Catalytic performance of iron oxide loaded on electron-rich surfaces of carbon nitride

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Abstract

Carbon nitride (CN) in CN encapsulated Ni/Al₂O₃ (denoted as CN/Ni/Al₂O₃) catalyst was evidenced previously as a material in electron-rich state and possessed H₂-dissociative adsorption activity due to the electron doping effect from underlying nickel. In this report, iron oxide loaded on the CN/Ni/Al₂O₃ was synthesized and investigated by Fischer-Tropsch (F-T) synthesis to test the special effect of electron-rich support on the catalytic activity of iron oxide. The Fe/CN/Al₂O₃ and CN/Ni/Al₂O₃ samples were accordingly synthesized for comparison. In Fe/CN/Ni/Al₂O₃, the iron oxide was reduced to magnetite by syngas as evidenced by the in-situ XPS measurements and XRD pattern of used catalyst. Compared with Fe/CN/Al₂O₃, more light hydrocarbons over Fe/CN/Ni/Al₂O₃ were observed. It should be understood by the interaction between iron oxide and support mainly due to the effect of electron-rich state and thus enhanced H₂ adsorption ability. In addition, such a novel support facilitated the CO conversion and retarded the water-gas shift reaction and CO₂ formation. The new type of adjustment on electronic state should be useful for novel catalyst design.

Key words: Electron-rich state; Fischer-Tropsch synthesis; Iron-based; H₂-dissociation

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1. Introduction

Since carbon materials especially single layer graphene and carbon nanotube have been extensively discussed, their application has been widely spread [1–3]. Carbon nitride (CN) or nitrogen doped carbon materials with a similar structural with sp^2 bonded carbon materials has unique and versatile properties. It has been popularly used in photocatalysis water splitting [4,5], oxygen reduction [6,7], and some heterogeneous reactions [8,9]. Nitrogen atoms in CN alter the surface properties of the material mainly on surface defects, electron localization, and the active site anchoring, which leads it to be a competitive candidate to support metal nanoparticles [7,10–12]. Previous work reported that Ni-CN interaction, as electron doping from nickel to CN, made CN/Ni/Al₂O₃ in an electron-rich state and further favored the hydrogen dissociation process on the surface of the CN [11].

Fischer-Tropsch (F-T) synthesis is an approach to transfer CO to a clean liquid synthetic fuel through hydrogenation with growing interests due to the continued application of fossil fuels are highly problematic [12]. Literatures reported that only the VIII group metals such as Fe, Ni, Co and Ru have the required activity for commercial application [13]. For instance, iron-based catalysts with low cost and high water-gas shift reaction activity usually are optimized for liquefaction of CO to gasoline [14,15], while nickel-based ones show high activities to produce light gaseous products especially CH₄ [16]. Among the published works, active metals as well as the promoters were typically co-dispersed on supports like oxides, carbon materials, and zeolites [12,17,18]. The electronic interactions between metallic particles or other active species and supports were rarely reported [19,20]. Only carbon has been found extracting electron from supported metallic particles [19]. At this stage, Ni was found to donate electron to CN in CN/Ni/Al₂O₃. In addition, noble metals, which are also F-T synthesis active, have been typically applied as promoters to directly tune the catalytic performance of the F-T catalysts [21]. Compared with co-loaded metallic promoter, the indirect electronic adjustment by underlying Ni could efficiently avoid the interference by the intrinsic F-T activity of metallic promoter. Therefore, it is interesting to introduce CN/Ni/Al₂O₃ as novel support in electron-rich state for iron-based F-T catalyst. The catalyst synthesis route is shown as the scheme below. The structure-activity and selectivity relationship of the Fe/CN/Ni/Al₂O₃ catalyst is also discussed on the basis of characteristic studies. It was suggested that CN with electron transfer from underlying nickel, maybe further interacted with loaded

Fe species, would lead to special influence on the F-T catalyst.

Scheme 1. Synthesis route for Fe/CN/Ni/Al₂O₃ catalyst.

