Carbon nanotube-supported bimetallic Pt–Fe catalysts for nitrobenzene hydrogenation

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Carbon nanotube (CNT)-supported Pt–Fe catalysts were prepared by a chemical reduction method using chloroplatinic acid and ferric nitrate as starting materials. The structure and the morphology of the catalysts were characterised by an X-ray diffractometer, transmission electron microscopy and inductively coupled plasma atomic emission spectrometry. The catalytic performance for nitrobenzene hydrogenation was evaluated under atmospheric pressure at an ambient temperature. The bimetallic Pt–Fe/CNT catalysts showed much higher activity than Pt/CNTs with a similar Pt content for nitrobenzene hydrogenation.

1. Introduction: Nitrobenzene hydrogenation is important in organic chemistry, as aniline is used as a basic raw material in the production of methylene diphenyl diisocyanate, as an additive in the rubber process, and in dyes, pigments, pesticides and herbicides [1–5]. Supported Pt or Pd nanocatalysts are reported as effective catalysts for nitrobenzene hydrogenation under milder conditions with better activity and selectivity [6–8]. The primary roles of the support are to finely disperse and stabilise small metallic particles and thus provide access to a much larger number of catalytically active atoms; a large surface area of support is favourable for improving the dispersion. Hence, Pt supported on carbon nanotubes (CNT) with a large specific surface area are widely used as catalysts for nitrobenzene hydrogenation [8–10]. However, the activity of the CNT supported Pt catalysts still needs to be improved at ambient temperature and atmospheric pressure. Introduction of Fe to the Pt catalysts improves the catalytic activity for the hydrogenation of p-choloronitrobenzene [11], however, the authors only utilised Pt–Fe catalysts with a higher Pt content and a lower Fe loading (the contents of Fe and Pt are 0.1 and 0.3 wt%, respectively) to catalyse the hydrogenation of p-choloronitrobenzene. Based on the low price and the cocatalytic action of Fe, it is interesting to investigate the effect of iron content (especially higher Fe content than Pt loading) on the catalytic performance of the Pt–Fe/CNTs. It is also important for developing bimetallic Pt–Fe catalysts with a high activity and a low cost.

In this Letter, we report on the synthesis of the Pt–Fe/CNT catalysts with different Fe loadings and similar Pt content by a chemical reduction method. The content of Pt is in the range of 1.15–1.35 wt% and the Fe loading is 0, 0.18, 0.27 and 2.91 wt%, respectively. The catalytic activities for nitrobenzene hydrogenation were investigated.

2. Experimental
2.1. Catalyst preparation: CNTs (0.5 g), obtained from Shenzhen Nanotech. Port. Co. Ltd, were dispersed in 150 ml of glycol using ultrasonication for 30 min, then the mixture was heated to 80°C. 1 g of $C_8H_5KO_4$ (potassium acid phthalate) was added. The solution of chloroplatinic acid and ferric nitrate was dropped with vigorous stirring. Afterwards, the solution of KBH_4 was dropped. The reduction reaction was run at 80°C for 8 h and at room temperature for 12 h. The slurry was filtered, washed with ethanol and water and dried at 80°C for 12 h in a vacuum oven.

2.2. Characterisation: Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku Ultima IV) at 40 kV and 40 mA, respectively, with Cu Kα radiation. The particle size and the distribution of the samples were analysed by transmission electron microscopy (TEM) (Hitach-7700) with an acceleration voltage of 100 kV. The loading of metals on to the surface of the CNTs was analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (ULTIMA).

2.3. Hydrogenation of nitrobenzene: The hydrogenation of nitrobenzene was performed at room temperature. The catalyst (25 mg) was put in a three-necked bottle and hydrogen was introduced into it to activate the sample at a 40 ml min^{-1} flow rate for 2 h. Then, 0.25 ml nitrobenzene and 25 ml ethanol, respectively, were injected with stirring. The samples were taken intermittently. The chemical analysis of the products was performed by liquid chromatography (ECHCOMO T2100P).

3. Results and discussion
3.1. Morphology and structure of the catalysts: Pt–Fe/CNT catalysts with different loadings were prepared. Table 1 lists the elemental chemical analysis data for the metals of the Pt–Fe/CNTs. The content of Pt is in the range of 1.15–1.35 wt% and the Fe loading is 0.18, 0.27 and 2.91 wt%, respectively. Pt/CNTs with 1.15 wt% of Pt loading were also prepared for comparison.

