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The role of carbon surface chemistry in N_2O conversion to N_2 over Ni catalyst supported on activated carbon

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Abstract

The effect of acidic treatments on N_2O reduction over Ni catalysts supported on activated carbon was systematically studied. The catalysts were characterized by N_2 adsorption, mass titration, temperature-programmed desorption (TPD), and X-ray photoelectron spectrometry (XPS). It is found that surface chemistry plays an important role in N_2O-carbon reaction catalyzed by Ni catalyst. HNO_3 treatment produces more active acidic surface groups such as carboxyl and lactone, resulting in a more uniform catalyst dispersion and higher catalytic activity. However, HCl treatment decreases active acidic groups and increases the inactive groups, playing an opposite role in the catalyst dispersion and catalytic activity. A thorough discussion of the mechanism of the N_2O catalytic reduction is made based upon results from isothermal reactions, temperature-programmed reactions (TPR) and characterization of catalysts. The effect of acidic treatment on pore structure is also discussed. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbon; Ni catalyst; Acid treatment; N_2O reduction

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1. Introduction

Acid treatments of activated carbons are known to produce significant changes in carbon surface chemistry [1–8] and these in turn can have dramatic effects on both catalyst dispersion [2–9] and catalytic activity [1–4]. Carbon-supported catalysts have been investigated extensively in recent years for NO_x reduction [1,3,10–12]. The general mechanisms of N_2O and NO reduction by carbon are essentially the same, and can be summarized (albeit somewhat simplistically) as follows:

NO adsorption:

$$2S + 2NO \rightarrow 2S - O + N_2 \qquad (1)$$

$$2C_f + 2NO \rightarrow 2C - O + N_2 \qquad (2)$$

Oxygen transfer:

$$C - O \leftrightarrow C(O) \qquad (3)$$

$$S - O \rightarrow C(O) \qquad (4)$$

Product desorption (including site ‘regeneration’ and catalytic cycle propagation):

$$2C(O) \rightarrow CO_2 + C_f^* \qquad (5)$$

$$2C_f^* + 2NO \rightarrow 2C - O + N_2 (\rightarrow CO_2 + C_f^*) \qquad (6)$$

where S represents a catalyst active site and C_f represents a free carbon active sites.

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It should be noted that the 'nascent' carbon active sites (C_f^*) play a key role in these reactions. These are transient species with a very short half-life; they are produced upon desorption of the carbon–oxygen surface intermediates, not only as a consequence of NO_x reduction but also from either pre-existing oxygen-containing functional groups on the activated carbon surface or when O_2 is present together with NO_x. Previous studies have shown that the rate constant for NO reduction on C_f^* sites is much greater than that corresponding to NO reduction on C_f sites [12]. Similar arguments apply for analogous rate-enhancing phenomena in coal hydrogasification [13–14] and steam-assisted char hydrogasification [15].

To better understand the reaction mechanisms of NO or N_2O-carbon reaction catalyzed by various catalysts, it is desirable to systematically investigate the role of surface chemistry of the carbon supports in terms of its effects on the above redox cycle. The relationship among the different surface oxygen groups and catalyst dispersion, reaction mechanism and catalytic activity and stability is not yet clearly established so far.

Gao and Wu [1] studied the influence of acid treatment on NO conversion over several Cu-activated carbon catalysts and found that HNO_3 provided surface oxygen complexes useful for NO conversion, while HCl treatment decreased the reaction rate in most cases. However, two important issues have not been addressed in their work: (1) they did not explain how the complexes affected NO conversion; and (2) the catalyst dispersion is another important issue that was not addressed in their work.

In the study of NO-carbon reaction catalyzed by transition metals, Illán-Gómez et al. [11] found that over ferromagnetic metals such as cobalt, nickel, iron etc., NO dissociative chemisorption can be easily observed at low temperatures (from ca. 373 K) while oxygen is still retained on catalysts, but for copper, a diamagnetic metal, such a process is hard to be observed as the release of carbon–oxygen complexes follows NO chemisorption very closely. This means that over ferromagnetic metals the separate processes of NO chemisorption, oxygen transfer, the release of carbon–oxygen surface complexes can be more easily observed. This is also useful for the study of effects of surface chemistry on catalytic activity. Generally, nickel is a very popular catalyst for either environmental or industrial catalysis.

Since N_2O is relatively simple as an oxidant, it is often used to evaluate the activities of a variety of catalysts for oxidation reaction and as a probe for catalyst characterizations [16–20]. As an intermediate of NO-carbon reaction [11] at low temperatures (below 573 K), N_2O possesses some common features with NO. For example, both N_2O and NO can be reduced by carbon involving a similar redox cycle. The reaction can be catalyzed by common catalysts such as transition metal, alkali metal, alkali earth metal etc. However, N_2O is generally more reactive than NO over the same catalyst [12] (this may be related to the different molecular structure, for the N–O bond has a bond order of 1.61 in N_2O, but a much higher order of 2.5 in NO). Therefore, with the increasing concerns over both N_2O and NO emissions, it is useful to use firstly N_2O instead of NO as a test agent to study the fundamental mechanisms and effect of acid treatment of the carbon support as N_2O should be more sensitive to the changes of surface chemistry. However, to our knowledge, much less has been reported so far on N_2O conversion than NO conversion.

