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Unique reactivity in Pt/CNT catalyzed hydrolytic dehydrogenation of ammonia borane⁺

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We demonstrate an unprecedented H_2 generation activity in the hydrolytic dehydrogenation of ammonia borane over acid oxidation- and subsequent high temperature-treated CNT immobilized Pt nanocatalysts to combine the merits of defect-rich and oxygen group-deficient surfaces and unique textural properties of supports as well as optimum particle size of Pt.

Hydrogen is an ideal energy carrier for a long-term solution to current energy problems owing to its high energy-efficiency and non-polluting nature, and its safe and efficient storage is of great significance to fulfill the goal of hydrogen-powered transport systems.¹ With a high hydrogen capacity of 19.6 wt%, good stability and being non-toxic, ammonia borane (AB, NH₃BH₃) has recently attracted considerable attention as a hydrogen reservoir.² Typically, the hydrogen stored in AB can be released by thermal dehydrogenation and hydrolysis. Compared to the thermal dehydrogenation, the hydrolysis, proceeding by means of NH₃BH₃ + 2H₂O \rightarrow NH₄⁺ + BO₂⁻ + 3H₂↑, is more attractive because of the mild reaction conditions and high H₂ selectivity.^{3–5} Various catalysts have been tested for AB hydrolysis, among which Pt exhibits the highest activity.^{2,3}

Taking into account the practical applications of this system, many efforts have been made to reduce the cost of supported Pt catalysts and achieve high Pt utilization by preparing Pt-based alloy and core–shell nanoparticles (NPs) as well as highly dispersed Pt NPs.^{3,6–11} Compared with oxide supports, carbon supports have the controllable arrangement of the carbon atoms in terms of primary and secondary structures, and exhibit unique and tunable surface chemistry (*e.g.*, defects and oxygen groups) and textural properties (*e.g.*, pore structures and curvature of graphene sheets), which opens up an unprecedented opportunity to tailor the properties (*e.g.*, electronic properties and metal particle size) of supported metal NPs.^{12–14} An attempt is therefore necessary to clarify the nature of the relationship between the surface chemistry and textural properties of carbon supports, Pt particle size and H_2 generation activities in AB hydrolysis over supported Pt nanocatalysts.

In this work, the H_2 generation activities (TOF_{H2}, mol_{H2}, mol_{H2} mol_{Pt}⁻¹ min⁻¹) in Pt-catalyzed hydrolytic dehydrogenation of AB will be correlated with the types of carbon supports, the defects and the surface concentration of oxygen groups on the supports, and the Pt particle size, aiming at a rational design of the high-performance Pt nanocatalysts.

Two types of carbon supports, i.e., activated carbon (AC) and close carbon nanotubes (CNTs), were used to immobilize Pt NPs by incipient wetness impregnation for AB hydrolysis, in which the Pt particle size was tuned by changing Pt loading (Table S1 and Fig. S1, ESI[†]). Both support effects and size effects of Pt catalysts in principle have a significant influence on the catalytic activity, and thus excluding the size effects will make a fair comparison for the support effects. It can be clearly seen that at the identical Pt particle size, CNT supported Pt nanocatalysts exhibit much higher TOF_{H2} than AC supported Pt nanocatalysts (Fig. 1a), indicating a profound support effect. The reasons for this particular behavior could be related to the unique surface chemistry and textural properties (e.g., the absence of microporosity with elimination of mass-transfer limitation and the introduction of curvatures of graphene sheets with a strong interaction with Pt NPs) of close CNTs with respect to AC.14 Unexpectedly, during the batch AB hydrolysis reaction, both Pt/CNT and Pt/AC nanocatalysts with a low Pt loading of 0.5 wt% show much lower volume of H₂ generation than those with high Pt loadings (Fig. 1b and Fig. S2, ESI⁺). This strongly implies that the difference in the textural properties of the two carbon supports is not the dominant reason, while the difference in the surface chemistry is mainly responsible for the above support effect.

To explore the difference between the surface chemistry of CNTs and that of AC, Raman, TG and XPS techniques are employed, and the results are provided in Fig. 2 and Table S2 (ESI[†]). Obviously, CNTs have lower I_D/I_G and thus less disorders (defects) as well as lower surface concentration of oxygen groups than AC, in which the oxygen groups on the surfaces

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Fig. 1 (a) TOF_{H₂} as a function of Pt particle size over Pt nanocatalysts, and (b) volume of H₂ generation as a function of time over Pt/AC, Pt/CNTs and Pt/CNTs-HT catalysts with 0.5 wt% of Pt loading. Reaction conditions: 30 °C, $n_{\rm Pt}/n_{\rm AB} = 4.7 \times 10^{-3}$ and $C_{\rm AB} = 0.01$ g mL⁻¹.



