

# Effect of Residence Time and Carrier Gas on the Dehydrogenation of n-Hexane over Alumina-supported Chromium Catalyst

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**Abstract.** CrOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetness impregnation method, and the influence of residence time and carrier gas on the dehydrogenation of n-hexane were studied. It is found that n-hexane dehydrogenation over CrOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with H<sub>2</sub> as carrier gas exhibits totally different catalytic behaviors with that of diluting n-hexane with N<sub>2</sub>. When diluting feed with N<sub>2</sub>, the selectivity to dehydrogenation product is promoted while the cracking reaction is exhibited with reducing residence time. However, the selectivity to dehydrogenation product is significantly decreased while the isomerization of n-hexane is promoted when using H<sub>2</sub> as carrier gas. It is proposed that H<sub>2</sub> undergoes dissociation on the dehydrogenation active site, and further facilitates the olefinic dehydrogenation products to form carbocation, which performing isomerization reaction on the acid site on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. Therefore, the isomerization of n-hexane is promoted in cost of the selectivity to dehydrogenation product when using H<sub>2</sub> as carrier gas.

**Keywords:** n-hexane, dehydrogenation, isomerization, selectivity, CrOx catalyst.

## 1. Introduction

Alumina-supported chromium oxide is widely used for dehydrogenation reaction due to the excellent C-H activation ability and olefin selectivity [1-3], like the Catofin process for C<sub>3</sub>/C<sub>4</sub> dehydrogenation [4, 5], and the Catodiene process for C<sub>4</sub>/C<sub>5</sub> dehydrogenation [6, 7]. Many studies have indicated that the selectivity to olefin can be improved by reducing the residence time and using hydrogen as carrier gas for the dehydrogenation process of low-carbon alkanes (C<sub>2</sub>-C<sub>5</sub>) [8, 9]. However, little research about this aspect has been done for n-hexane (or the other long-chain alkanes), and the likelihood of isomerization of n-hexane is increased due to the increased carbon-chain length. Thus, in this work, CrOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with 13 wt%Cr content was prepared, and the influence of residence time and carrier gas on the dehydrogenation of n-hexane were studied. N<sub>2</sub> and H<sub>2</sub> were used as the diluent gas, and the residence time in the range of 1-11 seconds were used in experiment are listed in Table 1.

Table 1. Flow rate of carrier gas (N<sub>2</sub>/H<sub>2</sub>) and residence time of n-hexane.

Flow rate of carrier gas, mL/min	10	20	30	60	100
Residence time, s	10.2	5.1	3.4	1.7	1.0

## 2. Experimental

### 2.1 Catalyst preparation

The CrOx/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetness impregnation method using chromium nitrate (AR. Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) solution. The impregnated sample was dried at 60 °C for 12 h, and then calcined at 600 °C for 2 h. The actual Cr content is measured to be 13.9 wt% by XRF analysis.

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support with a specific surface area of 189.9 m<sup>2</sup>/g was obtained by calcining the pseudoboehmite powder (AR. 67 wt%) at 650 oC for 6 h.

## 2.2 Catalyst characterization

The surface area and pore structure of samples were measured by the BET and BJH method, using Quadrasorb SI multifunctional adsorption equipment. The crystal structure was determined by an X-ray diffractometer (X'Pert PRO MPD), using Cu K $\alpha$  radiation with a scanning speed of 50 /min, operated at 40 mA and 40 kV. The actual Cr content of sample was measured by X-ray fluorescence spectrometer (ARL9800 XRF), operated at 50 mA and 50 kV.

Temperature programmed desorption (NH<sub>3</sub>-TPD) was performed on a PCA-1200 chemisorption analyzer. About 0.1 g samples were pretreated under He (30 mL/min) at 600 oC for 1 h, then cooled down and stabilize at 100 oC, followed by adsorbing NH<sub>3</sub> (20 vol% NH<sub>3</sub>/N<sub>2</sub>) for 45 min. Finally, the temperature rose from 100 °C to 600 °C under He (30 mL/min) with a rate of 10 °C/min. Pyridine fourier-transform infrared spectroscopy (Py-FTIR) analysis was performed to describe the acid type of catalyst, which using a Tensor 27 FTIR spectrometer. The spectra were recorded with the resolution of 4 cm<sup>-1</sup> and 64 scans.