In the present paper, we compare the influences of HCl and HNO_3 treatments on N_2O reduction by Ni catalyst supported on activated carbon. A detailed characterization of supports and catalysts was carried out and the work was focussing on how the catalyst dispersion and the activities of Ni catalysts are affected by surface chemistry.

2. Experimental

2.1. Preparation of activated carbons and catalysts

A commercial activated carbon (AC) sample (Calgon, 4 × 6 mm) was treated with 2 N HCl, 2 N HNO_3, respectively for about 24 h. After the treatment, samples were washed with distilled water and dried in air at 376–378 K overnight. The ash content was determined by burning off the carbon at 1023 K. The carbon supports treated by acids were then referred to as AC–HCl, AC–HNO_3, respectively.

The catalysts were prepared by wet impregnation method. The precursor used was $Ni(NO_3)_2{\cdot}6H_2O$

(BDH chemicals, AR grade). The supports were impregnated with aqueous solution of the precursor in the appropriate concentration (0.6 g/ml) to obtain Ni loadings of about 5%. The solutions were heated and constantly stirred until total elimination of the liquid. All catalysts were dried at 376–378 K overnight. Ni loadings were determined by burning off the carbonaceous supports.

2.2. Characterization of carbon supports and catalysts

The point of zero charge (PZC), termed as the pH value required to give zero net surface charge, is related to the two intrinsic acidity constants. Noh and Schwarz [21] proposed a mass titration method to estimate the PZC of amphoteric solid including activated carbon and it proved to be effective. To measure the PZC of the carbon samples, three different initial pH solutions were prepared using HNO_3 (0.1 M) and NaOH (0.1 M), such as pH = 3, 6, 11. $NaNO_3$ was used as the background electrolyte. For each initial pH, six containers were filled with 20 ml of the solution and different amounts of carbon were added (0.05%, 0.1%, 0.5%, 1% and 10% by weight). The equilibrium pH was measured after 24 h. The plot of pH versus mass fraction of carbon shows a plateau and the PZC is identified as the point at which the change of pH is zero. The PZC is then taken as the average of the three asymptotic pH values.

The N_2 adsorption/desorption isotherms at 77 K of the samples were obtained using a gas sorption analyser (Quantachrome, NOVA 1200). Samples were degassed for 3 h at 573 K prior to the adsorption analysis. The BET surface area, total pore volume, and average pore radius were obtained from the adsorption isotherms. Dubinin–Radushkevich method was used to calculate the micropore volume and the mesopore volume was determined by subtracting the micropore volume from total pore volume.

Thermogravimetric (TGA) experiments were carried out in a thermobalance (Shimadzu TGA-50) to study the thermal composition of Ni catalyst. Samples were loaded into a platinum pan and heated under N_2 atmosphere from ambient temperature to 383 K and held at this temperature for 20 min, and then heated to 1273 K with a control heating rate of 10 K/min.

The XPS measurements were conducted to study the surface characters of catalysts by using PHI-560 ESCA system (Perkin–Elmer). All spectra were acquired at a basic pressure of 2×10^{-7} Torr with Mg K_α excitation at 15 Kv and recorded in the ΔE = constant mode, pass energy 50 and 100 eV. C, O and Ni concentrations on different carbon surfaces are calculated by converting measured peaks areas to atomic concentrations through dividing the area by experimentally determined sensitivity factors [22].

XRD patterns of Ni catalysts were obtained with a Philips PW 1840 powder diffractometer. Cobalt K_α radiation was employed covering two angles between 2° and 90°. The mean crystallite diameters of Ni catalysts were estimated from application of the Scherrer equation.

Temperature-programmed desorption (TPD) experiments were carried out in a vertical tube furnace. 1 g sample was placed in a quartz tube and helium of ultrahigh purity was flowed as the carrier gas. After holding at 383 K for 60 min, the temperature was raised at 5 K/min to 1073 K. The gases evolved during the TPD runs were continuously analysed using a gas chromatography (Shimaduz GC-17A) equipped with a thermal conductivity detector and a Carbosphere column.

2.3. Catalyst activity measurements

The N_2O reaction was carried out under atmospheric pressure in a fixed-bed flow reactor (10.0 mm ID; 200 mg sample), and the gaseous products were analyzed by a gas chromatograph (Shimadzu GC-17A) equipped with a thermal conductivity detector and a Carbosphere column. Two modes of experiments were carried out: (i) TPR: the sample was first subjected to an in situ heat treatment in He at 25 K/min to 773 K and kept there for 1 h, then the temperature was lowered to room temperature followed by heating the sample at 4 K/min until 100% of N_2O conversion was reached in a N_2O/He mixture; and (ii) isothermal reaction at 673 K. Before isothermal reactions, the samples were treated in He at 573 or 773 K for 1 h. The feed gas, with a gas hourly space velocity (GHSV = 22 500 cm^3/g h), contained 3000 ppm N_2O in He.

