dioxide. The results indicated that the carbon modification can decrease the total acidity of the NiO/ γ -Al₂O₃ catalyst and it has low acidity and anticoking performance, so it is effective on suppressing the coke formation and side reactions occurrence. Therefore, the catalyst stability and the isobutene selectivity are improved significantly by the carbon modification.

Key Words: Carbon modification, Dehydrogenation, Isobutane, Isobutene, NiO/ γ -Al₂O₃, Carbon dioxide.

INTRODUCTION

It is well known that lower unsaturated hydrocarbons are valuable sources for modern chemical industry. The most important among them are ethene and propene used for production of polymers. Since the 1990s the demand for isobutene has considerably increased, which has been a consequence of its application for alkylation of gasoline and for production of methyl-*tert*-butyl ether (MTBE), an important octane number enhancer for gasoline. Isobutene is also used for production of plastics (polyisobutene and butyl rubber). At present, isobutene is typically obtained by catalytic dehydrogenation of isobutane. 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. On the other hand, the oxidative dehydrogenation is an effective way to increase the conversion and/or lower the reaction temperature¹. However, the desirable dehydrogenation product is vulnerable by deep oxidation when using oxygen as oxidant².

Many researchers have attempted to employ CO₂ as a mild oxidant in the oxidative dehydrogenation of isobutane³⁻⁸, where the dehydrogenation is coupled with reverse water gas shift (RWGS):



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 CO₂. Furthermore, CO₂ can suppress the carbonaceous deposition by reaction with coke to form CO^{6,8}, so the deactivation of catalyst was suppressed and the stability of catalyst was enhanced. The catalysts V-Mg-O^{4,6}, VO_x^{3,5}, Cr₂O₃⁷ and Fe-O⁸ have been used for this reaction. However, there are some disadvantages on them. For example, low isobutene yield, poor catalyst stability and so on. The experimental results are still unsatisfactory for practical application. Therefore, it is necessary to exploit some new sorts of catalysts used in the dehydrogenation of isobutane to isobutene in carbon dioxide.

The catalyst nickel supported on alumina (NiO/ γ -Al₂O₃) exhibited excellent performance for the dehydrogenation of isobutane in presence of CO₂. It is well known that alumina is widely used support material for the dehydrogenation catalysts due to its superior capability in holding high dispersion of active phase^{9,10}. However, the alumina supported catalyst for dehydrogenation may suffer from its acidity. It is generally accepted that the side reactions of the dehydrogenation of alkanes such as isomerization and catalytic cracking may occur on the acid sites. If there are abundant acid sites, especially the strong acidity sites, the olefins will move to the acid sites

to induce the side reactions and finally the formation of the coke and the coke formation is an important factor of catalyst deactivation for the process of the alkanes dehydrogenation^{11,12}. Therefore, elimination of acidic sites during catalyst preparation is one way of suppressing undesired reactions and improving the stability and selectivity of catalyst¹³. Some researches¹⁴⁻¹⁷ reported that the catalysts supported on alumina were modified by carbon addition, because the carbon has the favourable surface properties (low acidity and anticoking performance), which are advantageous to the dehydrogenation of alkanes.

Therefore, to weaken the negative effects of the acidity of alumina on the dehydrogenation of isobutane, the carbon modified NiO/ γ -Al₂O₃ catalyst (NiO-C/ γ -Al₂O₃) was prepared in this work. Moreover, the effects of carbon modification on the performance of NiO/ γ -Al₂O₃ catalyst for the dehydrogenation of isobutane to isobutene in the presence of carbon dioxide were investigated.

EXPERIMENTAL

NiO/ γ -Al₂O₃ catalyst with a Ni loading of 0.5 mmol/ γ -Al₂O₃ was prepared by incipient wetness impregnation of alumina with an aqueous solution of Ni(NO₃)₂·6H₂O. To obtain the catalyst modified with deposited carbon (NiO-C/ γ -Al₂O₃), an aqueous solution of Ni(en)_x(NO₃)₂ was first prepared by dissolving Ni(NO₃)₂·6H₂O into the solution of ethylenediamine (en) (ratio of mol (en)/Ni being 4.0). Then the alumina was impregnated with an aqueous solution of Ni(en)_x(NO₃)₂. Both impregnations lasted for 24 h at room temperature and then the catalysts were dried at 383 K in nitrogen atmosphere for 12 h and calcined at 550 °C in Ar for 1 h.

General procedure: The catalytic test of isobutane dehydrogenation was carried out 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 catalyst was loaded and placed in the constant temperature zone of the microreactor. The temperature of reactor was programmed up to the reaction temperature under an argon atmosphere, then the argon flow was switched to the reaction stream (a mixture of isobutane + CO₂ with the mole ratio of CO₂/isobutane being 15). The volumetric hourly space velocity (VHSV) of the gas flow for the heat treatment and the feed for the dehydrogenation was 5280 h⁻¹. The effluent was analyzed using an on-line gas chromatograph (Shimadzu GC-14C, TCD, C₁₈ packed column).

