



## Catalytic Decomposition of Propane and Catalytic Performance of CO<sub>2</sub> Reforming of C<sub>3</sub>H<sub>8</sub> Over Ni Catalyst

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The decomposition and reaction of propane with CO<sub>2</sub> had been investigated on Ni/SiO<sub>2</sub> catalysts. It was found that the decomposition of propane is a temperature sensitive process. The amount of deposited carbon decreases with the increasing temperature. At lower temperature, a large proportion of H-rich carbon species was observed, which might locate mainly on the surface of the support. However, the order of graphitization of the deposited carbon increased with the temperature and might be formed mainly on the surface of nickel particles. The conversion of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> reached nearly 100 % and 88.5 % on the Ni/SiO<sub>2</sub> catalyst under the chosen test conditions (C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub>/Ar = 10/30/260 (V/V/V, GHSV = 18000 h<sup>-1</sup>). According to the catalytic performance of Ni/SiO<sub>2</sub> at different temperature, it was confirmed that the higher reaction temperature favours the CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub>.

**Key Words:** Propane, Ni catalyst, Carbon deposition.

### INTRODUCTION

Crude natural gas may contain 10 vol.% of light alkanes (C<sub>2</sub>-C<sub>4</sub>) and up to 30 vol. % of CO<sub>2</sub> in addition to methane. Synthesis gas production is an important step in the conversion of natural gas to fuels and petrochemical products. In order to convert it into syngas *via* reforming reactions without prior separation, an overall understanding of both CH<sub>4</sub> and higher alkanes dry reforming mechanisms is required for developing catalysts with a high activity and selectivity towards CO and H<sub>2</sub>, a high stability and a low selectivity to coke formation. While many articles exist on the catalytic dry reforming of methane to synthesis gas<sup>1-3</sup>, only few studies address the specificity of propane dry reforming, in general using supported noble metal catalysts (Rh, Ru)<sup>4-6</sup>. Recently, more attention has been paid to the production of synthesis gas towards dry reforming of propane over Ni based catalysts<sup>7-9</sup>. This choice was based on the lower vapour pressure of propane compared with methane at ambient temperature, making it more suitable for use in fuel cell cars.

Supported Ni catalysts are the preferred choice as catalysts for the reforming reaction, due to the low cost and easy availability of Ni metal. The main disadvantage of Ni/support catalysts compared with noble metal catalysts is a lower stability with respect to carbon deposition<sup>10</sup>. In this contribution, the decomposition of propane and catalytic performance of

CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub> on the Ni/SiO<sub>2</sub> were studied and the possible correlation between the forms and activation of medial carbon species and propane decomposition over Ni-based catalysts was discussed.

### EXPERIMENTAL

**Catalyst preparation:** Ni/SiO<sub>2</sub> catalyst was prepared by direct incipient-wetness impregnation of [Ni(en)<sub>3</sub>]<sup>2+</sup> (en, ethylenediamine) onto a spherical SiO<sub>2</sub> support (special product for fluidized reactor, S<sub>BET</sub> = 330 m<sup>2</sup> g<sup>-1</sup>, average diameter 0.25-0.38 mm, Qingdao, China). [Ni(en)<sub>3</sub>]<sup>2+</sup> were prepared as described previously<sup>11</sup>. The loading amount of Ni was controlled at 5 wt % of the support. The precursors were dried at 80 °C in vacuum and calcined at 800 °C in stagnant air for 4 h.

Before the experiment, catalyst was reduced under H<sub>2</sub> flow at 700 °C for 1 h. Subsequently, sample was treated in 10 % C<sub>3</sub>H<sub>8</sub>/Ar (50 mL/min) at 400, 500, 600 or 700 °C for 10 min. After coking reaction, O<sub>2</sub>-TPO was carried out in a flow of 10 % O<sub>2</sub>/Ar from 50 to 800 °C at 15 °C/min. All gases in effluent were detected by a quadrupole mass spectrometer (OmniStar<sup>TM</sup>, GSD301, Switzerland). The amounts of carbon formed after coking was detected *via* TG (PE-TGA7, USA). TEM images were obtained using an accelerating voltage of 200 kV (TEM, JEOL-2020F). The quality was identified by Raman spectroscopy using a 514 nm line of an argon laser operated at a laser power of 30 mW.

