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Fe_2O_3 nanoparticles anchored *in situ* on carbon nanotubes *via* an ethanol-thermal strategy for the selective catalytic reduction of NO with NH_3^{\dagger}

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Fe₂O₃ nanoparticles were anchored *in situ* on carbon nanotubes (CNTs) *via* an ethanol-thermal route, for the selective catalytic reduction (SCR) of NO with NH₃. The structure and surface characteristics of the obtained catalysts were measured by transmission electron microscopy, X-ray diffraction, N₂ adsorptiondesorption isotherms, Raman, X-ray photoelectron spectroscopy, H₂-temperature programmed reduction, and NH₃-temperature programmed desorption. Compared with catalysts prepared *via* impregnation or co-precipitation methods, the synthesized catalyst showed better catalytic activity and a more extensive operating-temperature window. The TEM and XRD results suggested that the iron species was uniformly anchored on the surface of the CNTs. The Raman and XPS results indicated that the catalyst has a relatively higher number of defects, a higher atomic concentration of Fe present on the surface of the CNTs and a higher content of chemisorbed oxygen species. The H₂-TPR and NH₃-TPD results demonstrated that the catalyst possesses a more powerful reducibility and stronger acid strength than the other two catalysts. Based on the above-mentioned physicochemical properties, the obtained catalyst showed an excellent performance in the SCR of NO to N₂ with NH₃. Additionally, the catalyst also presented outstanding stability, H₂O resistance and SO₂ tolerance.

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1. Introduction

Nitrogen oxides (NO_x), which arise from the combustion of fossil fuels in industrial processes, can result in environmental contamination, such as acid rain, photochemical smog and air haze.¹⁻⁴ Nowadays, certain processes have been employed to remedy these environmental problems.⁴⁻¹⁰ Among these methods, selective catalytic reduction (SCR) technology is a state-of-the-art process which, through a reductant-NH₃ selective chemical reaction with NO_x, forms the environmental products N₂ and H₂O.^{5,6} The commercial catalyst V₂O₅–WO₃ (MOO₃)/TiO₂ has been widely used for NO_x elimination.⁴⁻⁶ However, there still remain some inevitable unsolved problems, such as low N₂ selectivity at high temperatures, and the volatility and toxicity of V₂O₅.^{5,11-13} What's more, the oxidation of SO₂ to SO₃ could cause etching of the equipment and blocking of the pores of the catalyst.^{5,11,12} So it is meaningful to design and develop a suitable nonvanadium catalyst with a relatively low working temperature and a great resistance to SO₂ toxicity.^{11,14,15}

Iron oxide, as an ordinary transition metal oxide, has been widely investigated either as an active ingredient or promoter for DeNO_x catalysts, due to its inherently environmentally friendly character, its prominent thermal stability and its outstanding SO₂ resistance; for example, as Fe₂O₃,¹⁶ Fe/ZSM-5,^{11,17-22} Fe/HBEA,^{23,24} Au/Fe₂O₃,²⁵ Fe₂O₃-TiO₂,²⁶ and Fe₂O₃-CeO₂/TiO₂.²⁷ The catalytic performance and mechanism of Fe zeolites in NH₃-SCR have been systematically studied,^{11,17-24} and ferric oxides have also been applied as additive agents.^{13,14,27} However, as the application of the NH₃-SCR of NO is always downstream of the desulfurizer and electrostatic precipitator, it is still necessary to improve the low temperature activity of ferric oxide catalysts.

Recently, it was demonstrated that carbon nanotubes (CNTs) possess the feature of outstanding adsorption of ammonia, nitric oxides and other gaseous substances.^{28–31} Besides, CNTs could decompose and directly reduce NO,^{32,33} and improve the SO₂ resistance with a decrease in the decomposition temperature of sulfates and bisulfates.^{34,35} Hence, CNTs have attracted great attention for the NH₃-SCR of NO.^{36–39} It is considered that a good dispersion of active ingredients on the support could favor activity during the



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[†] Electronic supplementary information (ESI) available: TEM images of Fe₂O₃/ CNTs-IM, Fe₂O₃/CNTs-CP, Fe₂O₃/TiO₂; XRD patterns of the samples; nitrogen adsorption–desorption isotherm, H₂-TPR, NH₃-TPD profiles and NO conversion *vs.* temperature over the Fe₂O₃/TiO₂, and Raman spectrum of CNTs. See DOI: 10.1039/c4cy00789a



Scheme 1 Schematic illustration of the *in situ* synthetic process for the Fe₂O₃/CNTs-ET catalyst.

