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Granulated Carbon Nanotubes as the Catalyst Support for Pt for the Hydrogenation of Nitrobenzene

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Granulated Pt/carbon nanotubes (CNTs) were found to have a much better catalytic activity in the liquid phase hydrogenation of nitrobenzene than Pt/activated carbon (AC). The granulated CNTs had much larger pores than the AC particles, which gave a faster mass transfer rate of H_2 that helped produce aniline with high selectivity.

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Numerous works have indicated the potential application of carbon nanotubes (CNTs) as catalysts or catalyst supports in heterogeneous catalytic processes.[1–8] In these studies,[1–8] the CNTs were used in a loosely packed or mono-dispersed state because the aim was to evaluate the intrinsic activity of the catalyst. In an industrial application however, there is a need to granulate the CNTs into the 10 μm to mm scale to avoid catalyst carry over by the fluid flow and the tedious filtration of nanosized powders. Compared with mono-dispersed or loosely packed particles, the granulated large powders often have the problem of mass transfer limitation for the diffusion of reactants and products in their pores.[9] This effect however, has been rarely studied.

In the present work, we used a liquid-induced densification method to make granulated Pt/CNT particles.[10,11] The catalytic activity of the granulated Pt/CNT catalyst was compared with that of Pt/active carbon (AC) particles using the liquid phase hydrogenation of nitrobenzene (NB). This is a reference reaction that is often used to evaluate the performance of hydrogenation catalysts.[12–15] The granulated Pt/CNT catalyst, as compared with the Pt/AC catalyst, exhibited a higher activity in the conversion of NB and a higher selectivity to aniline (AN). Gas chromatography-mass spectrometry (GC-MS) characterization showed the presence of many intermediates with larger molecular sizes than aniline in the hydrogenation reaction on the Pt/AC catalyst. Nitrogen adsorption characterization confirmed that the two catalysts had significantly different pore structures. The large pores (50–100 nm) of the CNT particles gave a faster mass transfer rate of H_2 in the stepwise hydrogenation of NB, as compared with the AC particles with pores of 2–3 nm. These results suggested a promising commercial application of the CNT supported catalyst.

The pristine CNTs (P-CNTs) used were mostly longer than 30 μm. They tended to form loosely packed agglomerates with a density of only 200–300 $\mathrm{kg\,m^{-3}}$ (Fig. 1a).[16,17] HNO_3 oxidization was performed to shorten the CNTs to only several μm.[2–6,18] The Pt particles dispersed well on the oxidized CNT (O-CNT) wall and were mostly smaller than 2 nm (Fig. 1b), which was a similar size to the Pt particles deposited on the AC support. The liquid-induced densification method made the Pt/CNTs (these CNTs were the same as the O-CNTs) into cubic or irregular particles 1–20 nm in size (Fig. 1c) with a bulk density of 1300 $\mathrm{kg\,m^{-3}}$. These granulated Pt/CNTs had a similar morphology to Pt/AC (Fig. 1d) and remained unchanged after the liquid hydrogenation of NB, which was carried out under a condition with continuous (4–6 h) stirring (Fig. 1e). Scanning electron microscopy (SEM) images indicated that the relatively short CNTs interacted tightly inside the Pt/CNT powder (Fig. 1f), and suggested that these CNTs could not be easily broken again once they had been granulated by the liquid induced densification, which can be seen to be an irreversible process.[10,11] Such a stable structure can be used in applications for extended reaction times.

The Pt/CNT catalyst (granulated) gave a higher activity in the conversion of NB to AN than Pt/AC catalyst (Fig. 2a). The biggest difference in the conversion of NB over the latter two catalysts was 20% from 70 to 90 min. Moreover, the Pt/CNT catalyst gave a much higher selectivity to AN than the Pt/AC catalyst (Fig. 2b). The selectivity to AN over Pt/CNT was higher than 80% initially and reached 100% after 120 min. But selectivity was only 50–60% even after 200 min over Pt/AC. These observations demonstrated the excellent catalytic performance of granulated Pt/CNTs. Of course, if compared with the monodispersed Pt/CNT catalyst, the granulated one shows slightly lower activity and low selectivity.

