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Communication

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N-doped Graphene as an Electron Donor of Iron Catalyst for CO Hydrogenation to Light Olefins

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N-doped graphene used as an efficient electron donor of iron catalyst for CO hydrogenation can achieve a high selectivity of around 50% for light olefins, significantly superior to the selectivity of iron catalyst on conventional carbon materials, e.g. carbon black with a selectivity of around 30% at the same reaction conditions.

CO hydrogenation to light olefins is regarded as one of the most important conversion ways of methane (natural gas and shale gas) and coal to chemical feedstock and fuels.¹⁻⁴ Especially, with the increasing discovery of shale gas, several governments such as America, Canada and China, have given more attentions to methane conversion. Therefore, CO hydrogenation to light olefins has become a hot topic in the field of energy and chemical engineering. However, due to the limit of Anderson-Schulz-Flory (ASF) distribution in Fischer-Tropsch (FT) synthesis, most products of CO hydrogenation are saturated alkanes and long chain hydrocarbons.^{5, 6} It is difficult to control the product distribution for light olefins with high selectivity.⁷⁻¹⁰ Different metals including Fe, Co, Ni and Ru are often used as the catalysts for CO hydrogenation.^{1, 11} Among them, Fe based nanomaterials have been regarded as the low-cost, high-efficient catalysts to enhance the selectivity of light olefins in CO hydrogenation. Previous research indicated that the iron based catalysts for light olefins are very sensitive to the electronic properties of the additives and supports. For example, Na and K additives can be used as the electron donor to increase the selectivity of the light olefins.¹²⁻¹⁴ Different supports such as silica, alumina, magnesia, zeolite, carbon, SiC etc. also have a crucial effect on the selectivity of these catalysts due to the different electronic interactions between them.^{13, 15-21} Among them, carbon materials have attracted great attentions as the potential candidate because of their unique structural and electronic properties. For example, our previous research showed that Fe catalysts confined inside carbon nanotubes (CNTs) can significantly affect the catalytic selectivity of CO hydrogenation compared with the Fe catalysts supported on the outside of CNTs due to the different electronic environment inside and outside the CNTs.²²⁻²⁴

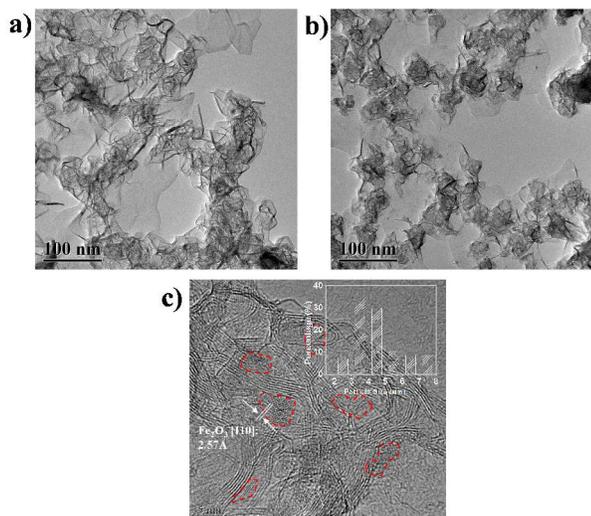
Recently, graphene has attracted wide attention as a catalyst

support due to its high surface area and exotic electronic properties.²⁵⁻²⁷ However, perfect graphene is inert in chemistry. It is reported that doping heteroatoms such N and B atoms into the matrix of graphene can tailor its electronic structure and chemical activity, which can be used as an electron donor or acceptor according to the types of dopants.²⁸⁻³² Inspired by this, we report herein that the N-doped graphene can be used as an efficient electron donor for iron catalyst to enhance the performance of CO hydrogenation to light olefins.