Supported Pt/CNT and Pt–Fe/CNT catalysts were prepared by a reduction reaction using pristine CNTs as supports, potassium acid phthalate as a ligand and a cross linker [12], KBH_4 as a reductant and chloroplatinic acid and ferric nitrate as the starting material. It is hard to keep Pt loading as a constant when using this process. Potassium acid phthalate has two carboxyl groups and a benzene ring. Thus, under alkaline conditions, the metal ions

Table 1 Elemental chemical analysis data for the metals of the Pt–Fe/CNT catalysts

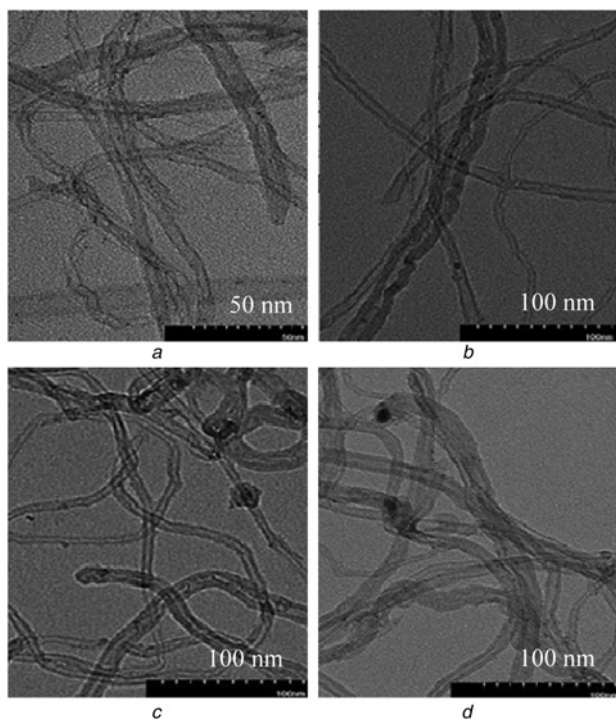| Sample	ICP-AES
1	Pt (1.15 wt%)/CNTs
2	Pt (1.20 wt%)–Fe (0.18 wt%)/CNTs
3	Pt (1.15 wt%)–Fe (0.27 wt%)/CNTs
4	Pt (1.35 wt%)–Fe (2.91 wt%)/CNTs

Figure 1 *TEM images of the Pt–Fe/CNT catalysts*
a Pt (1.15 wt%)/CNTs
b Pt (1.20 wt%)–Fe (0.18 wt%)/CNTs
c Pt (1.15 wt%)–Fe (0.27 wt%)/CNTs
d Pt (1.35 wt%)–Fe (2.91 wt%)/CNTs

Figure 2 *XRD patterns of*
a Pt (1.15 wt%)/CNTs
b Pt (1.20 wt%)–Fe (0.18 wt%)/CNTs
c Pt (1.15 wt%)–Fe (0.27 wt%)/CNTs
d Pt (1.35 wt%)–Fe (2.91 wt%)/CNTs

could co-ordinate with the carboxyl groups of potassium acid phthalate, and the π–π stacking interaction between the CNTs and potassium acid phthalate may also be existent. This results in the preferred dispersion of the metal ions on the surface of the CNTs through the cross linking effect of potassium acid phthalate. Such an interaction also makes the CNTs easily dispersible and more accessible to the aqueous solution of the metal precursor. When the KBH_4 solution is added dropwise, the metal ions dispersed on the surface of the CNTs are reduced in situ, forming monodispersed metal nanoparticles on the CNTs' surface. Pristine CNTs are used as supports for the preparation of the Pt–Fe/CNT catalysts by using potassium acid phthalate. However, it is hard to keep Pt loading as a constant because of the complicated action between the potassium acid phthalate and the pristine CNTs, and between the potassium acid phthalate and the Pt ions. Pt loading was in a reasonable range of 1.15–1.35 wt%.

Fig. 1 shows the typical TEM images of the Pt/CNTs and the Pt −Fe/CNTs. The supported metal particles are in the range of 2–5 nm and most of them are around 2 nm. They are separately dispersed on the surface of the CNTs.

Fig. 2 shows the XRD patterns of the Pt/CNTs and the Pt–Fe/CNTs. The peaks at 2θ of 26.5 and 42.4 could be assigned to the diffractions, respectively, from the (0 0 2) and the (1 0 0) planes for the CNTs. No diffraction peaks of the metallic Pt and Fe are observed. As shown in Fig. 1, the supported metal particles for the Pt–Fe/CNT catalysts with different metal loadings are all in the range of 2–5 nm and most of them are about 2 nm. They are in a microcrystalline phase because of their small size [13], therefore no significant peaks are observed in the XRD. In addition, the loadings of Pt (1.15–1.35 wt%) and Fe (0.18–2.91 wt%), respectively, are also low, which is under the detection limit of the ordinary X-ray powder diffraction [14].