The Haber mechanism (Fig. 3a) suggested that the stepwise hydrogenation needed 3 mol of H_2 to convert 1 mol of NB to 1 mol of AN.[19] The main intermediate is nitrosobenzene (with an NO group) (NSB). An insufficient supply of H_2 would result in the interaction of NSB with other intermediates or AN to produce many by-products, including azobenzene (with an N=N group) (AZB). GC-MS characterization indicated that the major

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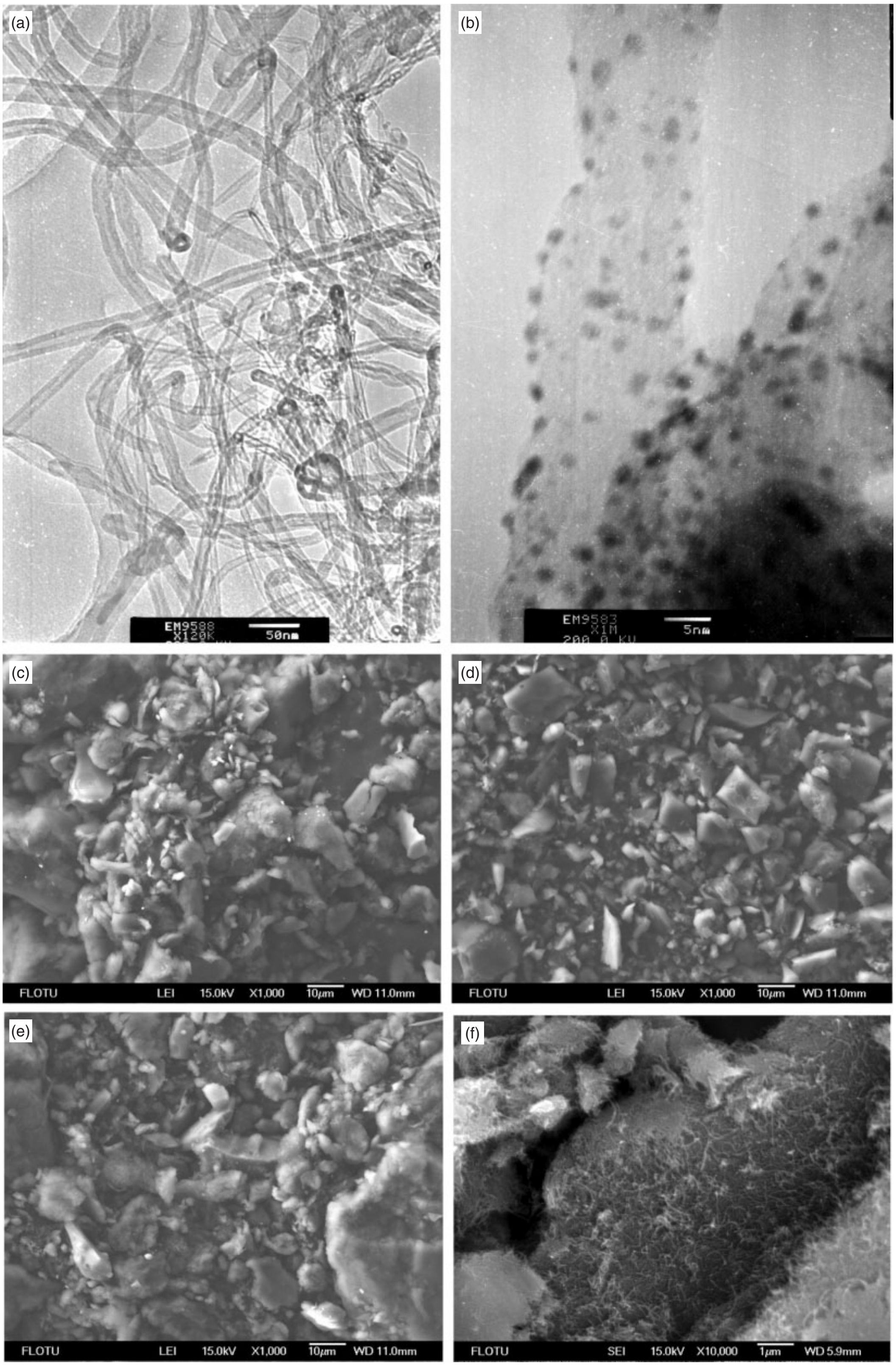