N-doped graphene (NG) was synthesized by an one-pot solvothermal method with the Li₃N and CCl₄ as the precursors as our previous report.³³ The nitrogen content in NG can be efficiently controlled with the aid of the cyanuric chloride during the reaction (see supporting information for more details). In this study, three different nitrogen content, i.e. 4.5%, 8.4%, 16.4% (N/C) in NG was prepared according to the X-ray photoelectron spectroscopy (XPS) measurement (Figure S1,2 and Table S1), which was denoted as NG_{4.5}, NG_{8.4} and NG_{16.4}, respectively. The Raman spectra (Figure S5) showed that these NG samples had the characteristic D (1335 cm⁻¹), G (1585 cm⁻¹) and 2D (2660 cm⁻¹) bands of graphene, and the G bands split into two peaks with a D' band at 1620 cm⁻¹ probably introduced by nitrogen doping which was also observed in nitrogen-doped graphene by other preparation methods.^{34, 35} The iron was loaded on NG samples (Fe/NG) via an ultrasound-assisted impregnation method (see supporting information for more details), which was denoted as Fe/NG_{4.5}, Fe/NG_{8.4} and Fe/NG_{16.4}, respectively. For comparison, we also prepared XC-72 and nitrogen doped XC-72 (denoted as XC-N) loading iron catalysts, which was denoted as Fe/XC and Fe/XC-N, respectively (see supporting information for more details). The iron content in all samples is around 8 wt.% according to the inductively coupled plasma optical emission spectrometry (ICP-OES) analysis in Table S2.

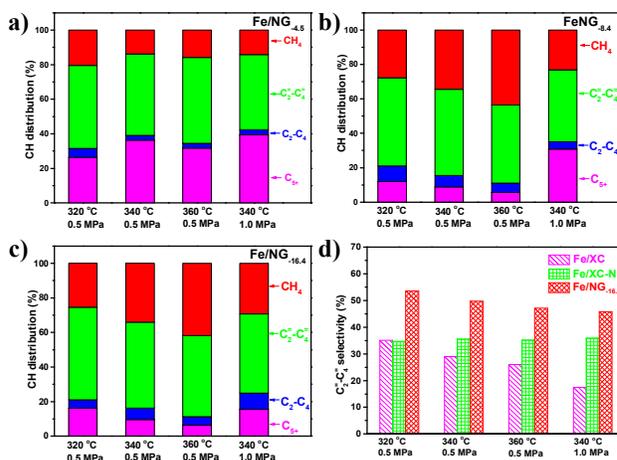
TEM images showed the morphology and structure of these Fe/NG samples. Taking any scanning area of the samples, one can see the morphology of Fe/NG samples (Figure 1b and S9) remain nanosheet structure as the original NG samples (Figure 1a). HRTEM images showed that these nanosheets in Fe/NG contain well-dispersed nanoparticles with an average size of c.a.

4 nm. The planar d of these particles is 2.57 ± 0.05 Å, corresponding to [110] plane of hematite (Fe_2O_3), in accord with the XRD analysis (Figure S6).



5 Figure 1. The morphology and structure of NG and Fe/NG samples. (a) TEM image of NG_{16.4}. (b) TEM image and (c) HRTEM image of Fe/NG_{16.4} before reaction. The area with red dashed circles in (c) shows the dispersed Fe_2O_3 nanoparticles on the graphene nanosheets. The insert in (c) shows the size distribution of Fe_2O_3 nanoparticles. The Fe/NG samples were first treated at 350 °C in Ar for 1 h before TEM measurement.