Table 1
Effect of acid treatments on activated carbon structure

	Ash (%)	Ni (%)	S_{BET} (m^2/g)	V^a (cm^3/g)	$V_{micro}{}^a$ (cm^3/g)	$V_{meso}{}^a$ (cm^3/g)
AC	7.44		972	0.528	0.495	0.033
AC–HCl	5.80		1015	0.548	0.513	0.035
AC–HNO_3	5.56		987	0.534	0.498	0.036
Ni/AC		4.98	888	0.478	0.448	0.030
Ni/AC–HCl		4.54	864	0.465	0.434	0.031
NI/AC–HNO_3		4.48	836	0.453	0.422	0.031

[a] Total pore volume.

3. Results

3.1. Characterization of supports

Table 1 gives the results of the pore structure variations of the activated carbon samples treated by different acids and the ash contents. It is evident that the original carbon (AC) has a high surface area and a well-developed porosity. According to the results of Miguel et al. [23], BET surface area and total pore volume are generally enhanced due to the removal of ash during acid treatment, the increase in surface area and pore volume was mostly pronounced in micropores. However, this trend in the present study is not very clear. The difference between specific surface area S_{BET} for AC–HNO_3 and AC is only 15 m^2/g, which is within experimental errors. The difference for AC–HCl is also rather small. Therefore, it should not be ascribed to ash removal. The argument about experimental error stands for V_{micro} of 0.495 cm^3/g (AC) and 0.498 cm^3/g (AC–HNO_3). In the study of Miguel et al. [23], most of the ash (ca. 10 wt%) was removed, so they observed a clear improvement in pore structure. In the present study, ash contents just decreased slightly after the acidic treatment resulting in the negligible change in pore structure. We should concentrate more on the surface chemistry instead of pore structure.

The PZC of carbons can give a good indication about the surface oxygen complexes and the electronic surface charges of carbons. This surface charge arises from the interaction between the carbon surface and the aqueous solution, and will determine the strength of interaction with the metal precursor in the catalyst preparation step. The complexes on carbon surface are generally classified as acidic, basic, or neutral groups. Carboxylic, anhydride, and lactone are acidic groups, while phenolic, carbonyl, quinone and ether groups are neutral or weakly acidic. Basic complexes are mainly the pyrone and chromene groups. Based on the PZC of carbons the nature of the surface oxygen groups of supports and the dominant complexes can be deduced.

Table 2
PZC of treated and untreated activated carbon supports

	AC	AC–HCl	AC–HNO_3
PZC	8.60	6.70	2.98

The values of PZC of various carbon supports are shown in Table 2. It is seen that the as-received activated carbon shows a basic property. AC–HCl is near neutral and AC–HNO_3 has a high acidity. Acid treatment is seen to increase the acidity of the support. The surface complexes on carbon have changed and more acidic groups (such as carboxylic) have been produced.

The increase in acidity of the support upon HCl treatment may also be attributed to the removal of inorganic compounds (ash) leaving sites on the carbon surface which can chemisorb oxygen upon exposure to atmospheric air at room temperature. This would result in more oxygen surface complexes which are more acidic. HNO_3 removed no more ash than HCl, thus would not result in much difference in the active site creation due to ash removal. It is further deduced that the much strong acidity of AC–HNO_3 is primarily due to the strong oxidation by HNO_3.

Using XPS it is possible to measure directly the concentration of oxygen and other elements on or near the surface, and to detect the different classes of surface functional groups in the outermost atomic layers of supports. In Table 3, C and O concentrations on surfaces of different carbon supports are given. It is obvious that the surface oxygen

Table 3
Results of XPS analyses

Support	C (%)	O (%)
AC	94.6	5.4
AC–HCl	94.2	5.8
AC–HNO_3	91.0	9.0

concentration is significantly increased by HNO_3 treatment. Surface oxygen on carbon consists of inorganic and organic components. Acid treatment mainly removes the inorganic oxides and increases the organic oxygen-contained functional groups, which is reflected in the results of PZC and ash content.

TPD experiments can also provide interesting information about the amount, thermal stability, and nature of the surface oxygen groups. During the TPD process the oxygen surface complexes desorb primarily as CO and CO_2. CO_2 proceeds from the decomposition of carboxylic, anhydride (acidic groups), and lactonic groups, whereas CO results from the decomposition of phenolic, carnonyl, quinone, pyrone, and anhydride (acidic) groups [24]. The application of this technique to the study of the supports shows pronounced differences in surface chemistry among them.

Fig. 1 presents the CO and CO_2 evolution profiles from three AC supports. In general, the desorption profiles are typical of those found on carbons [24]. The CO_2-forming complexes, which are responsible for the acidic nature of the carbon surface, evolved at much lower temperatures than the CO complexes. AC treated with HNO_3 generates an intense oxidation that results in a large evolution of CO_2 and CO. AC–HCl and AC have comparable amounts of CO_2 complexes, but with different thermal stability. AC and AC–HNO_3 seem to have more stable CO complexes than AC–HCl because no maximum is found up to 1073 K whereas a maximum at 1033 K is observed for AC–HCl. The CO_2 evolution curves of AC–HNO_3 show three peaks at about 553, 673 and 923 K. For AC and AC–HCl there is a broad peak occurring at 423–573 K. The above results indicate that a greater amount of stable carboxylic, anhydride and lactonic groups are formed on AC–HNO_3, which is consistent with its PZC value. AC treated by HCl has less thermal stability. Hence, it is deduced that some chemical groups may have transformed or been removed from the AC–HCl support during the acid treatments.