2. Experimental

2.1. Preparation of Fe/CN/Ni/Al₂O₃

CN/Ni/Al₂O₃ was prepared in accordance with the synthesis route documented [11,22]. Briefly, The NiO/Al₂O₃ with a nickel loading of 4 wt% was prepared by incipient impregnation method using Ni(NO₃)₂·6H₂O as precursor. Encapsulation with CN was conducted through three steps including polymerization of ethylenediamine (2 g) and carbon tetrachloride (4 g) with NiO/Al₂O₃ (1 g) in m-xylene (80 mL) at 140 °C for 2 h, filtration, and calcination at 600 °C for 6 h under N₂. The obtained black powder was labeled as CN/Ni/Al₂O₃. Fe/CN/Ni/Al₂O₃ with an Fe loading of 20 wt% was prepared by impregnation method using Fe(NO₃)₃·9H₂O as precursor. Briefly, Fe(NO₃)₃·9H₂O aqueous solution was added into CN/Ni/Al₂O₃. The resulting mixture was dried at 120 °C for 12 h. The catalyst was allowed to be reduced at 280 °C for 6 h by using syngas (H₂:CO=1.7, GHSV=2 L/(h·g_{cat}), 0.1 MPa) before use.

2.2. Preparation of Fe/CN/Al₂O₃

Fe/CN/Al₂O₃ was similarly prepared using the above-described methods. Typically, the encapsulation of CN was conducted on γ-Al₂O₃ then processed by thermal treatment to give CN/Al₂O₃. The resulting powder was then impregnated with Fe(NO₃)₃·9H₂O, dried at 120 °C for 12 h and reduced before catalytic test.

2.3. Catalyst structural characterization

Fourier transform infrared spectra (FT-IR) were carried out using the Bruker Vertex 70 spectrophotometer using KBr pellets.

Thermogravimetric curves were taken on a STA 449C Thermal Star 300 instrument in air atmosphere with a heating rate of 10 °C/min.

Nitrogen adsorption-desorption isotherms was carried out at 77 K on Quantachrome Autosorb-1 Surface Area and Pore Size Analyzer. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated from the corresponding desorption branch of N₂ isotherm by Barrett-Joyner-Halenda (BJH) method.

Transmission electron microscopy (TEM) measurements were carried out with a JEOL JEM-200CX instrument at an accelerating voltage of 200 kV.

X-ray powder diffraction (XRD) patterns were recorded using a Phillips X'Pro diffractometer. The X-ray source was a sealed, 2.2 kW Cu X-ray tube (40 kV, 30 mA).

H₂ temperature programmed reduction (TPR) was recorded using a gas chromatograph equipped with a thermal conductivity detector from room temperature to 800 °C at a heating rate of 10 °C/min. 80 mg of catalyst was pretreated at 200 °C in a He flow (30 mL/min) for 1.5 h to remove moistures and then cooled to room temperature. The H₂ TPR curve was recorded until a stable baseline was reached when H₂/N₂ (5% H₂ + 95% N₂, 20 mL/min) flow through the catalyst bed.

H₂ temperature programmed desorption (TPD) was carried out on the same instrument with TPR analysis. About 60 mg samples was allowed to be reduced at 450 °C in a H₂/N₂ flow for 6 h then cooled down. The N₂ was introduced for an additional 1 h until a stable baseline was achieved. The H₂ TPD curve was recorded from room temperature to 800 °C at a heating rate of 10 °C/min.

Compositions on the catalysts surface and their corresponding binding energies were determined by in-situ X-ray photoelectron spectroscopy (ESCALAB 250Xi XPS) equipped with a monochromatic Al K α X-ray source under pressure of 10⁻⁷ mbar. The sample was firstly evacuated at 120 °C (10 °C/min) for 1 h and cooled down to room temperature. XPS was obtained to evaluate the sample states before reduction. Then the sample was allowed to reduce at 350 °C in the chamber connected to XPS system using syngas (H₂:CO=1.7, 30 mL/min) for 1 h. After cooling down to room temperature, XPS analysis was conducted. Binding energies were calibrated using C1s peak (284.6 eV) as a reference.