Detection method: Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out to analyze the acidic properties of the catalysts. NH₃-TPD was performed in a quartz microreactor and about 100 mg sample was used in each measurement. The samples were pretreated at 500 °C for 1 h under argon stream (20 mL min⁻¹). After cooling to 100 °C, NH₃ (99.96 %) was adsorbed for 1 h. The desorption was carried out with a temperature ramp of 10 °C min⁻¹ and the amount of desorbed NH₃ was measured by a thermal conductivity detector (TCD). 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.

RESULTS AND DISCUSSION

The conversion of isobutane, the selectivity and yield to isobutene over the NiO/ γ -Al₂O₃ catalyst were compared with those of the NiO-C/ γ -Al₂O₃ catalyst, as shown in Fig. 1.

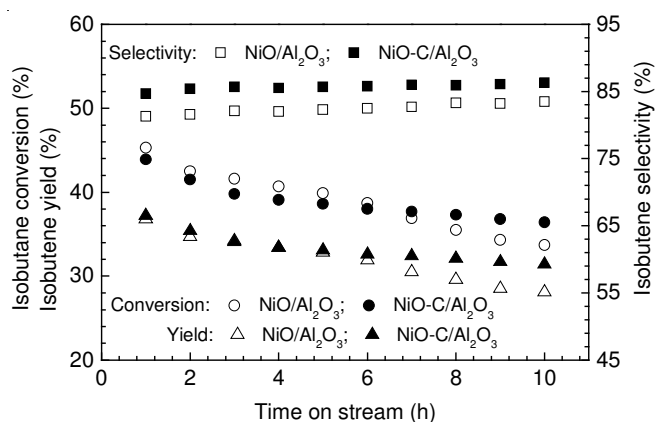


Fig. 1. Dehydrogenation of isobutane over the catalysts NiO/ γ -Al₂O₃ and NiO-C/ γ -Al₂O₃ in carbon dioxide. Reaction conditions: 550 °C, 0.1 MPa, VHSV of 5280 h⁻¹, mole ratio of CO₂ to isobutane being 15; data was acquired after reaction last for 1 h

NiO/ γ -Al₂O₃ catalyst, over which the conversion of isobutane during the first hour reached 45.3 %, performed the highest catalytic initial activity, but its activity lost rapidly with increasing the reaction time. Although, the NiO-C/ γ -Al₂O₃ catalyst exhibited a bit lower catalytic initial activity (43.9 %), it showed better stability with respect to the reaction time than that of NiO/ γ -Al₂O₃ catalyst. After 6 h, the conversion of isobutane over NiO-C/ γ -Al₂O₃ catalyst was higher than that of NiO/ γ -Al₂O₃ catalyst. And the selectivity and yield to isobutene over NiO-C/ γ -Al₂O₃ catalyst are higher than that of the NiO/ γ -Al₂O₃ catalyst during the successive reaction.

The temperature programmed desorption profiles of NH₃ adsorption on NiO/ γ -Al₂O₃ and NiO-C/ γ -Al₂O₃ catalysts were shown in Fig. 2. The strength of the acid sites can be determined by the temperature at which the adsorbed NH₃ desorbs. Based on the desorption temperature, the acid sites can be classified as weak (150-250 °C), medium (250-350 °C) or strong (350-450 °C)^{18,19}. A broad desorption peak with a maximum at about 232 °C, 320 °C and a shoulder at 365 °C are clearly observed over NiO/ γ -Al₂O₃ catalyst. However, the desorption peak of NH₃ on the NiO-C/ γ -Al₂O₃ shift left to lower temperature obviously. The weak, medium and strong acid sites on the NiO-C/ γ -Al₂O₃ catalyst was at about 225, 305 and 358 °C, respectively.

The amounts of acid sites on NiO/ γ -Al₂O₃ and NiO-C/ γ -Al₂O₃ were determined by integrating NH₃ desorption peaks, as shown in Table-1. NiO-C/ γ -Al₂O₃ has much less weak and strong acid sites than NiO/ γ -Al₂O₃, although a slight increase in the quantity of medium acid sites on NiO-C/ γ -Al₂O₃ was observed, the total acid sites on NiO/ γ -Al₂O₃ catalyst are more than those of NiO-C/ γ -Al₂O₃ catalyst. These results strongly suggest that the carbon deposited on the NiO-C/ γ -Al₂O₃ catalyst may overlay the acid sites on the catalysts and then eliminate the quantity of acid sites in the catalyst and lower the acidity of the catalyst.

