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Growth of carbon nanofibers synthesized from CO_2 hydrogenation on a $K/Ni/Al_2O_3$ catalyst

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ABSTRACT

We used a commercially available Ni/Al_2O_3 sample containing K additive to enable carbon deposition from CO_2 exposure by means of catalytic hydrogenation. Our experimental results suggest that K additives induce the formation of carbon nanofibers (CNFs) or carbon deposition on Ni/Al_2O_3 during the CO_2 hydrogenation reaction. We propose that the rate of carbon deposition depends on the reaction temperature, on H_2 and CO_2 partial pressures, and on the reactant residence time. Furthermore, we suggest that the creation of a K-relevant active phase may be involved in the carbon deposition process. Our results also indicate that the degree of CNF graphitization can change with reaction time.

1. Introduction

Carbon dioxide, primarily generated by combustion, is the most important and abundant greenhouse gas and is the main contributor to the greenhouse effect. To address this problem, researchers have proposed the catalytic chemical conversion of atmospheric CO_2 into solid carbon [1]. This would be a very powerful CO_2 recycling technique with an easily stored end product. The reverse water gas shift (RWGS) reaction is known to provide high-efficiency CO production from CO_2 ($H_2 + CO_2 \rightarrow CO + H_2O$) [2–7]. Recently, we have described a novel method for converting CO_2 to solid carbon through the hydrogenation of CO_2 on $K/Ni/Al_2O_3$ catalysts at 500 °C [8]; we discovered that enhancing the Ni catalyst with K can enable the formation of carbon nanofibers (CNFs) from CO_2. The rate of formation of solid carbon can be enhanced by increasing the K content of the Ni catalyst. A variety of potential applications for CNTs and CNFs have been reported [9–18], such as catalyst supports, electrode materials, gas storage materials, gas sensors, flat panel displays and adsorbents. Both reactions in CO_2 hydrogenation on $K/Ni/Al_2O_3$ may occur:

$$H_2 + CO_2 \rightarrow CO + H_2O \quad \Delta H^\circ = +41\ \text{kJ/mol}$$

$$2H_2 + CO_2 \rightarrow C + 2H_2O \quad \Delta H^\circ = -90.5\ \text{kJ/mol}$$

The overall energy of CO_2 hydrogenation is −49.5 kJ/mol. Methanol is a leading candidate as hydrogen carrier [19,20], due to its relatively low reforming temperatures, easy availability and yielding large amount of hydrogen. Hydrogen can be extracted from methanol via two process alternatives: partial oxidation and steam reforming reactions.

$$2CH_3OH + O_2 \rightarrow 2CO_2 + 4H_2 \quad \Delta H^\circ = -192.2\ \text{kJ/mol}$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \Delta H^\circ = +49.5\ \text{kJ/mol}$$

One can see that carbon formation in CO_2 hydrogenation may be thermodynamically favored in the typical temperature range, when H_2 is formed from methanol reactions.

In the present paper, we report on our use of a variety of techniques to carry out a detailed kinetic analysis of CNF formation from H_2/CO_2, and a detailed characterization of CNFs in the growth process using X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). We also discuss the effects of H_2 and CO_2 concentrations on carbon deposition and on the growth mechanisms of CNFs in the carbon structure.

2. Experimental

2.1. Catalyst preparation

The catalyst used in the present study was a commercially available Ni/Al_2O_3 formulation (12 wt.%) manufactured by

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Süd-Chemie Catalysts, Inc. (catalyst # FCR-4). All K/Ni catalysts were prepared by adding the requisite volume of aqueous KNO_3 to the Ni/Al_2O_3 catalyst without pretreatment; impregnated samples were subsequently air-dried at 80 °C for 10 h. All catalysts were used after calcination in air and reduction in H_2 at 500 °C for 5 h.

2.2. Synthesis of carbon nanofibers

The RWGS reaction and all carbon syntheses were carried out in a fixed-bed reactor (outer diameter: 0.95 cm) at atmospheric pressure. Fifty milligrams samples of catalyst were used for all reactions, which were carried out by feeding a stream of H_2/CO_2 over the catalyst at 100 mL/min. The impact of residence time on carbon formation was assessed through experiments in a H_2/CO_2 (1:1) stream that was controlled by varying the flow rate from 40 to 140 mL/min. Rates of carbon formation were inferred from linear plots of yields (g-carbon/g-cat.) *versus* reaction time within an initial 5 h period. All gaseous products were analyzed via gas chromatography using a thermal conductivity detector and a 12-ft Porapak-Q column.

2.3. X-ray photoelectron spectroscopy (XPS)

XPS data were obtained using a Thermo VG-Scientific Sigma Probe spectrometer at the Precision Instrument Center of the College of Engineering at the National Central University, Taiwan. The spectrometer was equipped with an Al Kα X-ray source (1486.6 eV; 1 eV = 1.602×10^{-19} J) that operated at 108 W and a hemispherical analyzer that operated at a pass energy of 50 eV. The instrument typically operated at an analysis chamber pressure of approximately 1×10^{-9} torr.