2.4. Catalytic test

Catalytic activity was evaluated in a fixed-bed reactor. The catalyst was diluted using 80–100 mesh SiC with a weight ratio of 1:5 to avoid hot spots and in-situ reduced by syngas as mentioned above.

After reduction, the GHSV was decreased to 1 L/(h·g_{cat}). The system was allowed to age at 170 °C, 1.5 MPa for 24 h. Then the temperature was increased and maintained at different temperatures (290 °C, 300 °C, 310 °C, and 320 °C) for 12 h to stabilize the reaction system. After the analysis of gaseous products, the reactor was kept for 24 h at 320 °C for liquid samples collection. Gaseous products were on-line analyzed by gas chromatography (Agilent 3000A Micro GC). CO conversion and selectivities were calculated as reported in literature [23].

3. Results and discussion

3.1. Properties of samples

3.1.1. TG and IR

CN was detected by FT-IR spectroscopy as shown in Fig. 1(a). Characteristic absorption bands of CN are found in both supports [11,24]. The CN contents in CN/Ni/Al₂O₃ and CN/Al₂O₃ are about 20% according to the TG analysis (Fig. 1b).

Fig. 1. (a) FT-IR spectra and (b) TG results of CN/Ni/Al₂O₃ and CN/Al₂O₃.

3.1.2. Nitrogen adsorption-desorption isotherms

Nitrogen adsorption-desorption measurements were conducted to further identify the physic-chemical details of the as-prepared materials. The basic parameters of the supports and the used catalysts are listed in Table 1. The obtained single point BET surface area is 137.6 m²/g for CN/Ni/Al₂O₃. The pore volume and the average pore size are about 0.32 mL/g and 14.35 nm, respectively. CN/Al₂O₃ shows little higher results as compared with CN/Ni/Al₂O₃. After reduction and catalytic tests, the used catalysts exhibit lower surface area, pore volume, and pore size than that of the corresponding supports. Because of the influence of supports, the surface area, pore volume, and pore size of Fe/CN/Ni/Al₂O₃ are lower than

that of the Fe/CN/Al₂O₃.

Table 1 Physic-chemical parameters of the supports and the used catalysts

Sample	BET surface area (m ² /g)	BJH pore volume (mL/g)	Average pore size (nm)
CN/Ni/Al ₂ O ₃	137.6	0.32	14.35
CN/Al ₂ O ₃	143.5	0.35	14.84
Fe/CN/Ni/Al ₂ O ₃	117.7	0.24	16.89
Fe/CN/Al ₂ O ₃	127.3	0.28	18.50

3.1.3. TEM and XRD

The morphologies and structures of the samples before reduction are studied by TEM as depicted in Fig. 2. The γ -Al₂O₃ shows a uniform rod-like structure with diameters of about 20 nm. The HRTEM of Fe/CN/Ni/Al₂O₃ only shows the CN encapsulated metallic Ni and Al₂O₃, as shown in Fig. 2(b), while Fe(NO₃)₃ is not detected. The as-prepared samples are in good accordance with the standard PDF cards as analyzed by XRD (Fig. 2c). CN layers cannot be detected due to its amorphous phase. Meanwhile, characteristic diffractions of metallic Ni are not discovered because of the low loading and high dispersion. Fe/CN/Ni/Al₂O₃ and Fe/CN/Al₂O₃ catalysts before reduction show good crystal structure of Fe(NO₃)₃. After catalytic tests for 4 days, Fe/CN/Al₂O₃ and Fe/CN/Ni/Al₂O₃ catalysts were recycled immediately and analyzed by XRD instrument. The corresponding results, as shown in Fig. 2(d), evidence a characteristic and stable crystalline of Fe₃O₄, which turns out to be the active phase(s) in F-T synthesis in such catalysts. Furthermore, it is found that the calculated crystal sizes for used Fe/CN/Al₂O₃ and Fe/CN/Ni/Al₂O₃ by Scherrer's equation are similar, which allows us to ignore the influence of particle size on catalytic performances.