NH₃-SCR reaction,^{40,41} and thus it is significant to realize active species with a smaller size that are highly dispersed on the support. Normally, CNT-carried catalysts are synthesized by an impregnation method^{36,42} or sol–gel method.^{26,35,43,44} However, the active nanoparticles can't be uniformly dispersed on the surface of the CNTs when using these routes. Therefore, there still remains a great challenge to uniformly disperse the active species on the CNTs. Recently, we accomplished *in situ* the production of MnO_x –CeO_x nanoparticles supported on CNTs, *via* a surfactant assisted reflux route⁴¹ and a pyridine-thermal route,⁴⁵ and found that they all displayed enhanced NH₃-SCR activity and improved resistance to SO₂ and H₂O when compared with the same catalyst synthesized by an impregnation method.

Herein, we have rationally designed and prepared for the first time, highly dispersed Fe₂O₃ nanoparticles on CNTs via an ethanol-thermal route. As illustrated in Scheme 1, Fe₂O₃ nanoparticles were anchored in situ on the CNTs by an ethanol-thermal strategy. Firstly, the Fe³⁺ interacts with the hydroxyl and carboxyl groups on the surface of the pretreated CNTs due to the electrostatic effect. Secondly, the ethanol may bond with the Fe³⁺ through the strongly electronegative end to afford the Fe³⁺ electric neutrality. After the solvothermal process and calcination, the Fe₂O₃ nanoparticles were anchored in situ on the CNTs. In this synthetic process, the steric hindrance of ethanol can effectively separate each of the Fe³⁺ particles, and thus highly dispersed Fe₂O₃ nanoparticles were formed in situ on the CNTs. The obtained catalysts were systematically characterized, and their NH₃-SCR activities, stabilities, H₂O resistances and SO₂ tolerances were also investigated.

2. Experimental

2.1 Catalyst preparation

The multiwall carbon nanotubes (CNTs) were furnished by Qinhuangdao Tai Chi Ring Nano-products Co. Ltd (China). All other chemicals were purchased from the Sinopharm Chemical Regent Company and were used without any further purification. The raw CNTs were 1–10 μ m in length and 10–30 nm in diameter. The CNTs were pretreated by refluxing in dilute HNO_3 (6 mol L⁻¹) under stirring for 6 h at 120 °C, to remove metal species and impurities that existed in the surface of the raw CNTs; they were then washed with an excess of deionized water until the pH was neutral, and were dried at 100 °C in oven overnight.

In a typical synthesis, 0.23 g of pretreated CNTs, 0.03 g of iron(III) nitrate nonahydrate and 80 mL of ethanol were mixed with subsequent ultrasonic treatment at room temperature for 0.5 h. Then the mixture was poured into a stainless steel autoclave with PTFE lining (100 mL) and maintained at 120 °C for 24 h. After the autoclave was cooled to an ambient temperature, the suspension was filtered and washed, and then dried at 100 °C for 12 h. Finally, it was calcined in a N₂ stream at 450 °C for 4 h, with a heating rate of 2 °C min⁻¹. The obtained catalyst was denoted as Fe₂O₃/CNTs-ET.

For comparison, the catalysts were also separately prepared by impregnation and co-precipitation methods. In the impregnation procedure, 0.69 g of pretreated CNTs were added to a solution of iron(III) nitrate nonahydrate (0.09 g) and H₂O (80 mL) with stirring until the solution dried at 80 °C, and was then calcined in a N_2 stream at 450 °C for 4 h, with a heating rate of 2 °C min⁻¹. The catalyst synthesized by this method was denoted as Fe₂O₃/CNTs-IM. In the co-precipitation procedure, 0.23 g of pretreated CNTs, 0.03 g of iron(III) nitrate nonahydrate, 0.5 g of urea and 80 mL of H₂O were mixed in a beaker with subsequent ultrasonic treatment for 0.5 h. Then the mixture was transferred into a stainless steel autoclave with PTFE lining (100 mL) and maintained at 120 °C for 24 h. After the autoclave was cooled to room temperature, the suspension was filtered and washed with an excess of water, and then dried at 100 °C for 12 h. Finally, it was calcined in a N₂ stream at 450 °C for 4 h, with a heating rate of 2 °C min⁻¹. The obtained catalyst was denoted as Fe₂O₃/CNTs-CP. The Fe₂O₃ supported on TiO₂ was synthesized by an impregnation method with the iron content unchanged, and was denoted as Fe₂O₃/TiO₂.