Fig. 1. TEM and SEM images of the supports and catalysts. (a) P-CNTs, (b) Pt NPs on the 2.5% Pt/CNTs, (c) ∼2.5% Pt/CNT particles (fresh), (d) 2.5% Pt/AC particles (fresh), (e) 2.5% Pt/CNT particles after reaction, (f) short CNTs in the 2.5% Pt/CNT particles after reaction.

by-products were NSB and AZB in the present work. They were always found in the hydrogenation reaction over the Pt/AC catalysts (Fig. 3b). When the NB was nearly 100% converted after 200 min, the solution contained 60% AN, 30% NSB, and 10% AZB. A similar result was observed with the use of a 5% Pt/AC catalyst (data not shown here), which suggested that the presence of NSB and AZB was independent of the Pt loading. In comparison, the concentrations of NSB and AZB were both near zero

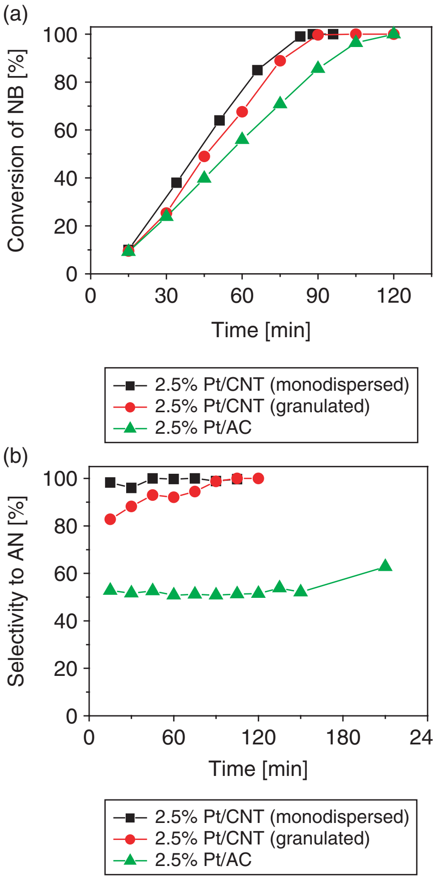

Fig. 2. (a) Conversion of NB versus time over the different Pt catalysts. (b) Selectivity to AN versus time over the different Pt catalysts.

in the entire hydrogenation process over the Pt/CNT catalysts (Fig. 3c). Since the Pt loading, Pt dispersion state and functional groups (including –COOH, –OH and –C=O) on the catalyst support were all the same, these activity and selectivity differences should be attributed to the different structures of the different carbon supports. In blank hydrogenation experiments at 30°C, performed by directly using AC and O-CNT particles that had some functional groups but without Pt loading, no detectable activity was found by GC for both supports. This observation excludes the contribution of the pure carbon supports or the functional groups on them as a reason for the difference in catalytic activity, as in other catalytic systems.[5] Thus, the structural difference of the carbon supports was responsible for the different catalytic performances.