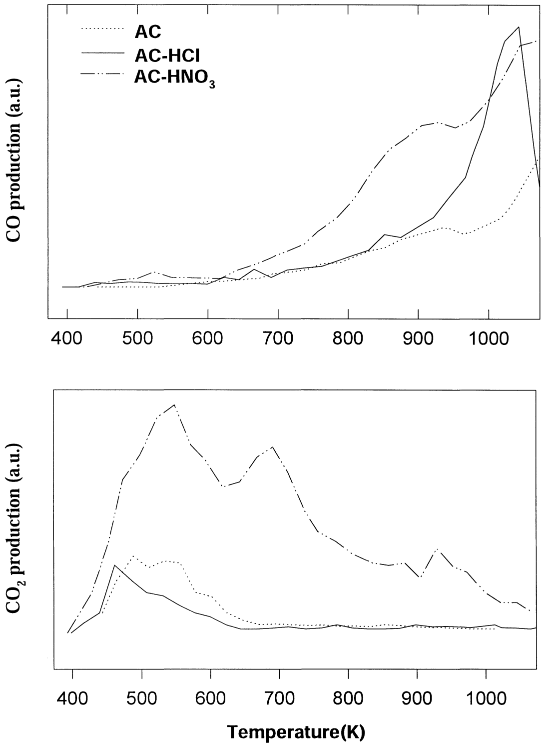

Fig. 1. TPD profiles of untreated and acid-treated carbon supports.

3.2. Characterization of Ni catalysts

From Table 1, it is seen that the impregnation of $Ni(NO_3)_2$ resulted in a decrease in both the specific surface area and pore volume. It is probably due to the pore blockage by NiO as the degassing temperature of 573 K is used in this study, at which nickel nitrate is decomposed to NiO according to the TGA results in Fig. 2 and XRD results in Fig. 3. It is also found that S_{BET} decrease was less than that reported by Gandia and Montes [25] where they used 423 K as the degassing temperature. However, in their studies, the surface area decrease was recovered when $Ni(NO_3)_2$ was decomposed upon higher temperature treatment because the NiO particles formed during the decomposition have considerably smaller diameters than that of $Ni(NO_3)_2$ particles.

Listed in Table 4 are decreases in pore volume of catalysts due to impregnation. Impregnation generally produces larger decrease in micropores than that in mesopores and acid treated carbons show more decrease in pore volume than that in the as-received

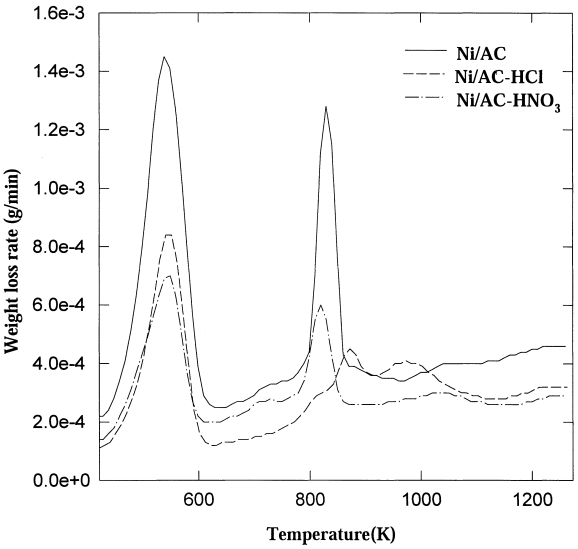

Fig. 2. Thermal analysis of Ni catalysts at 10 K/min in N_2 atmosphere.

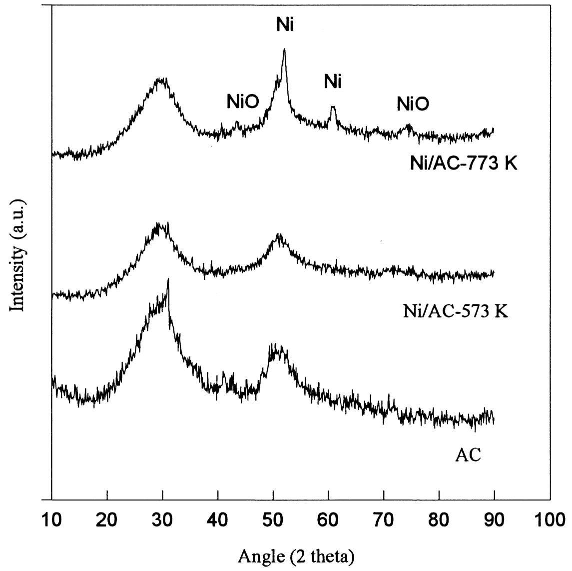

Fig. 3. XRD patterns of Ni catalysts heat treated at different temperatures.

Table 4
Decreases in porosities resulting from catalyst impregnation

Carbon	V_{micro} (%)	V_{meso} (%)
AC	9.5	9.1
AC–HCl	15.4	11.4
AC–HNO_3	15.3	13.9

Table 5
Comparison between Ni/C molar ratios from XPS and gravimetric analyses

Catalyst	$(Ni/C)_{XPS}$	$(Ni/C)_b$	$(Ni/C)_{XPS}/(Ni/C)_b$	D_{XRD} (nm)
Ni/AC	0.040	0.010	4.0	10.4
Ni/AC–HCl	0.021	0.0093	2.2	21.8
Ni/AC–HNO_3	0.0089	0.0092	0.97	9.0

samples. This seems to suggest that treated carbons have larger adsorption capacity for nickel ion, and nickel ion can more easily diffuse into the inner pores of treated carbons.