2.2 Characterization

The morphologies and surface structures of the catalysts were observed using a transmission electron microscope (TEM, JEOL JEM-200CX) and a field emission high resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). The energy dispersive X-ray spectroscopy (EDS) was carried out on a TEM (JEOL JEM-2100F). Powder X-ray diffraction (XRD) was performed with a Rigaku D/MAX-2200 X-ray diffractometer, using Cu Ka (40 kV, 40 mA) radiation and a secondary beam graphite monochromater. Nitrogen adsorption-desorption isotherms of the samples were taken at 77 K using an ASAP 2020 volumetric adsorption analyzer. Before the measurements, all the samples were degassed overnight at 573 K in a vacuum line. The specific surface areas and the pore volumes of the samples were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distributions were derived from the adsorption branches of the isotherms, using the Barrett-Joyner-Halenda (BJH) model. The Raman spectra

were recorded on a spectrometer (JY H800UV) equipped with an optical microscope at room temperature. X-Ray photoelectron spectroscopy (XPS) was recorded on a Perkin-Elmer PHI-5000C ESCA system equipped with a dual X-ray source, using an Mg Ka (1253.6 eV) anode and a hemispherical energy analyzer. The background pressure during data acquisition was kept below 10⁻⁶ Pa. The XPS species of the elements in these catalysts were recorded and fitted by XPS PEAK 4.1 software, which had been calibrated against the standardized C 1s peak at 284.6 eV. Temperatureprogrammed reduction by hydrogen (H2-TPR) was obtained on a Tianjin XQ TP5080 auto-adsorption apparatus. 50 mg of the catalyst was outgassed at 300 °C under a N2 atmosphere. After cooling to room temperature under a N₂ atmosphere, the flowing gas was switched to 5% H_2/N_2 and the sample was heated to 840 °C at a heating rate of 10 °C min⁻¹. The H₂ consumption was monitored by a thermal conductivity detector (TCD). Temperature-programmed desorption experiments on ammonia (NH₃-TPD) were conducted on a Tianjin XO TP5080 auto-adsorption apparatus. Before the TPD, each sample was pretreated with high-purity (99.999%) He (35 mL min⁻¹) at 300 °C for 0.5 h, then saturated with high-purity anhydrous ammonia at 100 °C for 1 h and subsequently flushed at the same temperature for 1 h to remove physicallyadsorbed ammonium. Finally, the TPD experiment was carried out from 100 °C to 525 °C at a heating rate of 10 °C min⁻¹. The amount of NH₃ that was desorbed was monitored by a TCD.

2.3 Catalytic tests

The NH₃-selective catalytic reduction activity tests were completed in a fixed-bed quartz reactor using 0.2 g catalyst (40–60 mesh). The gas mixture was composed of 500 ppm NO, 500 ppm NH₃, 3 vol.% O₂, N₂ balance, 200 ppm SO₂ (when used) and 4 vol.% H₂O (when used). The gas hourly space velocity (GHSV) was about 18 000 h⁻¹ while the total flow rate of the feed gas was approximately 220 mL min⁻¹. The reaction temperature was from 150 °C to 400 °C. All the concentrations of the feed gas and the tail gases were detected by a KM9106 flue gas analyzer when the reaction reached 15 min.