3.2. Catalytic activity: As shown in Fig. 3, the Pt–Fe/CNTs show excellent activity for nitrobenzene hydrogenation at room
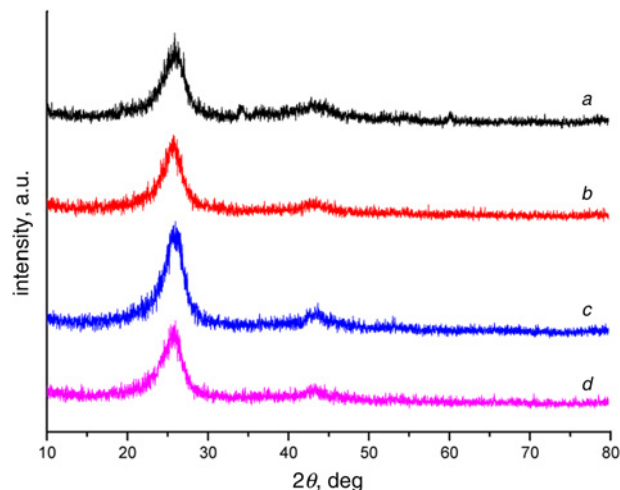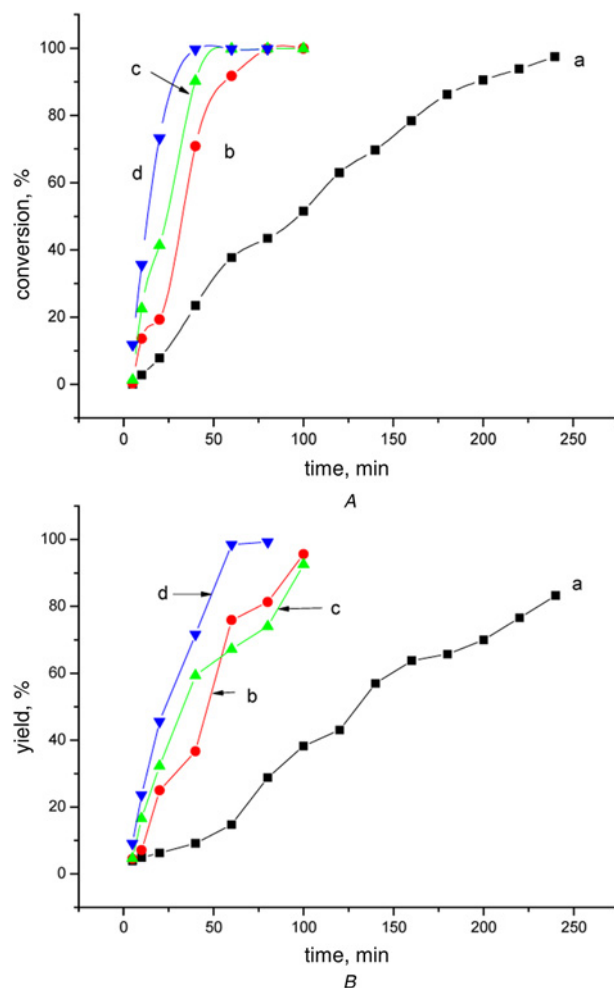

Figure 3 *Catalytic behaviours of*
A Conversion of nitrobenzene
B Yield of aniline
a Pt (1.15 wt%)/CNTs
b Pt (1.20 wt%)–Fe (0.18 wt%)/CNTs
c Pt (1.15 wt%)–Fe (0.27 wt%)/CNTs
d Pt (1.35 wt%)–Fe (2.91 wt%)/CNTs

temperature. The bimetallic Pt–Fe/CNT catalysts show a much higher activity than the Pt/CNTs with a similar Pt content for the nitrobenzene hydrogenation reaction. In addition, the activities of the bimetallic Pt–Fe/CNTs increase with the increase of Fe loading. Nitrobenzene conversion and aniline yield are both close to 100% after 80 min by the bimetallic Pt–Fe/CNT catalysts. The introduction of Fe greatly enhances the catalytic property of Pt for nitrobenzene hydrogenation.

4. Conclusion: Pt–Fe/CNT catalysts with different loadings were prepared by a chemical reduction technique. The content of Pt is in the range of 1.15–1.35 wt% and the Fe loading is 0, 0.18, 0.27 and 2.91 wt%, respectively. 2–5 nm of metal particles were dispersed on the surface of the CNTs. The bimetallic Pt–Fe/CNT catalysts showed a much higher activity than the Pt/CNTs with a similar Pt content for nitrobenzene hydrogenation. The activities of the bimetallic Pt–Fe/CNTs increased with the increase of the Fe loading. The introduction of Fe greatly improves the catalytic property of Pt for nitrobenzene hydrogenation.

6 References

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