**Catalytic reaction:** The CO<sub>2</sub> reforming of propane was carried out in a quartz fluidized-bed reactor (i.d. = 20 mm, h = 750 mm) at atmospheric pressure. C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub> and Ar were controlled by three sets of mass flow controller (Brooks, 5850E, USA) with a molar ratio C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub>/Ar = 10/30/260 (V/V/V) and a total flow rate of 300 cm<sup>3</sup> min<sup>-1</sup>. The catalyst was firstly reduced at 700 °C for 1 h under H<sub>2</sub> flow. The effluent gas was then cooled in an ice-water trap and analyzed with an online gas chromatograph (SHIMADZU, GC-8A) equipped with a packed column (Porapak Q) and a thermal conductivity detector. The conversion and the selectivity were calculated as follows.

$$X(\text{C}_3\text{H}_8)(\%) = \frac{F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}}}{F_{\text{C}_3\text{H}_8,\text{in}}} \times 100$$

$$X(\text{CO}_2)(\%) = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100$$

$$S(\text{H}_2)(\%) = \frac{F_{\text{H}_2,\text{out}}}{4(F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}})} \times 100$$

$$S(\text{CO})(\%) = \frac{F_{\text{CO},\text{out}}}{(F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}) + 3(F_{\text{C}_3\text{H}_8,\text{in}} - F_{\text{C}_3\text{H}_8,\text{out}})} \times 100$$

where, X: conversion; S: selectivity; F: flow of reactant or product.

## RESULTS AND DISCUSSION

**Decomposition of propane and catalytic characterizations:** Table-1 presents the carbon deposition on the Ni/SiO<sub>2</sub> catalyst from propane decomposition. The amount of deposited carbon is smaller at 400 °C. However, it increases remarkably to 9.17 mmol/g-cat at 500 °C and then decreased to 0.72 and 0.35 mmol/g-cat at 600 and 700 °C, respectively, which indicated that propane decomposition is a temperature sensitive process.

Temperature (°C)	Coke (mmol/g <sub>cat</sub> )
400	0.50
500	9.17
600	0.72
700	0.35

Raman spectra of deposited carbon derived from C<sub>3</sub>H<sub>8</sub> decomposition on Ni/SiO<sub>2</sub> are shown in Fig. 1. Raman analysis found that two main bands were observed at 1605-1590 and 1340 cm<sup>-1</sup>. The strong peak located at 1340 cm<sup>-1</sup> corresponds to the disorder-induced D band, contributed to the structural imperfection of graphite. In addition, the band at 1605 cm<sup>-1</sup> (D' band) might be attributed to imperfect graphite<sup>12</sup> and this peak shifts gradually to 1590 cm<sup>-1</sup> (G band) with the temperature increased<sup>13</sup>, which was inferred to the in-plane carbon-carbon stretching vibrations of graphite layers. The half-band width of G band decreased with the temperature, which suggests that, the order of graphitization of the deposited carbon increased<sup>14,15</sup>. The band at 2926 cm<sup>-1</sup> is ascribed to the H-rich carbon species. Bands at 1150 and 1490 cm<sup>-1</sup> were

observed at 500 °C [Fig. 1(B)], which are assigned to C-C and C=C stretching vibrations, respectively<sup>15</sup>.