CO hydrogenation was carried out on a fixed bed reactor using a typical syngas with a H_2/CO ratio of 1:1. The reaction was first performed at 340 °C with a pressure of 0.5 MPa and a gas hourly space velocity (GHSV) of 5000 h^{-1} . After reaching the pre-set temperature, the reaction was continued at least 8 hours to get a steady state. It should be noted that there was no obvious activity for pure NG samples since the CO conversion was almost negligible (lower than 0.1%). The activity and selectivity of Fe/NG samples were summarized in Table S3 and Figure 2. One can see that all Fe/NG catalysts showed high selectivity, i.e. around 50% towards light olefins in all CH products at 0.5 MPa. When increasing the pressure to 1.0 MPa, the CO conversion will significantly increase while the selectivity of light olefins will reduce but still more than 40%. It is quite remarkable since iron based catalysts usually give a wide distribution of hydrocarbons with a low selectivity toward light olefins (usually no more than 40%) when directly supported on carbon materials without promoters like S, K and Mn.^{10, 12, 14} The nitrogen here may play the role like the K and Mn promoters that inhibited the hydrogenation of olefins and thus increased the selectivity of olefins. In addition, as shown in Table S3, with nitrogen content increasing from 4.5% to 16.4%, CH_4 selectivity will increase from 14.2% to 29.2%, while the selectivity of C_{5+} will reduce from 39.4% to 15.5% at GHSV = 5000 h^{-1} , 340 °C and 1.0 MPa, indicating that the growth of carbon chain was also restrained by increasing the nitrogen content.



40 Figure 2. The performance of CO hydrogenation to light olefins by Fe/NG catalysts. The product distribution of CO hydrogenation by Fe/NG_{4.5} (a), Fe/NG_{8.4} (b) and Fe/NG_{16.4} (c) at various reaction temperature and pressure. (d) $\text{C}_2\text{-C}_4$ selectivity of Fe/XC, Fe/XC-N and Fe/NG-16.4 at various reaction temperature and pressure. Reaction condition: 100 mg catalyst, Fe loading = 8 wt.%, GHSV = 5000 h^{-1} , H_2 : CO = 1:1.

To further confirm the nitrogen doping effect to CO hydrogenation, we also test the catalytic reaction by using iron catalyst supported on pure conductive carbon black (XC-72) and nitrogen doped XC-72 (XC-N). As shown in Table S4, the light olefins selectivity of Fe/XC is only 29.0% and 17.5% in 0.5 MPa and 1 MPa at 340 °C, respectively. In comparison, the light olefins selectivity of Fe/XC-N significantly increase to 35.6% and 35.9% in 0.5 MPa and 1.0 MPa, respectively. Nevertheless, the selectivity of light olefins of Fe/XC-N is still lower than that of Fe/NG samples at the same conditions (Figure 2d), which may be attributed to the NG samples possess more nitrogen content than XC-N sample, as shown in Table S1. This result further convinced that the introduction of nitrogen atom in graphene can enhance the selectivity of CO hydrogenation to light olefins.

Table 1. The performance of CO hydrogenation by Fe/NG_{16.4} catalyst at various space velocity.

| GHSV (h^{-1}) | 5000 | 2000 | 1000 | 600 |
|---|------|------|------|------|
| CO conversion (%) | 1.4 | 3.2 | 8.8 | 21.1 |
| CO_2 selectivity (%) | 11.5 | 14.2 | 22.6 | 35.1 |
| CH distribution (%) | | | | |
| CH_4 | 37.8 | 35.8 | 28.7 | 21.4 |
| $\text{C}_2\text{-C}_4$ | 48.2 | 47.0 | 48.0 | 49.6 |
| $(\text{C}_2\text{-C}_4)/(\text{C}_2^0\text{-C}_4^0)$ | 8.2 | 5.6 | 4.5 | 5.4 |
| C_{5+} | 8.1 | 8.8 | 12.7 | 19.8 |