2.4. Temperature-programmed desorption (TPD)

TPD experiments were performed using H_2 and He streams at atmospheric pressure in a fixed-bed flow system. The temperature was increased from 25 to 1000 °C at a rate of 10 °C/min over the course of the TPD process. Concentrations of CH_4, CO and CO_2 were measured with a VG Smart IQ$^+$ 300D mass spectrometer. The desorbed products were admitted into the vacuum chamber through a leak valve using H_2 or He as the carrier gas. The chamber operating pressure was approximately 3×10^{-7} torr, and the chamber base pressure was approximately 2×10^{-9} torr.

3. Results

3.1. Effect of reaction parameters on CNF synthesis

Table 1 compares the rates of carbon deposition on 7% K + Ni/Al_2O_3 catalyst ($K/Ni/Al_2O_3$) obtained with a variety of H_2 and CO_2 partial pressures. As evident from the data, carbon formation was improved by increasing both H_2 and CO_2 concentrations. A low ratio of H_2/CO_2 concentration was insensitive to measurements of carbon deposition in our investigation, thus a partial pressure of CO_2 below 380 torr was suggested.

Fig. 1A reveals the effect of temperature on the formation rates of carbon, CO and CH_4 on the $K/Ni/Al_2O_3$ catalyst. The growth of CNFs increased as the temperature was raised from 440 to 500 °C, with the highest rate of formation at 500 °C, consistent with our previous data [8]. A similar temperature dependence was previously reported for CNF formation from methane decomposition [21,22], suggesting that a lower CNF yield from methane at higher temperatures may be due to increased catalyst deactivation. CO formation was apparently enhanced with increasing temperature, but CH_4 exhibited a low formation rate at 440–520 °C. Fig. 1B plots the rate of carbon formation as a function of residence time, suggesting an optimum carbon growth rate at a flow of 80 mL/min (GHSV = 96 L h^{-1} g^{-1}).

Table 1
Effect of H_2 and CO_2 partial pressures on the formation rate of carbon using a $K/Ni/Al_2O_3$ catalyst.

Partial pressure (torr)			Initial rate of carbon formation (g-carbon/g-cat. h)
CO_2	H_2	H_2/CO_2	7% K + Ni/Al_2O_3
152	608	4.00	0.27
152	456	3.00	0.23
152	380	2.50	0.18
152	304	2.00	0.15
380	228	0.60	0.05
380	304	0.80	0.07
380	380	1.00	0.27
304	380	1.25	0.19
228	380	1.67	0.12
76	380	5.00	0.10

Fig. 1C and D shows relevant kinetic data for carbon deposition on the $K/Ni/Al_2O_3$ catalyst. An Arrhenius plot suggests an apparent activation energy for CNF formation at a value of 71.1 kJ/mol between 440 and 500 °C; the reaction rate law for carbon formation at 500 °C was $r_C = kP_{CO_2}^{0.55}P_{H_2}^{0.9}$, suggesting that the reaction displayed a near-first-order dependence on H_2 pressure and a 0.5 order dependence on CO_2 pressure.

Fig. 1E compares the formation rates of gaseous products in the CO_2 hydrogenation reactions for Ni/Al_2O_3 and $K/Ni/Al_2O_3$ catalysts. All experiments were performed using a stream of H_2/CO_2 (1:1) at a flow rate of 100 mL/min at 500 °C. Ni/Al_2O_3 with and without K resulted in near-constant CO production, but the rate of CH_4 formation was inhibited by the presence of K additives. Fig. 1F depicts the variations of CO and CH_4 formation rate on the $K/Ni/Al_2O_3$ catalyst with changes in the partial pressures of H_2 and CO_2 at 500 °C. The red and blue symbols are the results under constant partial pressures of H_2 and CO_2, respectively. It is clear that CO formation is seemingly enhanced by increasing H_2 and CO_2 pressures, but CH_4 production was virtually insensitive to the reactant concentrations.

3.2. Effect of synthesis time on CNF growth

We used XRD spectroscopy to characterize the effect of the total reaction time on CNF formation in the context of K-enhanced Ni/Al_2O_3 catalysts. Our results suggest typical XRD patterns for the (0 0 2) graphitic basal plane at approximately $2\theta = 26.1°$ across multiple carbon deposition periods, and increased intensity with longer reaction times, as shown in Fig. 2A. All diffraction angles of the (0 0 2) graphite planes were slightly lower than is typically seen for graphite ($2\theta = 26.5°$) [23].

Fig. 2B shows the XRD spectra (30–35°) for Ni/Al_2O_3, $K/Ni/Al_2O_3$ and $K/Ni/Al_2O_3$ exposed to H_2/CO_2 at 500 °C for 10 min. Certain weak peaks near 32.1° and 34.1° were identified in the $K/Ni/Al_2O_3$ catalyst, as compared to spectra (a) and (c). We note that the peaks at 32.1° and 34.1° for the $K/Ni/Al_2O_3$ catalyst completely disappeared when a trace amount of carbon was formed by H_2/CO_2 feeding for 10 min, as shown in spectrum (c). We suggest that the new diffraction peaks at 32.1° and 34.1° were the result of new species generated by the addition of K. To date, we have been unable to confidently identify the peaks at 32.1° and 34.1°, whether by examining the existing literature, or by using the International Center for Diffraction Data (ICDD) library. The disappearance of the diffraction peaks at 32.1° and 34.1° suggests that the new K-related species may participate in the carbon formation process.

Table 2 lists the interplanar distances d_{002}, the average sizes of coherently scattering domains (CSD) along the *c*-axis of carbon (L_c),