Subsequently, the pore structures of the many carbon materials, including AC, P-CNTs, the compressed P-CNTs at 31 MPa, and O-CNTs produced by different oxidative methods, were investigated by N_2 adsorption characterization for a better understanding of the catalytic activity (Fig. 3d). The dominant pores of the P-CNTs were 0.1 μm–0.1 mm in diameter, in agreement with its very low bulk density and loosely packed state shown in Fig. 1a.[16,17] The compression of dry P-CNTs at 31 MPa significantly decreased the fraction of these large pores. However, because P-CNTs had a high mechanical strength and were not easily compressed,[17] the final fraction of these large pores in compressed P-CNTs was still much higher than that of O-CNTs and AC. In comparison, the short O-CNTs had a tendency to form densely packed particles that had dominant pores of 50–100 nm in diameter. A stronger acid oxidation (by the use of HNO_3-H_2SO_4) than HNO_3 oxidation did not decrease these pores significantly, which suggested that these pores were formed by the liquid phase densification and could be considered as the specific pores of the granulated powders that were independent of the oxidative method. However, the Pt/AC catalysts had

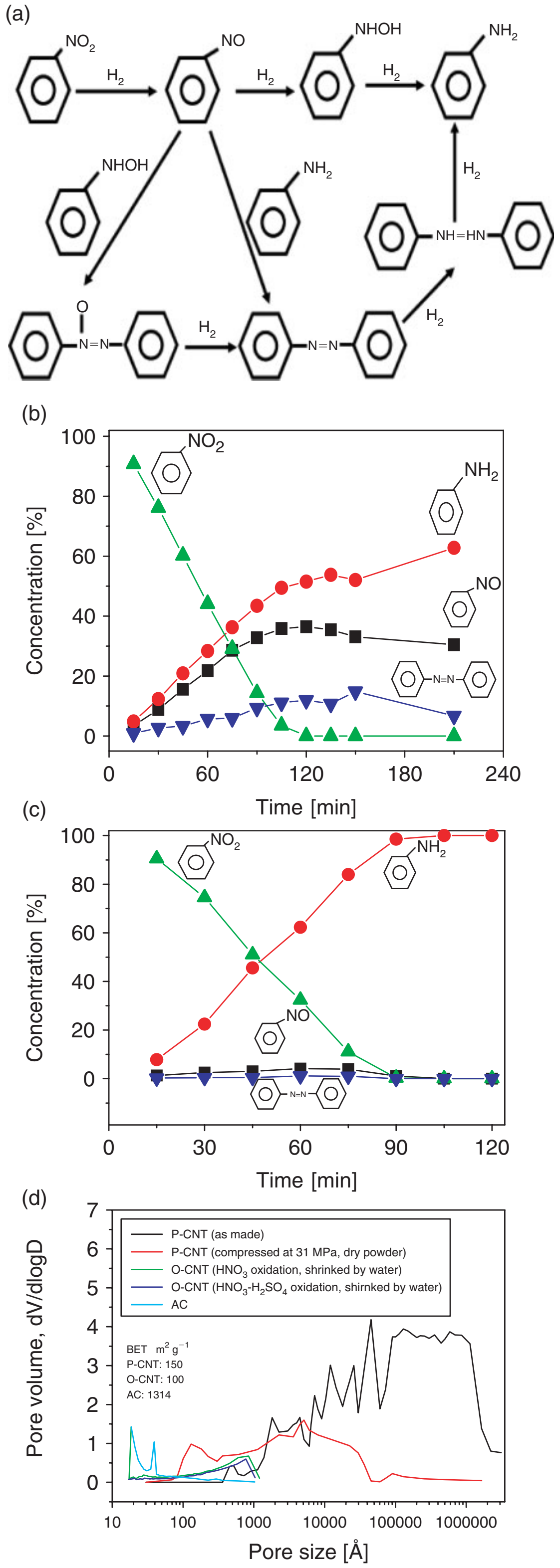

Fig. 3. (a) The Haber mechanism for the hydrogenation of NB to AN. (b) Evolution of intermediate products over the 2.5% Pt/AC catalyst. (c) Evolution of intermediate products over the 2.5% Pt/CNT catalyst. (d) Pore size distribution of the different carbon supports.

small pores of 2–3 nm in large amounts, consistent with its high specific surface area (1314 $m^2 g^{-1}$). The lack of large pores (> several 10 nm or even larger) in the AC support probably hindered the mass transfer of H_2 inside the Pt/AC catalyst, and would be responsible for the low selectivity of AN and the relatively low conversion of NB. From comparing the differences between the conversion of NB and the selectivity of AN over the two catalysts, the transfer of one H_2 molecular to convert NB into NSB would be relatively easy but the further conversion of NSB would be difficult because of the rapid consumption of H_2 inside the Pt/AC particles. Thus, this also gave an explanation for why a high pressure operation was often used in an industrial scale process using a Pt/AC catalyst (to increase the mass transfer rate of hydrogen in the inner pores of the AC).