Fig. 2. (a) TEM image of Al_2O_3 , (b) HRTEM images of $\text{Fe/CN/Ni/Al}_2\text{O}_3$, (c) XRD spectra of $\text{CN/Ni/Al}_2\text{O}_3$, $\text{Fe/CN/Al}_2\text{O}_3$, and $\text{Fe/CN/Ni/Al}_2\text{O}_3$. The XRD patterns are recorded before syngas reduction. (d) XRD spectra of $\text{CN/Ni/Al}_2\text{O}_3$, $\text{Fe/CN/Al}_2\text{O}_3$, and $\text{Fe/CN/Ni/Al}_2\text{O}_3$ after catalytic tests.

3.1.4. H_2 TPR and TPD

Fig. 3(a) shows the H_2 TPR profiles of all the catalysts. The reduction of $\text{Fe}(\text{NO}_3)_3$ species with CN can be accomplished through three typical processes. A: H_2 adsorption on CN accompanied with phase change of $\text{Fe}(\text{NO}_3)_3$ to $\alpha\text{-Fe}_2\text{O}_3$; B: reduction of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 ; and C: reduction of Fe_3O_4 to metallic iron [25–27]. CN adsorbed H_2 is detected in $\text{CN/Ni/Al}_2\text{O}_3$ suggesting metallic Ni phase, which is in agreement with the TEM result. In addition, the areas of peaks A and C for $\text{Fe/CN/Ni/Al}_2\text{O}_3$ are larger than that of $\text{Fe/CN/Al}_2\text{O}_3$, implying the presence of metallic Ni will further promote H_2 adsorption on CN and the reduction of iron oxides [26]. The H_2 adsorption and desorption play important roles in determining the catalytic performance of the catalysts [16,28]. Fig. 3(b) depicts the H_2 TPD curves of the samples. The $\text{CN/Ni/Al}_2\text{O}_3$ shows a single H_2 desorption peaks on CN species. Catalysts show a typically couple of H_2 desorption peaks: (i) desorption of H_2 by weak chemical interaction on CN species and metallic compounds, (ii) desorption of H_2 by strongly chemical adsorbed H_2 on metallic compounds. In addition, it is found that promotion with nickel shows a negative shift of desorption temperature.

Fig. 3. (a) H_2 TPR and (b) TPD profiles for the $\text{Fe/CN/Ni/Al}_2\text{O}_3$, $\text{Fe/CN/Al}_2\text{O}_3$, and $\text{CN/Ni/Al}_2\text{O}_3$.

3.1.5. In-situ XPS

Fig. 4 shows the core-level XPS patterns of prepared catalysts in the Fe 2p and N 1s regions. Before reduction in the XPS equipped chamber, the pressed samples were carefully treated in vacuum at 120 °C for 1 h to remove the weakly adsorbed impurities on the samples. The Fe 2p spectral lines for $\text{Fe/CN/Ni/Al}_2\text{O}_3$ and $\text{Fe/CN/Al}_2\text{O}_3$ before reduction are split into $2p_{3/2}$ (712.2 and 712.3 eV) and $2p_{1/2}$