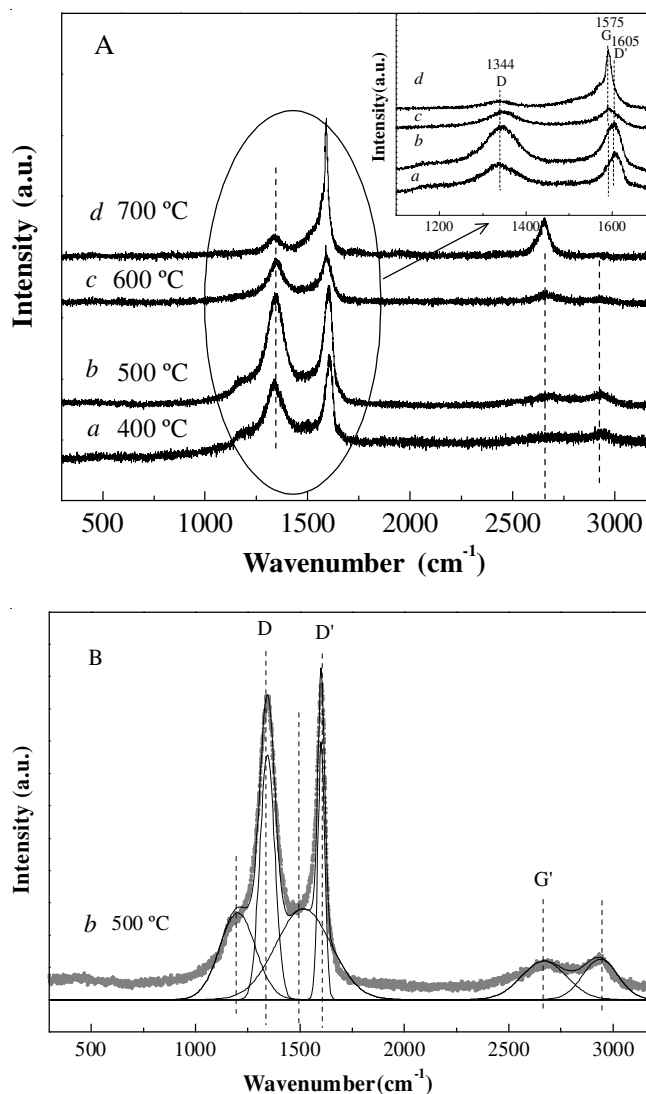


Fig. 1. Raman spectra of the carbons deposited on Ni/SiO<sub>2</sub> catalyst from propane decomposition

TEM image of the carbons deposited from C<sub>3</sub>H<sub>8</sub> on the Ni/SiO<sub>2</sub> catalyst are presented in Fig. 2. Large amounts of encapsulating carbon and tubular carbon formed at 500 °C exists the surrounding of the metal particles and the support [Fig. 2(A)]; however, carbon generated at 700 °C mainly locates on the surface of Ni particles [Fig. 2(B)].

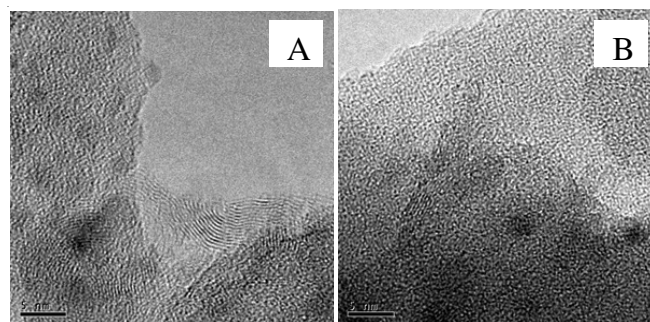


Fig. 2. TEM image for the carbons deposited from C<sub>3</sub>H<sub>8</sub> on the Ni/SiO<sub>2</sub> catalyst. (A) at 500 °C and (B) at 700 °C

Fig. 3 shows the oxidation profiles of carbon deposited on Ni/SiO<sub>2</sub> catalyst after decomposition reaction of 10% C<sub>3</sub>H<sub>8</sub>/Ar. All the profiles showed two main peaks, one in the low-temperature region, 300–450 °C and the other in the high-temperature region, 550–650 °C. The results are consistent with reported by Noronha *et al.*<sup>16</sup> and Souza *et al.*<sup>17</sup>. The various TPO peaks might not due to different forms of carbon but rather to different locations on the catalyst surface for Ni/SiO<sub>2</sub>. The low-temperature peaks observed in TPO of coked Ni/SiO<sub>2</sub> have been typically ascribed to carbon surrounding the metal particles, while those peaks at high temperatures are ascribed to the carbon deposition over the support. Deactivation is attributed to carbon formation surrounding the metal-support perimeter.

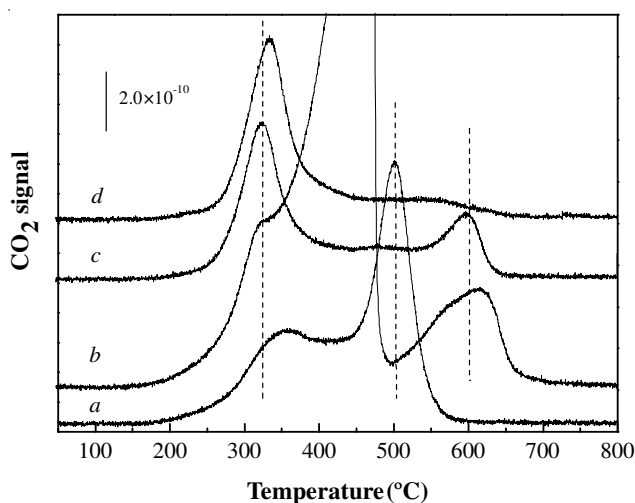


Fig. 3. MS signal of CO<sub>2</sub> during O<sub>2</sub>-TPO after C<sub>3</sub>H<sub>8</sub> decomposition