## 2.3 Catalytic tests

Catalytic performance was evaluated in a stainless fixed-bed reactor with a diameter of 12 mm. The dehydrogenation of n-hexane was carried out at 500 oC and 0.1 MPa. 0.5 g catalysts (40-60 mesh) were loaded in the middle of reactor and heated to 500 oC at a speed of 10 oC/min with 99.9% N<sub>2</sub> and kept 30 minutes to move the adsorbed impurities on the catalyst surface. The WHSV of n-hexane (99.4% purity) was 2.7 h<sup>-1</sup>. The composition of feed and product was analyzed by a gas chromatograph (PANNA GCA60) with an FID detector and a PONA column (50 m × 0.2 mm). The outlet products were kept 150 oC by the heater belt and delivered to the gas chromatograph. n-Hexane conversion and product selectivity are calculated as follows:

$$n\text{-Hexane conversion (wt\%)} = \frac{n\text{-hexane, in} - n\text{-hexane, out}}{n\text{-hexane, in}} \times 100\%$$
$$Product\ selectivity\ (wt\%) = \frac{product\ i,\ out}{n\text{-hexane, in} - n\text{-hexane, out}} \times 100\%$$

### 3. Result and discussion

#### 3.1 Catalytic performance of CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for n-hexane dehydrogenation

##### 3.1.1 Influence of residence time on the n-hexane dehydrogenation: N<sub>2</sub> as carrier gas

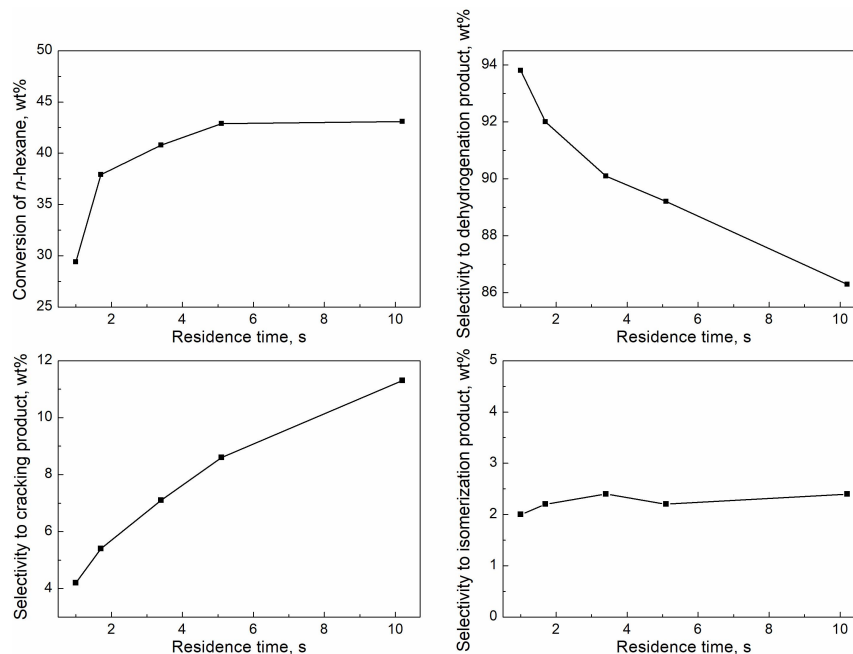


Fig. 1 Catalytic performance of CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst under different residence time (N<sub>2</sub> as carrier gas).

The evolution of n-hexane dehydrogenation performance changing with residence time on CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Fig.1. The products of n-hexane dehydrogenation reaction are classified as dehydrogenation products that including n-hexenes and deep dehydrogenation products (n-hexadiene and benzene), cracking products (the sum of C<sub>1</sub>-C<sub>5</sub> hydrocarbons), isomerization products (isomeric C<sub>6</sub> hydrocarbons), and other products. The conversion of n-hexane is 43.1 wt% at residence time of 10.2 s, and it is decreased with reducing residence time that to 29.4 wt% at residence time of 1 s. The selectivity to dehydrogenation products is increased with reducing residence time (83.6 wt% at residence time of 10.2 s to 93.8 wt% at residence time of 1s). At the same time, the cracking reaction is inhibited as the residence time became shorter. The selectivity to isomerization product fluctuates between 2.0 wt% and 3.0 wt% during the dehydrogenation reaction.