(725.7 and 725.8 eV) doublets due to the spin-orbit coupling [29–31], as shown in Figure 4(a). Fe 2p core-levels spectra for reduced Fe/CN/Ni/Al₂O₃ and Fe/CN/Al₂O₃ catalysts are divided into three couples of peaks in Fig. 4(b) referred to Fe₃O₄ (main) and Fe₂O₃ with associated satellite peaks due to partially reduction since Fe 2p_{3/2} for Fe₃O₄ does not have a satellite peak [32,33]. In addition, there exhibits a strong interaction between Fe₃O₄ and CN/Ni/Al₂O₃ since the binding energies for Fe/CN/Ni/Al₂O₃ are higher than that of Fe/CN/Al₂O₃ due to electron doping by underlying Ni. Combined with the XRD patterns of used catalysts, the catalysts were totally reduced to Fe₃O₄ in the fixed-bed F-T experiments. The exact identity of the active phase(s) for iron-based catalysts in F-T synthesis remains controversial [12,34–38]. Fe₃O₄ has been evidenced as efficient materials for F-T synthesis and water-gas shift [35–37]. The results we obtained are agreed with this viewpoint. The N 1s XPS profiles of catalysts before reduction can be fitted to five peaks, which are attributed to the nitrate N1 (~406.7 eV), graphitic N2 (~401.0 eV), pyrrol N3 (~399.9 eV), amine N4 (~399.0 eV), and pyridinic N5 (~398.4 eV) from high to low binding energy [12,39,40]. After treated by syngas reduction, nitrate N1 in the samples disappears and N2–N5 peaks shift to lower binding energies, especially in Fe/CN/Ni/Al₂O₃. It indicates CN in such a catalyst was in electron-rich state due to electron doping from underlying Ni, which has been fully studied in our previous work [11].

Fig. 4. In-situ Fe 2p and N 1s XPS spectra of Fe/CN/Ni/Al₂O₃ and Fe/CN/Al₂O₃. (a) Before reduction and (b) after reduction at 350 °C for 1 h using 30 mL/min of H₂/CO=1.7:1 syngas.

3.2. Catalytic Performance

Catalytic tests were conducted on a micro fixed-bed reactor equipped with an online gas analyzer.

Diluted catalysts were firstly reduced at 280 °C using syngas ($H_2/CO=1.7:1$, 0.1 MPa, 2 L/(h·g_{cat})). Then, the catalysts were aged at 170 °C for 24 h and pressure and GHSV were adjusted to 1.5 MPa and 1 L/(h·g_{cat}), respectively. Catalytic tests were then recorded every 10 °C from 290 to 320 °C.

Fig. 5 shows the evaluations of catalysts including (a) CO conversion & H_2 conversion, (b) CO_2 selectivity, and (c) CH_4 selectivity. Please note that in order to study the structural influences on catalyst performance, the diversity of the results was consciously enhanced by optimal conditions without consideration of optimization results. In Fig. 5(a), CO and H_2 conversions are increased with the system temperature. $CN/Ni/Al_2O_3$ shows a very low activity. $Fe/CN/Ni/Al_2O_3$ depicts a promoted activity as compared with $Fe/CN/Al_2O_3$. Herein, the influence of temperature on CN contained samples is more significantly. The other phenomenon that catches our eyes is that the catalysts modified with CN shows growing discrepancy between CO and H_2 conversion. It is worthy to note that $Fe/CN/Ni/Al_2O_3$ catalyst shows a stable performance since a slight decrease of 2.1% in CO conversion after 36 h at 320 °C is found. CO_2 is an important side product due to water-gas shift reaction. The selectivity to CO_2 is carefully studied as plotted in Fig. 5(b). Since nickel-based catalyst shows low water-gas shift reaction activity, $CN/Ni/Al_2O_3$ exhibits low selectivity to CO_2 and also independent of temperature. While Fe-based catalysts produce much more CO_2 due to water-gas-shift reaction. Along with the improved system temperature, CO_2 becomes an important part of resulting gaseous products. Due to supported on electron-rich material, $Fe/CN/Ni/Al_2O_3$ shows lower CO_2 selectivity than $Fe/CN/Al_2O_3$. Observed from Fig. 5(c), selectivity to CH_4 is relative low and not affected by thermal changes for $Fe/CN/Al_2O_3$. $CN/Ni/Al_2O_3$ produces almost CH_4 as traditional nickel-based catalysts [13,30,41]. Owing to the influence of $CN/Ni/Al_2O_3$, $Fe/CN/Ni/Al_2O_3$ depicts growing CH_4 selectivity with increased reaction temperature.