The large amounts of AZB found, but undetectable amounts of azoxylbenzene (with N(O)=N group) and phenylhydroxylamine (with NHOH group) (PHA) suggested that AZB was mainly produced by the reaction of NSB with AN, and not with PHA and the subsequent hydrogenation. Thus, it can be deduced that PHA, once produced, can be quickly converted into AN. Because PHA has a larger molecular size than AN but is smaller than AZB, the above results suggested that the mass transfer rate of the smaller molecule was sufficient for further reaction inside the catalyst. From this point of view, because H_2 has the smallest molecular size, a reason why it was present in insufficient amounts in the small pores of the Pt/AC catalyst was also because there was a mass transfer barrier from the bulk gas phase to the bulk liquid phase and then to the liquid phase inside the catalyst. In contrast, H_2 easily diffused into the large pores (50–100 nm) of the Pt/CNT particles where the liquid phase inside the catalyst was nearly the same as in the bulk liquid phase. Such tendency is more significant as using the mono-dispersed Pt/CNT catalyst considering the CNTs dispersed well in the bulk liquid phase. Thus, the hydrogenation of NB would follow the most favourable route to first produce NSB, then PHA, and finally AN. In addition, the sufficient supply of H_2 also favoured the simultaneous hydrogenation of any intermediate that existed (Fig. 3c). The advantages of the structure of the CNT particles may be general for any gas-liquid-solid heterogeneous catalytic processes and this would imply many promising commercial applications.

In summary, we have shown that granulated CNTs as the support of Pt catalysts are advantageous over a conventional AC support in the hydrogenation of NB. The large pores of the granulated CNTs give the advantage of a faster mass transfer rate for the reactants to enhance the conversion of NB into AN with high selectivity.

Experimental

P-CNTs[16,17] were first oxidized by 70% HNO_3 under reflux at 105°C for 3 h. After cooling to ambient conditions, the O-CNTs were filtered, washed with distilled water to pH 7, then dispersed into the $HPtCl_6$ solution. After sufficient impregnation, the catalyst precursor was filtered and dried at 110°C. The van der Waals forces produced on liquid evaporation[10,11] made the tubes shrink to a small and rigid cake with a bulk density of 1300 $kg\,m^{-3}$. Finally, the dried cake was crushed into small particles of 10–20 μm size. The Pt/AC catalyst was prepared following the same procedure as above. The acid group amounts on the different carbon supports were measured by the acid-base titration method.[20] Thus, we selected an AC support with nearly the same acid group amount as that of the O-CNTs, which would exclude the potential effect of functional groups on the hydrogenation catalysis if this existed. Generally, the acid group amount of AC and O-CNT was ~1.2 $mL\,g^{-1}$. The mechanical strength of the granulated Pt/CNT catalyst, measured by a crushing machine, was much higher than that of Pt/AC and was comparable to that of alumina powder.

Catalyst (0.05 g) was added into a 100 mL quartz flask and flushed with N_2 for 20 min, then H_2 for 10 min to remove air. The catalyst was calcined and reduced by H_2 at 350°C for 2 h. After cooling to ambient conditions, 50 mL ethanol containing 1% NB was added and H_2 was introduced for the hydrogenation at 30°C and 1 atm, with continuous stirring. Liquid samples were analyzed by GC-MS (Agilent 6890).

The catalysts were characterized by SEM (JSF7401F, 3–10 kV). The pore structures of the different carbon supports were characterized by a nitrogen adsorption instrument (ASAP2010, BET).

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