65 Reaction condition: 100 mg catalyst, Fe loading = 8 wt.%, H_2 : CO = 1:1, 340 °C, P = 0.5 MPa.

Apart from the selectivity enhancing with the nitrogen content increasing, we also found that increasing N content in Fe/NG samples can promote the CO conversion, i.e. with the N content increasing from 4.5% to 16.4%, the CO conversion increases from 1.3% to 5.0% at 340 °C under 1 MPa. We speculate that the introduction of nitrogen may introduce more defects in graphene

and subsequently promote the dispersion of the iron particles as shown in XRD spectra (Figure S6).^{36, 37} The nitrogen promotion to the dispersion of metal particles in carbon materials was also demonstrated in the literature. For examples, Hu and his co-workers have demonstrated that Pt loaded on N-doped carbon nanotubes shows higher electrocatalytic activity than that on pure carbon nanotubes, which was attributed to better dispersion of Pt nanoparticles on N-doped carbon nanotubes.³⁸ In addition, we also studied the catalytic performance of the Fe/NG samples with the effect of GHSV. As shown in Table 1, with decreasing GHSV of Fe/NG_{16.4} from 5000 h⁻¹ to 600 h⁻¹, the CO conversion increases significantly, i.e. from 1.4% to 21.1% at 340 °C and 0.5 MPa, while the selectivity of light olefins still remains around 50%. It is reported that the carbon chain growth increased with the decreasing GHSV, and usually lead a lower C₂⁼-C₄⁼ selectivity according to the literature.⁸ So it is surprising to find that the Fe/NG catalysts can still keep high C₂⁼-C₄⁼ selectivity at a lower GHSV since this high selectivity is often only gained by adding promoters like K and Mn or at a very high GHSV (usually over 10000 h⁻¹).^{13, 39} Furthermore, the optimized Fe/NG_{16.4} also shows long-term stability toward CO conversion and C₂⁼-C₄⁼ selectivity during the lifetime test of 90 h (Figure 3). These results indicate that the introduction of nitrogen in Fe/NG samples can significantly enhance both the activity and selectivity for CO hydrogenation to light olefins with a high durability.

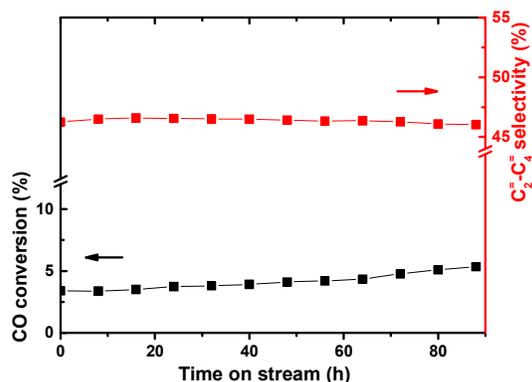


Figure 3. Life test of CO hydrogenation by Fe/NG_{16.4} catalyst. Reaction condition: 100 mg catalyst, Fe loading = 8 wt.%, GHSV = 2000 h⁻¹, H₂ : CO = 1 : 1. Temperature = 340 °C, P = 0.5 MPa.

To comprehend the nature of the nitrogen effect to the active sites of Fe/NG samples for CO hydrogenation, X-ray adsorption fine structure spectra (XAFS) and X-ray diffraction (XRD) measurements were employed to investigate the structural and electronic properties of these catalysts before and after the reaction. X-ray absorption spectra (XAS) of Fe L-edge analysis (Figure 4a) indicated that the original Fe/NG and Fe/XC samples have a similar energy at the Fe L_{3,2}-edge, corresponding to a typical Fe₂O₃ feature, which is in agreement with the XRD analysis (Figure S6).⁴⁰ But the intensity of the L_{3,2}-edge peak in Fe/NG samples has a significant decrease compared with that in Fe/XC sample and further decreases with nitrogen content increasing. The metal L-edge intensity is proportional to the number of half- or unoccupied metal d orbitals in the final state