Fig. 5. Results of catalytic experiments at different temperatures using $Fe/CN/Ni/Al_2O_3$, $Fe/CN/Al_2O_3$,

and CN/Ni/Al₂O₃: (a) CO conversion (solid) & H₂ conversion (open), (b) CO₂ selectivity, and (c) CH₄ selectivity.

Typically, iron-based F-T catalysts are applied to produce liquid hydrocarbons especially gasoline, whereas even lighter products are obtained by nickel-based materials. The liquid products were analyzed by off-line GC. Paraffins are the primary products as shown in Fig. 6. Fe/CN/Ni/Al₂O₃ shows a distribution with mono-peak curve from C₄ to C₂₈ hydrocarbons, whereas resulting liquid over Fe/CN/Al₂O₃ presents products from C₄ to C₃₁ hydrocarbons. Due to the influence of CN/Ni/Al₂O₃, the liquid distribution over Fe/CN/Ni/Al₂O₃ is shifted to short chain direction inordinately and becomes narrow. Alcohols, olefins, and isomers show similar results to paraffins.

Fig. 6. The resulting liquid distributions of (a) Fe/CN/Ni/Al₂O₃ and (b) Fe/CN/Al₂O₃. The vertical axis is liquid distribution (%) and the horizontal one is carbon number of C₅₊ products.

In order to explain the results above, Fig. 7 is introduced to briefly discuss the interaction among components in prepared catalysts. Main reactions are described as follows. In the structural model, nickel is highly dispersed on rod-like Al₂O₃ and then covered by CN. Fe species, actually Fe₃O₄ particles, are loaded on the external surfaces of CN/Ni/Al₂O₃. XPS results reveal a strong metal Ni-CN interaction, exhibiting as electron-rich CN by accepting electron donated by underlying Ni, which favors the adsorption and activation of hydrogen as process (a) in Fig. 7. Hydrogen is activated on the surfaces of CN, as shown in process (b) [11]. Then CO is converted to CH₄ by applying activated H* on CN, as exhibited by processes (c). The activated H* on CN is assumed to facilitate the chain terminal process [42], therefore CH₄ selectivity follows the order of CN/Ni/Al₂O₃>Fe/CN/Ni/Al₂O₃>Fe/CN/Al₂O₃ (without underlying Ni). CO₂ as a side product is mainly produced over Fe species via water-gas shift

reaction, see process (d). Due to the influence of CN in electron-rich state, the water-gas shift reaction is retarded. Process (e) is used to describe the F-T synthesis for hydrocarbons mainly occurred on Fe_3O_4 surfaces due to the high loading. Since there is a strong metal-support interaction between Fe_3O_4 and $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ and activated H^* on CN facilitates the chain terminal process, $\text{Fe}/\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ produces more light hydrocarbons during F-T process.

Fig. 7. Schematic show of the functions of components in one particle of $\text{Fe}/\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ for CO for CO hydrogenation (top-view).

4. Conclusions

In this paper, CN encapsulated $\text{Ni}/\text{Al}_2\text{O}_3$ was investigated as a material in electron-rich state, which was further applied as a support in $\text{Fe}/\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$. The interactions among the components of $\text{Fe}/\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ were discussed. CN, as in electron-rich state, offered the active sites for hydrogen dissociation. Therefore, a considerable amount of CH_4 was produced over $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Fe}/\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$. Due to the same reason, a unique liquid products distribution was found for $\text{Fe}/\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$. Moreover, $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ was identified to decline the emission of CO_2 by suppressing water-gas shift activity. These results were suggested to provide reference for studying electronic interactions and designing of new catalysts.

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Iron oxide was loaded on the electron-rich surfaces of CN/Ni/Al₂O₃ and investigated by Fischer-Tropsch (F-T) synthesis to test the special electron-rich support effect on the catalytic performance.