**Catalytic activity of Ni/SiO<sub>2</sub>:** The catalytic activity of the Ni/SiO<sub>2</sub> for CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub> in the fluidized-bed reactor is presented in Fig. 4. The conversion of C<sub>3</sub>H<sub>8</sub> was nearly 100% during the initial 2.5 h and decreased from 99.1 to 97.1% in the following 2.5 h to 5 h. The conversion of CO<sub>2</sub> decreased from 88.5 to 85.4%. Generally, carbon deposition was considered as a major reason for affecting the activity and stability of catalysts in the CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub>.<sup>4,6,10,18,19</sup>

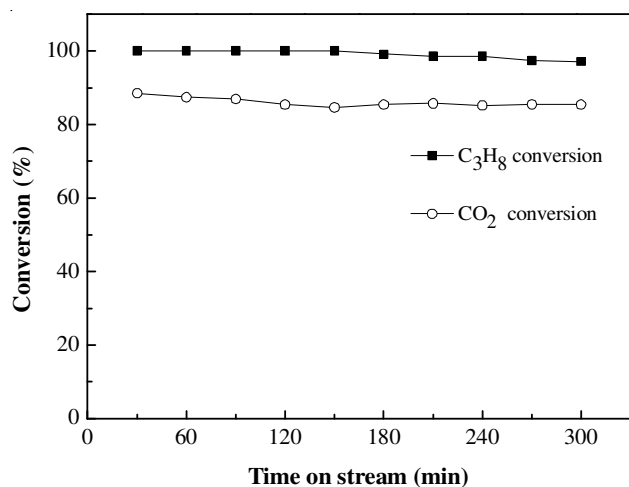


Fig. 4. Catalytic performance of CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub> over Ni/SiO<sub>2</sub>. Reaction condition: T=700 °C, GHSV = 18,000 h<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub>/Ar = 10/30/260 (v/v/v)

**Effect of reaction temperature:** Fig. 5 presents that the effect of reaction temperature on the catalytic activity of the Ni/SiO<sub>2</sub> catalyst. The conversion of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> increased with the increased temperature. The conversion of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> increased from 14.3% and nearly zero at 500 °C to 100% and 86% at 700 °C. C<sub>3</sub>H<sub>8</sub> was not detected in the effluent when temperature was above 600 °C. However, when the temperature is lower than 550 °C, the conversion of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> decreased to 44.3 and 25.3%, respectively. The results indicated that the CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub> on Ni-based catalysts can occur at higher reaction temperature.

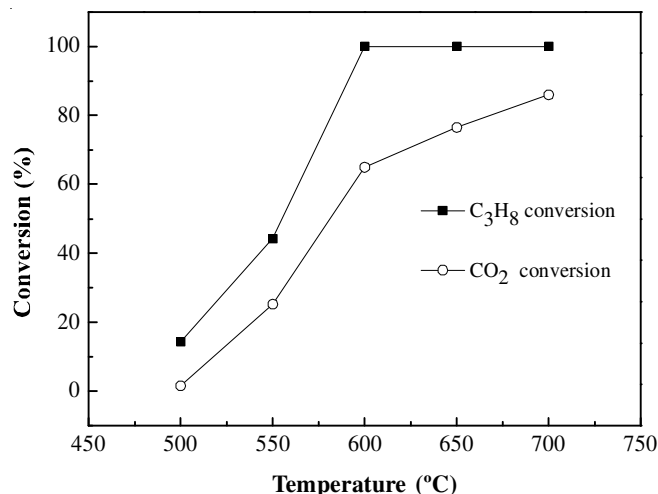


Fig. 5. Effect of temperature on the catalytic performance of CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub>. Reaction condition: GHSV = 18,000 h<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub>/Ar = 10/30/260 (v/v/v)

## Conclusion

The decomposition of C<sub>3</sub>H<sub>8</sub> is a temperature sensitive process. The amount of deposited carbon decreases with the increase of the temperature. The appearances and species of the deposited carbons were different at different temperature. The order of graphitization of the deposited carbon increased with the temperature and carbon deposited from the decomposition at different temperatures might exist on the support different locations on the catalyst surface for Ni/SiO<sub>2</sub>. It was found that the conversion of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> reached nearly 100% and 88.5% on the Ni/SiO<sub>2</sub> catalyst. According to the catalytic performance of Ni/SiO<sub>2</sub> at different temperature, it was confirmed that the higher reaction temperature favours the CO<sub>2</sub> reforming of C<sub>3</sub>H<sub>8</sub>.

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