Thus it can be seen that a shorter residence time is beneficial for the formation of dehydrogenation product, while exhibiting the cracking reactions. Furthermore, it is worth noting that the selectivity to isomerization product is independent with the residence time when using N<sub>2</sub> as carrier gas.

##### 3.1.2 Influence of residence time on the n-hexane dehydrogenation: H<sub>2</sub> as carrier gas

The catalytic behaviors of CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for n-hexane dehydrogenation change greatly after replacing N<sub>2</sub> with H<sub>2</sub>. As displayed in Fig. 2, the conversion of n-hexane is significantly decreased, to which 28.8 wt% at residence time of 10.2 s and 7.9 wt% at residence time of 1 s. Interestingly, the selectivity to dehydrogenation product is also increased with reducing the residence time, while it is obviously lower than the operation with N<sub>2</sub> as diluting gas (74.7 wt% at residence time of 10.2 s and 77.6 wt% at residence time of 1 s). Moreover, the selectivity to isomerization product is increased apparently, to which 7.6 wt% at residence time of 10.2 s and 16.2 wt% at residence time of 1 s. These results indicating that H<sub>2</sub> not only modifies the residence time of n-hexane, it may also participate in the reaction process and facilitate the isomerization reaction.

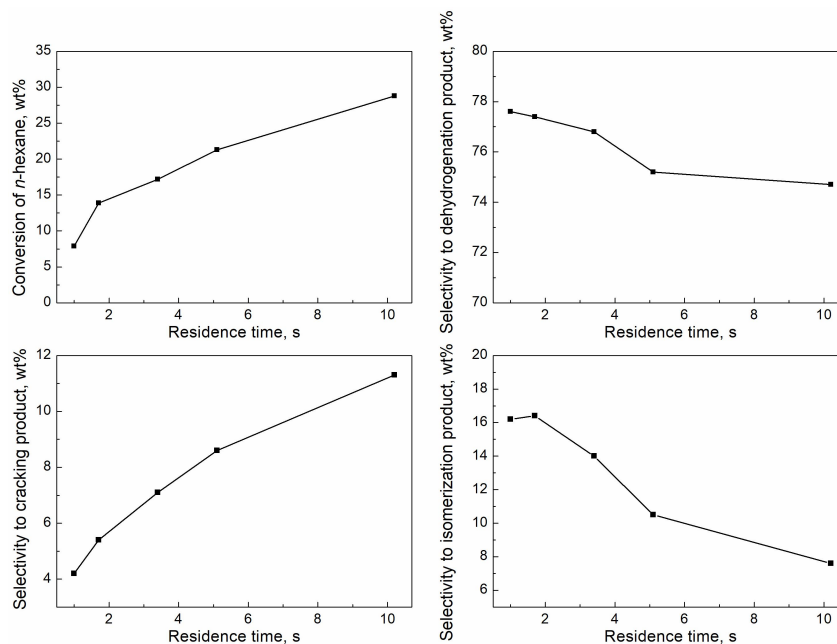


Fig. 2 Catalytic performance of CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst under different residence time (H<sub>2</sub> as carrier gas).

### 3.2 Structural and acidity properties of CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

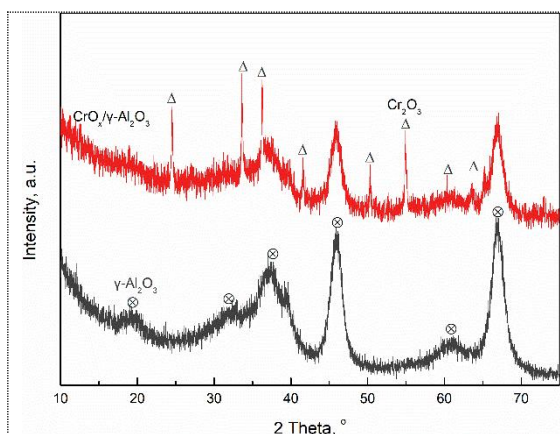


Fig. 3 XRD patterns of CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst and γ-Al<sub>2</sub>O<sub>3</sub> support.