Fig. 2 (a) Raman spectra of AC, CNTs, CNTs-O and CNTs-O-HT supports. (b) TG patterns of AC, CNTs, CNTs-O and CNTs-O-HT supports under an Ar atmosphere. (c) Molar ratio of oxygen to carbon from XPS for AC, CNTs, CNTs-O and CNTs-O-HT supported 1.5 wt% Pt catalysts. (d) Binding energy (B.E.) of Pt $4f_{7/2}$ over different Pt nanocatalysts as a function of Pt particle size (Note: for the same carbon support, the smaller sized Pt nanocatalyst corresponds to the lower Pt loading (Table S1, ESI†)).

of both carbon supports mainly consist of the electron donating groups (*e.g.*, phenolic hydroxyl) (Fig. S3, ESI[†]). Correspondingly, Pt/ CNT catalysts show the positive shifts of the Pt $4f_{7/2}$ binding energies compared to Pt/AC catalysts, in which the signals are mainly assigned to Pt⁰ species (*i.e.*, metallic Pt). In other words, the metallic Pt NPs supported on CNTs have higher binding energies. These surfaces seem to have stronger interaction with AB molecules to form the activated complex species, which has been assigned as the rate-determining step.^{9,15} As a result, it enhances the H_2 generation from AB hydrolysis. This is one reason for the higher activity of Pt/CNT catalysts. Moreover, these Pt catalysts especially Pt/AC catalysts exist clear shoulders in the XPS Pt 4f spectra at the side of high binding energies (*ca.* 78 eV), which could be linked to the number of Pt–O bonds (*i.e.*, ionic Pt) from the interaction of Pt NPs with oxygen groups. Performing the deconvolution analysis of Pt 4f spectra of 1.5 wt% Pt catalysts (Fig. S4, ESI†) for example, Pt/ CNT catalysts are found to have lower content of ionic Pt and higher content of metallic Pt than Pt/AC catalysts. This is another reason for the higher activity of Pt/CNT catalysts.

However, notably, for the low Pt loading of 0.5 wt%, Pt nanocatalysts show lower binding energy of Pt 4f7/2 (Fig. 2d), which may be due to Pt NPs preferentially anchored on the electron-rich oxygen groups not the electron-deficient defects and thus the electron transfer from surface oxygen groups to Pt.14,16,17 It is expected that Pt NPs immobilized on CNTs with more defects and the lower surface concentration of oxygen groups in principle show the improved Pt 4f_{7/2} binding energies as well as H₂ generation activity. To test this idea, pristine CNTs treated at a high temperature of 800 °C under an Ar atmosphere (i.e., CNTs-HT) are used to immobilize Pt NPs for AB hydrolysis. As expected, CNTs-HT exhibits higher I_D/I_G and thus more defects (Fig. S5a, ESI⁺) as well as lower surface concentration of oxygen groups (i.e., $n_0/n_c = 0.0059$ from XPS) than CNTs. The 0.5 wt% Pt/CNTs-HT catalyst shows much higher Pt 4f7/2 binding energy and content of metallic Pt (Fig. S5b, ESI[†]), which results in much higher volume and the rate of hydrogen generation (Fig. 1b) than the 0.5 wt% Pt/CNT catalyst. The preliminary results indicate that manipulating the surface chemistry of CNTs could be an effective method to remarkably increase the activity of Pt catalysts.

To this end, an acid oxidation and subsequent high temperature method is further employed to treat pristine close CNTs for introducing more defects on CNTs, and the as-obtained carbon supports are used to immobilize Pt NPs for optimizing their activities, in which only acid oxidation treated CNTs and acid oxidation followed by high temperature-treated CNTs in an Ar atmosphere at 800 °C are labelled as CNTs-O and CNTs-O-HT, respectively. As shown in Fig. 2 and Table S2 (ESI⁺), the acid oxidation followed by high temperature treatment significantly increases the number of defects, while the acid oxidation treatment remarkably increases the surface concentration of oxygen groups on CNTs. Correspondingly, the positive and negative shifts of Pt 4f7/2 binding energies are observed over Pt/CNTs-O-HT and Pt/CNTs-O nanocatalysts, respectively. These results indicate that the defects on CNTs promote the electron transfer from Pt to carbon supports, while the oxygen groups reverse the net electron transfer towards the opposite direction. This is in good agreement with previous results.^{16,17} In addition, CNTs-O and CNTs-O-HT show slightly higher surface area and pore volume than pristine CNTs from N₂-BET measurements (Table S1, ESI⁺), indicating that the ends of the as-treated CNTs are still close in most cases.¹⁶ This will help ensure that the supported Pt NPs mainly locate on the external surface of close CNT supports, and thus the confinement effect of Pt catalysts is almost negligible in this work.