3. Results & discussion

3.1 Characteristics of the catalysts

The microstructures of the catalysts and the size distribution of ferric oxide nanoparticles supported on the surface of the CNTs were investigated using a TEM. As shown in Fig. 1a and b, the TEM images show that $Fe_2O_3/CNTs$ -ET exhibited a homogeneous dispersion of ferric oxide nanoparticles supported on the surface of the CNTs, and that the particle size was uniform. The HRTEM image in Fig. 1c shows that the inter-planar distance was 0.23 nm, which is related to the (222) plane of Fe_2O_3 . Fig. 1d presents the EDS spectrum of $Fe_2O_3/CNTs$ which confirms the presence of iron elements, suggesting that the Fe species are supported on the



Fig. 1 (a, b) TEM images of $Fe_2O_3/CNTs$ -ET; (c) HRTEM image of $Fe_2O_3/CNTs$ -ET; (d) EDS spectrum of $Fe_2O_3/CNTs$ -ET; (inset) size distribution of ferric oxide nanoparticles of $Fe_2O_3/CNTs$ -ET.

surface of the CNTs. As can be seen in the Fig. 1 inset, it was observed that the sizes of the ferric oxide nanoparticles on the CNTs were in the range of 2.5–8.0 nm and that the average size of the nanoparticles was 4.8 nm. However, for $Fe_2O_3/CNTs$ -IM, the particles aggregated to some extent (Fig. S1a, ESI[†]); and for $Fe_2O_3/CNTs$ -CP and Fe_2O_3/TiO_2 , Fe_2O_3 nanoparticles displayed a distinct agglomeration (Fig. S1b and c, ESI[†]). This indicates that the active components are uniformly anchored on the surface of the CNTs by the ethanol-thermal method. Moreover, for Fe_2O_3/CNT -ET, the XRD peaks assigned to Fe_2O_3 were negligible, which suggests a good dispersion of Fe species (Fig. S2, ESI[†]). It was confirmed that the Fe_2O_3 nanoparticles can be highly dispersed on CNTs by the ethanol-thermal method.

The specific surface areas, pore volumes and pore sizes of the catalysts were analyzed using N_2 adsorption-desorption isotherms. As displayed in Fig. 2, the Fe₂O₃ nanoparticles



Fig. 2 N_2 adsorption–desorption isotherms of $Fe_2O_3/CNTs\text{-}ET,$ $Fe_2O_3/CNTs\text{-}IM$ and $Fe_2O_3/CNTs\text{-}CP.$

supported on CNTs by three different methods imply the IV isotherm with the relative pressure $P/P_o = 0.15$, indicating the existence of a mesoporous structure, and Fe₂O₃/TiO₂ also presents a mesoporous structure due to the stack of particles (Fig. S3, ESI[†]). In addition, the specific surface areas, pore volumes and pore sizes of the catalysts are summarized in Table 1. As shown directly in Table 1, there is no obvious difference between the three catalysts. Moreover, the BET surface area of the Fe₂O₃/CNTs catalyst was about 145 m² g⁻¹, which is higher than that of Fe₂O₃/TiO₂.

Raman spectroscopy is a powerful tool in probing the lattice vibrational states and dynamics of CNTs, under the variation of the layer number with respect to the CNT surface plane.⁴⁶⁻⁴⁹ The Raman spectra of Fe₂O₃/CNTs prepared by the three routes are displayed in Fig. 3. The G-band, at around 1580 cm⁻¹, is associated with an E_{2g} mode of graphite and is related to the vibration of sp² bonded carbon atoms in a 2-dimensional hexagonal lattice. The D-band, centred around 1360 cm⁻¹, corresponds to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite or glassy carbon.^{50–52} The I_D/I_G (the ratio of the intensities of the D and G bands) values over $Fe_2O_3/$ CNTs-ET, Fe₂O₃/CNTs-IM, Fe₂O₃/CNTs-CP and CNTs were around 1.02, 0.99, 0.89 and 0.81 (Fig. 3 and S4, ESI⁺), respectively. Compared with the value of I_D/I_G over CNTs, the value over Fe₂O₃/CNTs-ET is larger than the others, which suggest that more defects were created by introducing the active species.⁵² Furthermore, the increased ratio of I_D/I_G indicates an increase of surface defects in the Fe₂O₃/CNTs-ET,⁵³ which should be favorable to the NH₃-SCR of NO. The Raman results of Fe₂O₃/CNTs and CNTs demonstrate that the structure of multi-wall CNTs can be retained after being loaded with Fe₂O₃ nanoparticles.⁵⁰