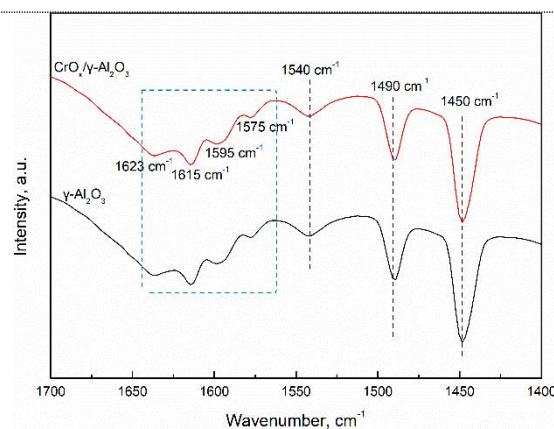


Fig. 4 Py-FTIR spectra of CrOx/ γ -Al<sub>2</sub>O<sub>3</sub> catalyst and γ -Al<sub>2</sub>O<sub>3</sub> support.

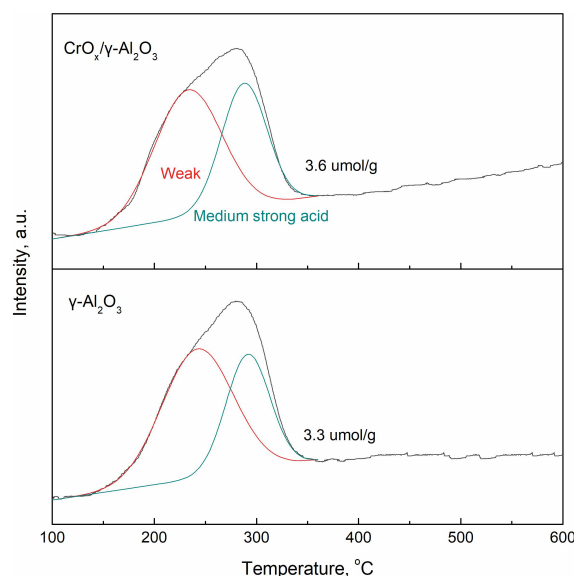


Fig. 5 NH<sub>3</sub>-TPD profiles of CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst and γ-Al<sub>2</sub>O<sub>3</sub> support.

The XRD patterns of CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst and γ-Al<sub>2</sub>O<sub>3</sub> support are shown in Fig. 3. The diffraction peaks corresponding to crystalline Cr<sub>2</sub>O<sub>3</sub> at 2θ of 24.5, 33.6, 36.3, 50.2, and 55.0 o [5, 10] are observed on CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The acid properties of CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst and γ-Al<sub>2</sub>O<sub>3</sub> support were determined by Py-FTIR and NH<sub>3</sub>-TPD analysis, with the results illustrated in Figs. 4 and 5. As seen, the CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst and γ-Al<sub>2</sub>O<sub>3</sub> support exhibit similar IR absorption bands at 1450, 1490, 1540, 1575, 1595 and 1615 cm<sup>-1</sup> [11, 12]. The IR absorption bands at about 1450 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> represent the Lewis and Brønsted acid sites, and the band at 1490 cm<sup>-1</sup> is assigned to the pyridinium ions chemisorbed on both Brønsted and Lewis acid sites [13]. The bands at 1575, 1595 and 1615 cm<sup>-1</sup> represent the medium strong Lewis acid sites, and the absorption band at 1623 cm<sup>-1</sup> is related to the pyridine ions interact with strong Lewis acid sites [14]. In addition, the NH<sub>3</sub>-TPD profiles of CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst are also similar with that of γ-Al<sub>2</sub>O<sub>3</sub> support, and the total acid amount of two samples are comparable (3.6 μmol/g v.s. 3.3 μmol/g). All of these indicating that the enhanced selectivity to isomerization product is not caused by the structural and acidic properties of CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, since the γ-Al<sub>2</sub>O<sub>3</sub> can not catalysis the isomerization of n-hexane.