Fig. 1a shows TOF_{H_2} as a function of Pt particle size over Pt/CNTs-O-HT catalysts as well as TOF_{H2} of Pt/CNTs-O at 30 $^\circ\text{C}.$ It is expected that at the identical Pt particle size, the defect-rich CNTs-O-HT immobilized Pt nanocatalysts exhibit much higher TOF_H, compared to Pt/CNT nanocatalysts, while the oxygen group-rich CNTs-O immobilized Pt nanocatalyst shows much lower TOF_H. This again verifies the fact that the surface oxygen groups and defects on CNTs are detrimental and beneficial to the Pt catalysis, respectively. Moreover, TOF_{H2} of Pt/CNTs-O-HT increases with Pt particle size to a maximum, *i.e.*, $\sim 567 \text{ mol}_{H_2} \text{ mol}_{Pt}^{-1} \text{ min}^{-1}$, at the mean size of \sim 1.3 nm followed by a decline with a further increase in the size, indicating a significant structure sensitivity for AB hydrolysis over Pt/CNTs-O-HT catalysts. To our knowledge, this is the first study by manipulating the surface chemistry of CNTs and Pt particle size to remarkably enhance the activity in AB hydrolysis, which will help future work on the catalyst design of Pt/C and the reaction mechanism.

Table 1 displays a comparison of the activities of Pt/CNTs-O-HT with various Pt-based catalysts taken from the literature. Clearly, the as-prepared Pt/CNTs-O-HT catalyst shows superior activity, and in particular ~2.1 times higher TOF_{H_2} at 25 °C than the most active supported Pt catalyst (*i.e.*, Pt/ γ -Al₂O₃) reported so far as well as slightly higher than the 2.0 wt%

Table 1 Activities of various Pt-based catalysts for AB hydrolysis

Catalyst	$n_{\rm metal}/n_{\rm AB}$	T (°C)	TOF_{H_2}	Ref.
Pt/CNTs-O-HT	0.0047	30	567	This work
Pt/CNTs-O-HT	0.0047	25	468^{a}	This work
Pt/γ - Al_2O_3	0.018	30	261	3
$Pt/\gamma - Al_2O_3$	0.018	25	222	3
Pt/CeO ₂	0.018	25	182	18
Pt/C	0.018	25	111	19
Pt black	0.018	25	14	19
PtO ₂	0.018	25	21	19
K_2PtCl_4	0.018	25	9	19
PtRu/C	0.03	25	8^b	7
Ni _{0.33} @Pt _{0.67} /C	0.018	25	81^b	8
$Co_{0.32}Pt_{0.68}/C$	0.038	25	67 ^b	9
Pt@MIL-101	0.0029	25	414	20

 a Obtained from the data in Fig. S6 (ESI). b Estimated from the slope of the fitting line.



Scheme 1 Possible pathway for the hydrolytic dehydrogenation of AB over two kinds of Pt particles immobilized on close CNT supports. Note: higher (yellow) and lower (brown) binding energy of Pt 4f.

Pt@MIL-101 (*i.e.*, Pt NPs immobilized inside the pores of MIL-101) catalyst. The higher activity of the Pt/CNTs-O-HT catalyst could be related to not only the unique textural properties of the support, which have no mass-transfer limitations and good capacity as electron reservoirs, but also the distinct surface chemistry. As illustrated in Scheme 1, the electron-deficient defects on CNTs effectively transfer the electrons from Pt to carbon supports and thus promote AB hydrolysis reaction to generate more H_2 , while the electron-rich oxygen groups reversely transfer electrons from carbon supports to Pt and thus inhibit the reaction.

In summary, we have demonstrated the defects not the oxygen groups on CNTs responsible for the improved Pt catalytic activity in AB hydrolysis. It is a facile and effective method to introduce a number of defects on CNTs by acid oxidation and subsequent high temperature treatments. Such defect-rich CNTs-O-HT support immobilized Pt nanocatalysts are highly active, and the optimum sized Pt catalyst shows an unprecedented H₂ generation activity up to $\sim 567 \text{ mol}_{H_2} \text{ mol}_{Pt}^{-1} \text{ min}^{-1}$ at 30 °C. The methodology reported here could be applicable for bi- or multi-metallic and other metallic catalysts.

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