The XPS technique provides valuable information on the location and distribution of metal in the porous structure of carbon. Table 5 lists the XPS and gravimetric analysis results of Ni/C molar ratios $(Ni/C)_{xps}$ — the Ni/C molar ratio on the surface is obtained from XPS measurements, and $(Ni/C)_b$ — the Ni/C molar ratio in the bulk can be easily calculated from Ni loading shown in Table 1. It is seen that the ratio $(Ni/C)_{xps}/(Ni/C)_b$, being indicative of the ratio of surface and bulk Ni concentration, is much higher than 1 for Ni/AC and Ni/AC–HCl. For Ni/AC–HNO_3 the ratio is close to 1. This means that for Ni/AC and Ni/AC–HCl, a higher concentration of nickel is on the surface but not in the bulk; while, for Ni/AC–HNO_3, the concentration of Ni on the surface and the bulk of support is almost the same. It is also found that the carbons treated by acids show lower $(Ni/C)_{xps}/(Ni/C)_b$ values compared with that of as-received carbon. This means that acidic treatments improve the nickel distributions by making more nickel ions diffused into inner pores of carbon. This deduction is further evidenced by the more reduction of micropore volume in acid-treated nickel catalysts compared with that of Ni/AC (see Table 4).

Another interesting calculation by using a simplified Kerhof–Mouljin model [26] can also offer useful information on Ni distributions. The equation is as follows:

$$P_p/P_s = (p/s)_b BC$$

where P_p and P_s are the XPS atomic concentrations of promoter and support respectively, p and s the corresponding bulk atomic concentrations. B is the function: $B = (\beta/2)(1 + e^{-\beta})/(1 - e^{-\beta})$, $\beta = \lambda_{ps}/(\rho_s\ S_{\mathrm{BET}})$, ρ_s the real density of catalyst, S_{BET} the specific surface, and λ_{ps} the mean free path of promoter electrons passing through the support. C depends on the average crystal size of the supported phase and λ_{pp} — the mean free path of promoter electrons passing through the promoter. C is a number <1 provided promoter dispersed on the total area of support uniformly. Otherwise C may be >1. In our calculation, P_p/P_s and $(p/s)_b$ could be easily obtained from $(Ni/C)_{xps}$ and $(Ni/C)_b$ respectively, and $\rho_s = 0.8\,cm^3/g$. Considering a typical parameter $\lambda = 1.7\,nm$, we calculated C value to be 3.33 for Ni/AC, 1.86 for Ni/AC–HCl and 0.79 for Ni/AC–HNO_3. It is deduced that for the as-received carbon, more nickel ions are distributed on the external surface but not on the overall surface uniformly as the calculated C value is much larger than 1. The decreased C value for Ni/AC–HCl means that more nickel ions have diffused into the interior surface due to HCl treatment but nickel concentration on the outside surface is still rather high. While C value is less than 1 for Ni/AC–HNO_3 indicating that nickel is well dispersed in the pores of the carbon. This is in good agreement with the results in Table 5 but more quantitatively shows the distribution of nickel in the surface of supports.

Conventional X-ray diffraction line broadening calculations have been performed in order to estimate the metallic crystallite diameter. These results are summarised in Table 5. As can be seen, the metallic crystallite size of the Ni catalysts varies depending on the acid employed for treatment and follows the order of Ni/AC–HCl > Ni/AC > Ni–HNO_3, and the latter two catalysts have a relatively close particle size. HCl treatment greatly increases the metal crystallite size of the catalyst while HNO_3 treatment decreases the particle size to some degree.

Some authors [2–4,9] have found that the interaction of metal precursor molecules with carbonaceous supports by means of surface oxygen complexes, leads to a high dispersion. However, in other studies [5–7], it is shown that the oxidation of activated carbon used as support has a negative influence on good catalyst dispersion. With respect to those apparent discrepancies, there is no general consensus available to date. The complicated influence of surface chemistry on metal dispersion was most comprehensively reviewed by Radovic and colleagues [27]. It is thought that the optimization of carbon's surface characteristics in preparation of carbon-supported catalysts is a delicated interplay between solution and surface chemistry. The degree and the strength of interaction between the catalyst precursor and the carbon surface impregnation are a critical factor as surface oxygen complexes are anchorage sites for the initial catalyst dispersion. However, this factor is not always dominant. To what extent this anchoring of catalyst precursor (to maximize catalyst dispersion) will be effective depends on the stability of anchoring sites in the stage of heat treatment. Before discussing the influence of acidic treatments on catalyst dispersion in the present study, we need to look into the interaction of catalyst precursor and the surface of carbons during impregnation stage. So Ni^{2+} isothermal adsorption on various carbons were conducted at 298 K. It is seen (Fig. 4) that the adsorption capacity of activated carbon is increased with acidic treatment. HNO_3-treated carbon shows the highest uptake of Ni^{2+}, while the as-received carbon has the lowest uptake. The reason is related to the change of surface chemistry of the supports [27]. HNO_3 treatment resulted in a very low PZC value thus greatly increasing the surface negative charge. As a consequence, the 'electrostatic' repulsion between the support and Ni^{2+} was weakened and Ni^{2+} ions became more accessible to the inner pores of AC–HNO_3. HCl treatment could not produce as much negative charge as HNO_3, this is why Ni^{2+} adsorption was weaker over