### 3.3 The role of H<sub>2</sub> in n-hexane dehydrogenation over CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

Different from the N<sub>2</sub>, changing the residence time with H<sub>2</sub> facilitates the isomerization reaction of n-hexane, and the higher selectivity to isomerization product is achieved when more H<sub>2</sub> is presented. According to the mechanisms of n-alkanes isomerization [15], H<sub>2</sub> usually undergoes dissociation on the dehydrogenation active site, and the dissociated H atoms preferentially migrating to the acid site on the catalyst surface, afterwards, the interaction between H atom and n-alkane leading to the formation of H<sup>+</sup>/H<sup>-</sup> and alkyl free radical, which is further converted to carbocation and initiating the isomerization reaction. In this case, H<sub>2</sub> occurs dissociation on the dehydrogenation active site, and the olefinic products (including n-hexenes and deep dehydrogenation products of n-hexane) obtained from dehydrogenation of n-hexane facilitate the formation of carbocation, both of those interacted in the acid site on the γ-Al<sub>2</sub>O<sub>3</sub> support and performed isomerization reaction. Therefore, when using H<sub>2</sub> as carrier gas, the selectivity to isomerization product is increased in cost of the selectivity to dehydrogenation product with decreasing residence time. The mechanism of n-hexane isomerization on CrO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst during the dehydrogenation reaction is depicted in Fig. 6.

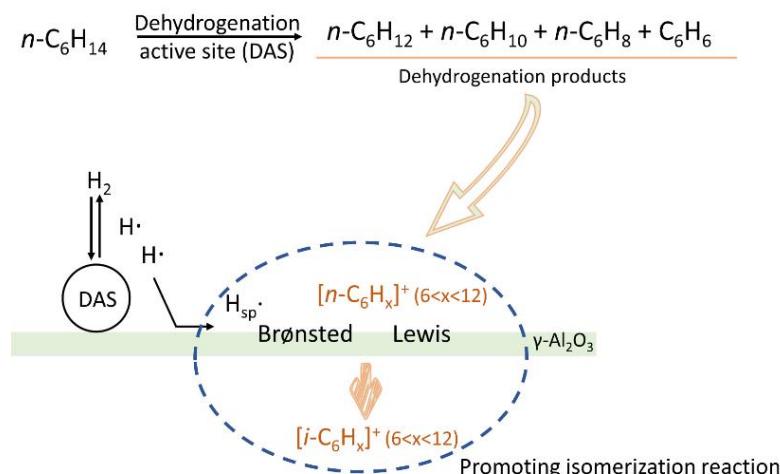


Fig. 6 The mechanism of n-hexane isomerization on CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst during the dehydrogenation reaction.

## 4. Conclusions

CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetness impregnation method, and the influence of residence time and carrier gas on the dehydrogenation of n-hexane over alumina-supported chromium catalyst were investigated. It is found that the conversion of n-hexane is suppressed with reducing residence time, and the cracking reaction is exhibited at the same time. While interestingly, the selectivity to dehydrogenation product is promoted only when diluting n-hexane with N<sub>2</sub>. The selectivity to dehydrogenation product is decreased while the isomerization of n-hexane is promoted when using H<sub>2</sub> as carrier gas. According to the mechanisms of n-alkanes isomerization, we proposed that H<sub>2</sub> undergoes dissociation on the dehydrogenation active site on the CrOx/γ-Al<sub>2</sub>O<sub>3</sub> catalyst surface, and the olefinic dehydrogenation products (including n-hexenes and deep dehydrogenation products of n-hexane) obtained from dehydrogenation of n-hexane facilitate the formation of carbocation, both of those interacted in the acid site on the γ-Al<sub>2</sub>O<sub>3</sub> support and performed isomerization reaction. Therefore, when using H<sub>2</sub> as carrier gas, the selectivity to isomerization product is increased in cost of the selectivity to dehydrogenation product.

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