In order to acquire information on the atomic concentrations and element chemical states of each catalyst's surface, the XPS spectra of the Fe 2p and O 1s in these catalysts were recorded. Fig. 4A shows the Fe peaks assigned to Fe species (Fe $2p_{3/2}$ and Fe $2p_{1/2}$). The Fe peaks of Fe₂O₃/CNTs were assigned to oxidized Fe species, most likely Fe³⁺ type species.^{13,54} The binding energies centered at about 709.8 eV and 711.2 eV may be assigned to Fe³⁺ in the spinel structure, and the binding energy centered at about 712.4 eV may be ascribed to Fe³⁺ bonded with a hydroxyl group.⁵⁵ It is interesting that the surface atomic concentration of Fe over Fe₂O₃/CNTs-ET is higher than those of Fe₂O₃/CNTs-IM and Fe₂O₃/CNTs-CP, as shown in Table 2. It has been demonstrated that accessible Fe³⁺ can participate in the reversible redox cycle, which is beneficial for SCR activity.¹³ Based on



Fig. 3 Raman spectra of $Fe_2O_3/CNTs\text{-}ET,\ Fe_2O_3/CNTs\text{-}IM$ and $Fe_2O_3/CNTs\text{-}CP.$

the above results, it is reasonable that $Fe_2O_3/CNTs$ -ET could display the best capacity for NH_3 -SCR performance among the three catalysts.

The XPS spectra of O 1s for the three catalysts are presented in Fig. 4B. All three catalysts show two overlapping peaks of the O 1s. The overlapping peaks of O 1s at a binding energy of 529.8 eV could be assigned to lattice oxygen (donated as O_{β}), and the overlapping peaks of O 1s at binding energies of about 531.7 eV could attributed to chemisorbed oxygen (donated as O_{α}), which could belong to defect oxide or hydroxyl-like groups.^{27,56-58} Table 2 summarizes the binding energies of O 1s and the atomic ratios of $O_{\alpha}/(O_{\alpha} + O_{\beta})$ for the three catalysts. As seen clearly in Fig. 4B and Table 2, Fe₂O₃/CNTs-ET had a higher ratio of $O_{\alpha}/(O_{\alpha} + O_{\beta})$ than Fe₂O₃/CNTs-IM and Fe₂O₃/CNTs-CP, mainly on account of the increase in chemisorbed oxygen species on the catalyst surface by the iron species.²⁷ The surface chemisorbed oxygen O_{α} has been reported to be the most active oxygen, and is highly active in the oxidation reaction due to its higher mobility. Besides, the high relative concentration ratio of $O_{\alpha}/(O_{\alpha}+O_{\beta})$ on the surface of the catalyst could be correlated with the high NH₃-SCR activity.⁵⁹ The loading of Fe₂O₃ nanoparticles on the CNTs by the ethanol-thermal route could create more vacancies on the catalyst surface, and lead to the increase of chemisorbed oxygen on the surface. It is reported that the NO₂ would enhance the NH₃-SCR reaction by participating in the "fast SCR" reaction route on the catalysts.¹⁵ It has been demonstrated that the chemisorbed oxygen plays an important role in oxidation reactions.⁵⁹ Therefore, the O_{α}

Table 1 BET surface areas and pore characterization of catalysts						
	Fe ₂ O ₃ /CNTs-ET	Fe ₂ O ₃ /CNTs-IM	Fe ₂ O ₃ /CNTs-CP	Fe ₂ O ₃ /TiO ₂		
BET surface area $(m^2 g^{-1})$	147	144	146	55		
Pore volume $(cm^3 g^{-1})$	0.41	0.48	0.43	0.33		
Pore size (Å)	95	110	101	199		



Fig. 4 (A) Fe 2p spectra and (B) O 1s spectra of the catalysts: (a) Fe₂O₃/CNTs-ET, (b) Fe₂O₃/CNTs-IM and (c) Fe₂O₃/CNTs-CP.

plays a crucial role in the NH₃-selective catalytic reduction process for promoting the oxidation of NO to NO₂.⁶⁰ Thus, the Fe₂O₃/CNTs-ET, which possess the highest O_{α} content, could be beneficial for improving the low-temperature NH₃-SCR catalytic activity, as expected.