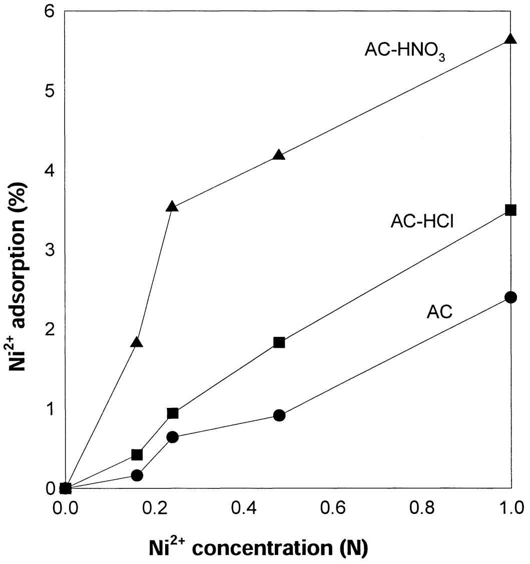

Fig. 4. Ni^{2+} isothermal adsorption on carbons at 298 K.

AC–HCl compared with AC–HNO_3. This is a further confirmation of the results of XPS and pore structure analysis of Ni catalysts as presented earlier.

Based upon the above discussion, the influence of surface chemistry on nickel dispersion is clear. Ni^{2+} adsorption capacity of the carbon support was significantly improved by HNO_3 treatment, so the thus produced acidic groups are ideal catalyst dispersing agents. Meanwhile, HNO_3 treatment produced CO-yielding complexes with good thermal stability, thus the catalyst dispersion could also be well maintained during the reduction reaction. This is why the catalyst dispersion was finally improved by HNO_3. Although HCl treatment could also increase the Ni^{2+} adsorption capacity of the support, AC treated by HCl showed less thermal stability. Hence, in this case more function groups decomposed during the reduction step, making the metal ions more mobile and aggregated as larger particles resulting in the largest crystalline size among the three catalysts.

It is noteworthy that the size of ca. 10–20 nm of nickel crystallites appears to suggest that nickel could not be introduced into micropores. This seems contradictory to the results obtained from the analysis of pore structure and XPS. A good agreement is obtained by considering that nickel ions diffuse into the inner pores of carbon during the adsorption (or loading) stage. However, the reaction between nickel nitrate and carbon during heat treatment consumed a large amount of pores of carbon, resulting in significant increase in catalyst crystallite size. This hypothesis is strongly supported by the largest crystallite size over Ni/AC–HCl.

Results of the thermal analyses of Ni–AC catalysts are shown in Fig. 2. There are two peaks in the TGA curves of Ni-catalysts. $Ni(NO_3)_2$ decomposed to NiO at the temperature of 473–573 K on the carbon support. The peak between 773 and 973 K corresponds to NiO reduction temperature of Ni/C catalysts which can be verified by the XRD results (Fig. 3).

The XRD pattern of the support corresponds to an amorphous material. The catalyst XRD pattern is very similar to that of the support, but heat treatment in N_2 at increased temperatures progressively show peaks corresponding to nickel oxide at 573 K and metal nickel at 773 K. The lower intensity of NiO peaks occurring on XRD pattern at 573 K is probably due to the low amount of Ni content and high dispersion. From XRD pattern at 773 K, it is seen that both Ni and NiO appear. During the preparation for XRD measurement, contamination and exposure of samples to air could lead to the oxidation of Ni to NiO. Hence, the complimentary information from TGA and XRD indicate that at 573 K nickel nitrate decomposes to produce nickel oxide and when heated to 773 K the interaction between nickel oxide and carbon leads to the redox reaction.

Gandia and Montes [25] studied the effect of thermal treatment on Ni activated charcoal supported catalyst and found that NiO can be reduced to metallic state when the catalysts were subjected to an inert atmosphere at 773 K. The interaction between the carbon and salts for impregnated carbon upon heat treatment in inert atmosphere was also reported by other researchers [28,29]. They found that there was a redox reaction between the metal salts and carbon, and the initial species Cr(IV) and Cu(II) were reduced to Cr(III), Cu(I), and Cu, respectively. It has been suggested that the mechanism is very similar to that of metal catalysed oxidation of carbon. When the Ni/C catalysts are treated in N_2 at a sufficiently high temperature, the oxides resulting from the nitrate decomposition transfer their oxygen atoms to the support, which in turn is oxidized.

From Fig. 2 it is seen that nickel nitrate decomposes at about the same temperature. For all catalysts the redox reaction occurred at different temperatures. These results suggest that acid treatment had little effect on nickel nitrate decomposition. However, it does affect the interaction between nickel oxide and carbon. HNO_3 treated carbon is more active than the untreated carbon, while HCl treated carbons show less activity, which is demonstrated by the peak shift and sharpness.