according to the literature.^{41, 42} Therefore, the decrease of L-edge peak intensity of the iron means iron gets more electrons at the 3d final state, suggesting that the introduction of N promotes the electron transfer from NG to iron. Furthermore, XANES Fe K-edge shows the Fe/NG samples after reaction possess more reduced state of iron compared with Fe/XC sample (Figure 4c). Further Fourier-transformed extended X-ray adsorption fine structure also indicates that the Fe/NG samples has a Fe-C bond at 1.4 Å and a Fe-Fe bond at 2.1 Å while the Fe/XC sample shows a double peak feature, i.e. a broad Fe-O bond at 1.4 Å (overlapped with Fe-C bond) and a Fe-O-Fe bond stretched to 2.6 Å, corresponding to the feature of Fe₂O₃. XRD patterns further confirmed that the iron mainly remains low-valence state in Fe/NG samples after reaction. As shown in Figure 4b, there are two main phases, i.e. the peaks at 42.6° and 44.9° corresponding to the [102] and [211] phase of Fe₇C₃, respectively, and the peaks at 43.4° and 44.0° corresponding to the [021] and [510] phases of Hägg Fe₃C₂, respectively, which is known as an active phase in Fischer - Tropsch synthesis.^{6, 43, 44} These broad and weak peaks in Fe/NG-FT samples also imply that these iron carbide species formed after reaction are still highly dispersed. These results indicate that graphene doped with N can offer the electron to keep iron particles at a low chemical valence state, which is similar with the role of alkali metal promoters in conventional FT synthesis and therefore enhance the selectivity of light olefins for CO hydrogenation.

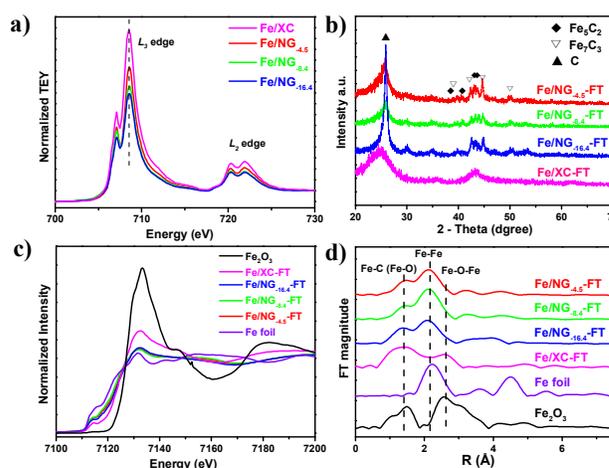


Figure 4. Structural and electronic characterization of the Fe/NG and Fe/XC samples before and after CO hydrogenation. (a) Normalized XAS of Fe L-edge of original Fe/NG and Fe/XC samples measured in a total electron yield (TEY) mode. The samples was treated in Ar at 350 °C for 1 h before XAS tests. (b) XRD patterns of Fe/NG and Fe/XC samples after reaction. (c) Normalized XANES spectra of Fe K-edge of Fe/NG and Fe/XC samples after reaction compared with standard Fe foil and Fe₂O₃ samples. (d) Fourier-transformed k₃-weighted EXAFS signal of Fe/NG and Fe/XC samples after reaction compared with standard Fe foil and Fe₂O₃ samples. Dashed lines are corresponding to the Fe-C (Fe-O) bond (1.4 Å), Fe-Fe bond (2.1 Å) and Fe-O-Fe bond (2.6 Å), respectively. All the samples after CO hydrogenation underwent the same reaction condition, i.e. 340 °C, GHSV = 5000 h⁻¹, 1.0 MPa and time on stream over 80 h.

In conclusion, we demonstrated that N-doped graphene can be used as an efficient electron donor of iron catalyst to enhance the performance of CO hydrogenation to light olefins. These Fe/NG samples exhibited a high selectivity toward light olefins with a long-term durability over 90 h. XAS results of Fe L-edge and K-edge and XRD indicated that the iron supported on N-doped graphene possess more reduced state before and after the reaction than that on XC-72, which could be the key factor to promote the selectivity of light olefins in Fe/NG samples. This study introduces a new way to enhance the performance of CO hydrogenation to light olefins and can further promote the understanding toward the nature of CO hydrogenation.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental section, Fig. S1-S9 and Table S1-S4. See DOI: 10.1039/c000000x/

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Table of content

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