 H_2 -TPR measurements were extensively performed to investigate the reducibility of the iron species in the different catalysts. Fig. 5 presents the H_2 -TPR profiles of the different samples. In the temperature range 100–840 °C, all three catalysts presented three distinct H_2 consumption peaks, which were assigned to the three-stepwise reduction of Fe₂O₃ → Fe₃O₄, Fe₃O₄ → FeO, and FeO → Fe.²⁵ For Fe₂O₃/TiO₂, the H_2 -TPR profile showed the sequential reduction of Fe₂O₃ to Fe (Fig. S5a, ESI†). Comparing the Fe₂O₃/CNTs made by each method, the corresponding reduction peaks of Fe₂O₃/CNTs-ET shifted to a relatively low temperature. It should be pointed out that the area of the reduction peak has a direct relationship with the consumed content of H_2 . It



Fig. 5 H₂-TPR profiles of the catalysts: (a) $Fe_2O_3/CNTs$ -ET, (b) $Fe_2O_3/CNTs$ -IM and (c) $Fe_2O_3/CNTs$ -CP.

can be seen clearly that the area of the reduction peak over $Fe_2O_3/CNTs$ -ET is the largest among the three catalysts. The H_2 consumption values of all the three $Fe_2O_3/CNTs$ are given in Table 3. As shown in Table 3, $Fe_2O_3/CNTs$ -ET exhibited the largest H_2 consumption among the three catalysts. In addition, the content of the reductive species was related to the degree of dispersion, which suggests that Fe_2O_3 nanoparticles were highly dispersed on the CNTs by the ethanol-thermal method. Thus, the $Fe_2O_3/CNTs$ -ET can offer more active species, which is in accordance with the XPS results. Since more reductive species could enhance the NH₃-SCR reaction, the $Fe_2O_3/CNTs$ synthesized by the ethanol-thermal route expose more reductive species, which should be beneficial to low-temperature NH₃-SCR performance.

The NH₃-TPD technique has been extensively used to characterize the adsorption of ammonia on the surface active sites of catalysts, which plays a significant role in the NH₃-SCR reaction. To investigate the surface acid amount and strength of the catalysts, NH3-TPD was performed. Fig. 6 shows the temperature-programmed desorption after ammonia adsorption over the three catalysts. It is clear that all three catalysts present three desorption peaks at desorption temperatures in the range 100-525 °C. The peaks around 150-160 °C were caused by the desorption of weak acid sites; the peaks around 200-220 °C were caused by the medium acid sites; and the peaks around 390-420 °C were caused by the strong acid sites.³⁵ It is generally accepted that Lewis acids attributed to coordinated NH3 molecules are more thermally stable than Brønsted acid sites attributed to NH₄⁺, so it can be inferred that the desorption peak at a low temperature

Table 2	The binding	energies a	and surfa	ice atomic	concentrations	of the	catalysts
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Catalysts	Surface atomic concentration/%			Binding energy/eV		The relative concentration ratios/%	
	С	Fe	0	O_{β}	Οα	$O_{\beta}/(O_{\alpha} + O_{\beta})$	$O_{\alpha}/(O_{\alpha} + O_{\beta})$
Fe ₂ O ₃ /CNTs-ET	92.93	0.43	7.64	529.8	531.7	34.45	65.55
Fe ₂ O ₃ /CNTs-IM	92.01	0.42	7.57	529.8	531.7	42.41	57.59
Fe ₂ O ₃ /CNTs-CP	92.19	0.23	7.59	529.8	531.7	47.81	52.19

$\label{eq: Table 3} \quad H_2 \ consumptions \ of \ the \ catalysts$

	Catalysts				
	Fe ₂ O ₃ /CNTs-ET	Fe ₂ O ₃ /CNTs-IM	Fe ₂ O ₃ /CNTs-CP		
Consumed hydrogen (mmol g^{-1})	0.072	0.056	0.034		



Fig. 6 NH₃-TPD profiles of the catalysts: (a) $Fe_2O_3/CNTs$ -ET, (b) $Fe_2O_3/CNTs$ -IM and (c) $Fe_2O_3/CNTs$ -CP.