3.3. Catalytic activity of Ni catalysts in N_2O reduction

Isothermal reactions were firstly conducted over activated carbon supports at 673 K. It was observed that the activity over as-received carbon was very low, being ca. 10% at the end of 90 min isothermal reaction. Acidic treatments have significant effect on N_2O reduction. HNO_3 treatment improved the activity

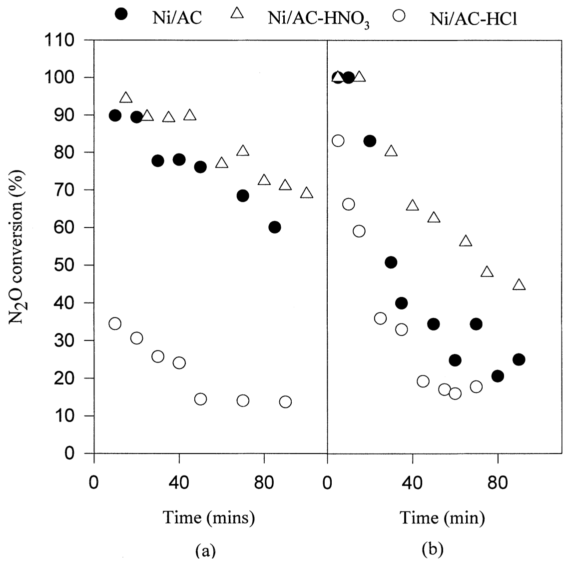

Fig. 5. N_2O conversion over Ni catalysts after heat treatment at (a) 573 K, (b) 773 K. (Other conditions: $P = 1$ atm, GHSV = 22 500 cm^3/g h, reaction $T = 673$ K, N_2O/He = 3000 ppm).

significantly to ca. 20%, while HCl treatment actually decreased the activity of carbon to 5%.

Results of isothermal experimental over Ni catalysts are shown in Fig. 5 and the following important observations can be made: (1) Impregnation of Ni catalyst improves N_2O conversion significantly. For example, ca. 5 wt% of Ni impregnated in the as-received carbon increased N_2O conversion from ca. 10% to more than 50% after a heat treatment at 573 K. (2) Similar to the case of carbon supports, acidic treatments of the supports also have a great effects on the activities of Ni catalysts. HNO_3 treatment increased the activity of Ni/AC, while HCl treatment almost destroyed the activities of Ni catalysts. A comparison of Fig. 5(a) and (b) shows that the activities of all catalysts are substantially influenced by heat treatment. A heat treatment at 773 K led to an extremely high N_2O conversion initially, followed by a quick deactivation. The initial activities after the heat treatment at 573 K were not as high as that after a treatment at 773 K. However, the deactivation of the catalyst prepared by the low-temperature heat treatment was also much less, resulting in a much higher stable N_2O conversion at the end of 90 min reaction over all the catalysts except for Ni/AC–HCl.

4. Discussion

The effects of acidic treatments on catalyst dispersion have been discussed above, and we are interested in how catalytic activities are influenced by carbon surface chemistry.

In the study of acid treatments of activated carbon on NO reduction over Cu/AC, Gao and Wu [1] also found that the conversion of NO reduction depends strongly on surface oxygen-containing groups on the activated carbons, among them the carboxyls and lactone favoured the NO reduction. However, HCl treatment led to the decomposition of carboxyls and lactones, decreasing their activities for NO reduction. Concentrated HNO_3 treatment of activated carbon produced higher conversion of NO reduction at relatively low temperatures due to the marked increase in the amounts of carboxyls and lactones. However, they did not explain how differently surface oxygen complexes affect reaction rates.

From previous studies [10–12], both N_2O- and NO-carbon reactions catalyzed by Cu are actually a redox cycle. N_2O or NO is firstly dissociatively chemisorped on the catalyst, followed by oxygen transfer from the metal (catalyst phase) to the carbon active sites and release of carbon–oxygen complexes from carbon surface. The prerequisite for the reaction is an effectively dissociative chemisorption. However, the reaction may slow down or even stop if the oxygen can not be transferred and released timely, and a quick oxygen transfer and release can greatly promote the overall reaction.

In order to look into the mechanism of how surface chemical properties of the carbon support affect the reaction, a detailed analysis of gaseous product evolution during the isothermal reaction corresponding to Fig. 5 was carried out with results in Fig. 6. It is seen that CO_2 selectivity defined as $CO_2/(CO_2 + CO) \times 100\%$ was 100%, no CO was detected at this relatively low temperature. Because one N_2O molecule reacting with a carbon generates one N_2 and 0.5 CO_2, normally the number of moles of N_2 doubles that of CO_2 in the products if no oxygen is retained on the catalyst surface. In order to clearly show the delay of oxygen-containing products with respect to N_2 in the product analysis, the CO_2 concentration was artificially doubled. In this way, N_2 concentration is equal to CO_2 concentration in the products if no delay for