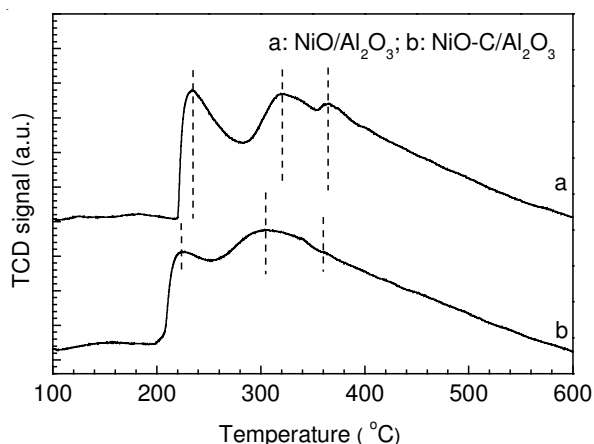


Fig. 2. NH₃-TPD profiles of NiO/ γ -Al₂O₃ and NiO-C/ γ -Al₂O₃ catalysts

TABLE-1
PEAK AREA AND MAXIMUM TEMPERATURE OF NH₃ DESORBED DURING THE TPD EXPERIMENTS OVER NiO/ γ -Al₂O₃ AND NiO-C/ γ -Al₂O₃ CATALYSTS

Catalysts	Peak area (a.u.)			Total peak area (a.u.)
	Weak (T _{max} (°C))	Medium (T _{max} (°C))	Strong (T _{max} (°C))	
NiO/ γ -Al ₂ O ₃	94.7 (232)	36.1 (320)	22.3 (365)	153.1
NiO-C/ γ -Al ₂ O ₃	32.3 (225)	40.1 (305)	5.2 (358)	77.6

Weak = 150-250 °C, medium = 250-350 °C and strong = 350-450 °C.

The content of coke of the used NiO/ γ -Al₂O₃, used NiO-C/ γ -Al₂O₃ catalyst and the content of carbon deposited on the fresh NiO-C/ γ -Al₂O₃ catalyst are calculated by TGA tests, as shown in Fig. 3. The quantity of coke formed during reaction can be determined by the mass loss during 350-650 °C. The carbon content of fresh NiO/ γ -Al₂O₃ and NiO-C/ γ -Al₂O₃ catalyst is 0 and 2.7 wt %, respectively. The carbon content of used NiO/ γ -Al₂O₃ and NiO-C/ γ -Al₂O₃ catalyst is 33.6 and 21.8 wt %, respectively. The coke formed on the NiO-C/ γ -Al₂O₃ catalyst during the isobutane dehydrogenation reaction was far smaller than that of the NiO/ γ -Al₂O₃ catalysts. From these results, it is inferred that the carbon deposited on the fresh NiO-C/ γ -Al₂O₃ catalyst may have anticoking performance, therefore, it could suppress the formation of coke during the reaction.

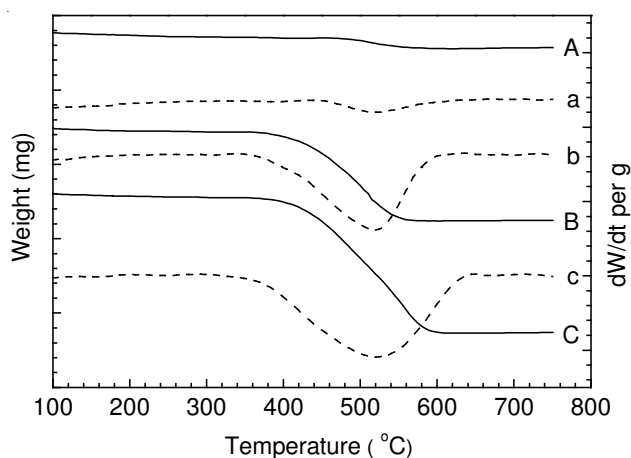


Fig. 3. Thermogravimetric profiles of catalysts: fresh NiO-C/ γ -Al₂O₃ (A): TG, a: DTG); used NiO-C/ γ -Al₂O₃ (B): TG, b: DTG); used NiO/ γ -Al₂O₃ (C): TG, c: DTG)

According to the results of NH₃-TPD and coke analysis, we know that the carbon deposited on the fresh NiO-C/ γ -Al₂O₃ catalyst can eliminate the quantity of acid sites in the catalyst, lower the acidity of the catalyst, so some side reactions and coke formation in isobutane dehydrogenation were suppressed. Therefore, the selectivity to isobutene and the catalyst stability were enhanced.

Conclusion

The carbon modification on the fresh NiO-C/ γ -Al₂O₃ catalyst for the dehydrogenation of isobutane to produce isobutene in the presence of carbon dioxide has distinct effects on enhancing the selectivity to isobutene and increasing the stability of the catalyst. According to the results of characterization, we know that the improvement of the selectivity and the stability may be attributed to the following reasons, respectively: the carbon modification on the fresh NiO-C/ γ -Al₂O₃ weakens the acidity of the catalyst and the carbon has low acidity and anticoking performance, so some side reactions and coke formation are suppressed during the catalytic process.

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