It is clear that the amounts of adsorbed NH_3 for $Fe_2O_3/$ CNTs-ET and Fe₂O₃/CNTs-IM are greater than that of Fe₂O₃/ CNTs-CP. However, it is notable that Fe₂O₃/CNTs-ET shows a higher amount of Lewis acid sites than the other two Fe₂O₃/ CNTs catalysts. For Fe₂O₃/TiO₂, the intensity of the desorption peaks for adsorbed NH₃ is very weak and mainly concentrates at low temperature (Fig. S5b, ESI[†]). It has been demonstrated that the CNTs themselves present both weak acid sites and strong acid sites as a catalyst support.^{28,29} Additionally, the results of the NH₃-TPD imply that the synthesis route has a crucial effect on the amount of acidic sites on the catalysts. As has been reported, the highly dispersed active species on the support could offer a large number of acidic sites and result in the best catalytic activity.²⁸ Therefore, the greater amount of the strongest acid sites over Fe₂O₃/CNTs-ET could be attributed to the highly dispersed Fe₂O₃ nanoparticles and the CNTs themselves.

3.2 Catalytic performance

Fig. 7 shows the NO conversion curves of the catalysts with reaction temperatures ranging from $150 \text{ }^{\circ}\text{C}$ to $400 \text{ }^{\circ}\text{C}$. It can clearly be observed that the reaction temperature has a



Fig. 7 NO conversion vs. temperature over the catalysts. Reaction conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] = 3$ vol.%, N₂ balance, and GHSV = 18 000 h⁻¹.

remarkable influence on the NO reduction efficiency over different catalysts. A negligible NO reduction efficiency was noticed for Fe₂O₃/CNTs-CP until the temperature reached 400 °C, whereas highly dispersed Fe₂O₃ nanoparticles on CNTs fabricated by the ethanol-thermal route displayed a favorable NH₃-SCR performance. The light-off temperature (at which the conversion of NO reaches 50%, T_{50}) of Fe₂O₃/CNTs-ET was 220 °C, and 96% NO conversion was achieved at 320 °C. The Fe₂O₃/CNTs-ET showed the best low-temperature NO conversion among the three catalysts and displayed excellent NH₃-SCR activity over a broad temperature window, varying from 250 °C to 400 °C, with NO conversions of more than 80%. It was noted that the Fe₂O₃/CNTs-ET also showed a better performance at low temperatures than Fe₂O₃/TiO₂ (Fig. S6, ESI[†]). The differences between the three catalysts could be due to the different physical chemical characterizations of them. The results of the TEM characterization and XRD demonstrated that the Fe₂O₃ nanoparticles were uniformly anchored on the surface of the CNTs for Fe₂O₃/ CNTs-ET, which could be beneficial for outstanding NH₃-SCR activity. Based on the results of the Raman spectroscopy and XPS for Fe₂O₃/CNTs-ET, it is clear that more defect Fe atoms exist on the catalyst surface, which indicates that more active sites are provided for the SCR reaction. Additionally, the high content of chemisorbed oxygen would enhance the lowtemperature NH₃-SCR reduction activity by accelerating the oxidation of NO to NO2 during the "fast SCR" reaction. The results of the H₂-TPR indicated that the reducibility of Fe₂O₃/ CNTs-ET was the strongest among the three catalysts, which

could promote the NH_3 -SCR reaction. Therefore, the robust interactions between ferric oxide and CNTs could cause the improvement in the NH_3 -SCR activity of Fe₂O₃/CNTs-ET.

Assessing the change in catalytic activity with different times on stream is a significant way to estimate catalysts' properties. Fig. 8A displays the catalytic activity of the different catalysts with different times on stream at 320 °C. All the catalysts remained unchanged and kept their highest conversion values during the whole test period, and Fe₂O₃/CNTs-ET showed the highest activity. It was noted that oxidation of the carbon nanotubes didn't occur at this temperature during the SCR process, which has also been confirmed in our previous work.^{41,61} As is well-known, some residual H₂O and SO₂ still exist in the exhaust gas after the desulphurization process, which can poison and devitalize the catalysts for the NH₃-SCR reaction.³ Thus, it is worth noting the NO conversions of the catalysts in the presence of H₂O and SO₂. The influence of H₂O on the NH₃-SCR activity of the Fe₂O₃ supported on CNTs by the three different methods, as a function of time at 320 °C, was investigated, as shown in Fig. 8B. When introducing 4 vol.% H₂O to the feed gas, the NO conversion of all catalysts remained unchanged during the whole test period whether or not H2O was present. It was confirmed that the competitive adsorption between H₂O and NH₃ on

the active sites of the catalyst surface could lead to the inhibition of the H₂O. This combined with the NH₃-TPD results (Fig. 6) suggests that the Fe₂O₃/CNTs-ET could preferentially adsorb NH₃ rather than H₂O in the feed gas, using the total amount of acid sites over Fe2O3/CNTs-ET, leading to an excellent H₂O resistance ability.¹⁶ The above results suggest that Fe₂O₃/CNTs-ET could be an appropriate candidate for H₂O resistance. Fig. 8C shows the effect of SO₂ on the NO conversion of the catalysts at the typical temperature of 320 °C. The total flow rate of the feed gas was 220 mL min⁻¹. As shown in Fig. 8C, the NO conversion of Fe₂O₃/CNTs-ET was 97% in the absence of SO₂, which decreased to 91% when SO₂ (200 ppm) was introduced to the feed gas. With the continual addition of 200 ppm SO₂, the NO conversion of the Fe₂O₃/CNTs-ET remained stable. In contrast, the addition of SO₂ to the reaction conditions induced a significant decrease in the NO conversion of the Fe₂O₃/CNTs-IM and Fe₂O₃/CNTs-CP, by 22% and 30% respectively. After cutting off the SO₂ supply to the feed gas, the NO conversion of Fe₂O₃/CNTs-ET was restored to 92% without any fluctuations during the test periods. However, for Fe₂O₃/CNTs-IM and Fe₂O₃/CNTs-CP, once the SO₂ stream was stopped, NO conversion was restored to a certain extent, and finally returned to 77% and 46%, respectively. The above results indicate that the Fe₂O₃/CNTs-ET



Fig. 8 (A) NO conversion vs. time on stream for the catalysts; (B) NO conversion vs. time on stream for the catalysts in the presence of H_2O ; (C) NO conversion vs. time on stream for the catalysts in the presence of SO₂; (D) NO conversion vs. time on stream for the catalysts in the presence of both H_2O and SO₂. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 3 vol.%, [SO₂] = 200 ppm (when used), [H₂O] = 4 vol.% (when used), N₂ balance, *T* = 320 °C and GHSV = 18 000 h⁻¹.

shows the best resistance to SO₂ among the three catalysts. It is well known that the SO₂ stream can poison and deactivate the catalyst with the formation and deposition of sulfates and bisulfates on the surface of the catalyst in NH₃-SCR reduction.^{34,35} At the same time, NH₃ reacts with SO₂ instead of reacting with NO, which could decrease the reaction between NH₃ and NO. Compared with Fe₂O₃/CNTs-IM and Fe₂O₃/CNTs-CP, Fe₂O₃/CNTs-ET presents a better resistance to SO₂. The results of NH₃-SCR activity under the reaction conditions in the presence of both H₂O and SO₂ over the catalysts were also investigated, as shown in Fig. 8D. As could clearly be seen, the activity of Fe₂O₃/CNTs-ET only decreased by about 6% after introducing 4 vol.% H₂O and 200 ppm SO₂ together, but the volume raised to 92% when the mixture of H₂O and SO₂ was eliminated. In contrast, the NO conversions of Fe₂O₃/CNTs-IM and Fe₂O₃/CNTs-CP radically decreased, by 18% and 26%, respectively, in the mixture of 4 vol.% H₂O and 200 ppm SO₂; they then recovered to 75% and 57%, respectively, once the H₂O and SO₂ were cut off. The above results show that Fe₂O₃/CNTs-ET possesses a good capacity for resistance to water and sulfur dioxide.

4. Conclusions

In summary, Fe_2O_3 nanoparticles anchored on CNTs were prepared *in situ*, *via* an ethanol-thermal route, for the selective catalytic reduction of NO with NH₃. Fe_2O_3/CNT -ET presented a better NH₃-SCR performance, higher H₂O-resistance and greater SO₂ tolerance than the catalysts synthesized by impregnation or co-precipitation routes. Additionally, it presented a better NH₃-SCR activity than Fe_2O_3/TiO_2 . The outstanding NH₃-SCR activity of the Fe_2O_3/CNT -ET could be attributed to the high dispersion of Fe_2O_3 nanoparticles on the CNTs, the greatest amount of defects on the surface, the robust reducibility, the stronger acid strength and the larger amount of chemisorbed oxygen. According to these excellent properties, the Fe_2O_3/CNT -ET catalyst might be a promising candidate for the NH₃-SCR of NO with NH₃.

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