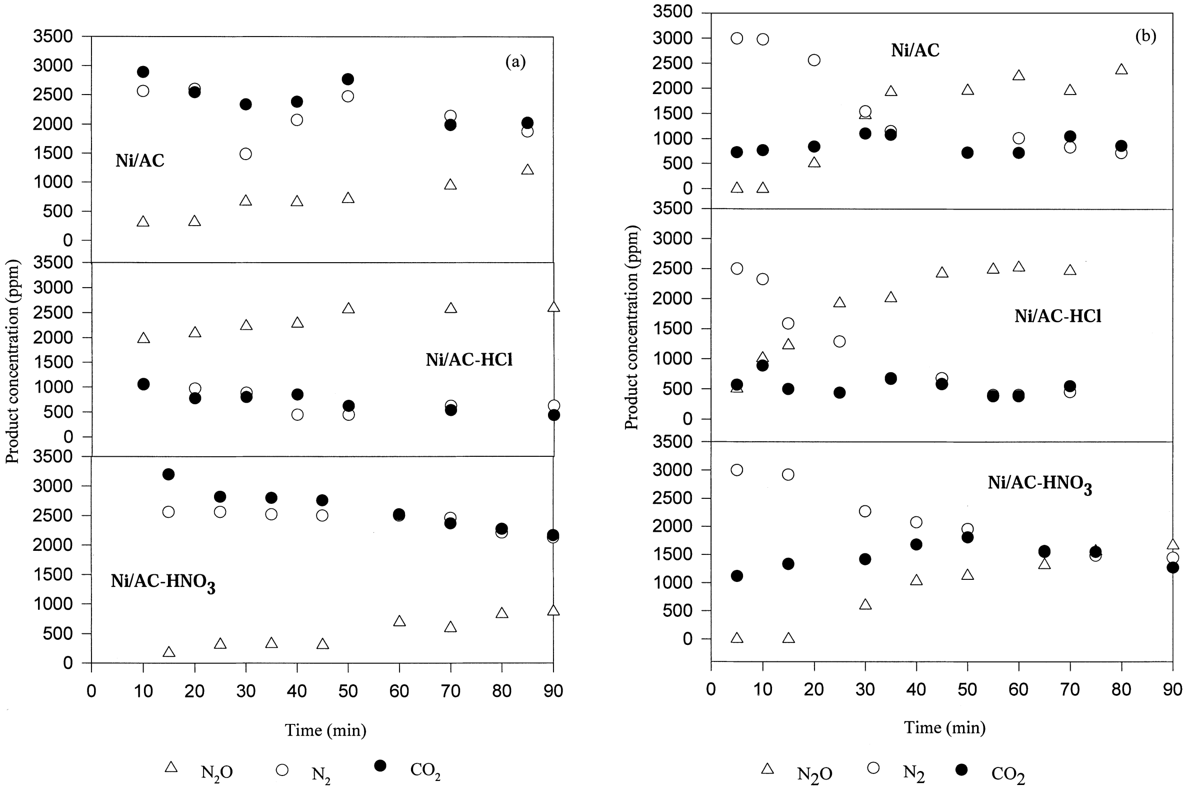

Fig. 6. Analysis of product evolution during isothermal reactions after heat treatment at (a) 573 K, (b) 773 K.

oxygen containing products. Otherwise, CO_2 concentration is less than N_2 concentration.

In Fig. 6(a), after heat treatment at 573 K, CO_2 evolution almost keeps the same pace with N_2 during the whole reaction over all these catalysts except that Ni/AC–HNO_3 shows a little higher CO_2 concentration than N_2 initially, which may be related to acidic groups produced by HNO_3. However, it is not clear enough to elucidate the reaction mechanism and the roles of acidic treatments. In Fig. 6(b), after heat treatment at 773 K, a great delay of CO_2 evolution with respect to N_2 is observed over all the catalysts. This delay means that most of the oxygen given by N_2O dissociative chemisorption was retained on Ni catalyst without being released. A 100% of N_2O conversion is observed over both Ni/AC–HNO_3 and Ni/AC initially, however, the initial CO_2 concentration over Ni/AC was ca. 750 ppm, much lower than ca. 1100 ppm over Ni/AC–HNO_3. Actually the CO_2 concentration from Ni/AC is always lower than from Ni/AC–HNO_3 during the whole duration of the reaction. It is thus concluded that, although Ni catalysts supported on the as-received carbon and HNO_3 treated carbon possess a close ability of N_2O dissociative chemisorption, oxygen can be more easily transferred from Ni to carbon and released from the carbon surface over Ni/AC–HNO_3, resulting in the improved stable N_2O conversion. This is indeed consistent with the surface chemistry nature of catalysts. The similar catalyst dispersion in Ni/AC and Ni/AC–HNO_3 explain their close abilities in N_2O dissociative chemisorption, and the more active acidic groups produced by HNO_3 account for the easy oxygen transfer as these surface groups can be more easily released from carbon surface (see TPD in Fig. 2) thus resulting in more active sites according to Eqs. (5) and (6). The initial N_2O conversion as well as N_2 evolution over Ni/AC–HCl is much lower than that over Ni/AC or Ni/AC–HNO_3, indicating the much weaker ability of Ni/AC–HCl in N_2O dissociative chemisorption due to its poorer catalyst dispersion or less catalyst active sites caused by HCl treatment. Furthermore, HCl treatment also greatly depresses the reaction by weakening the ability of oxygen transfer and release in Ni catalysts, which can be shown by the reduced CO_2 evolution. As has been noted, HCl treatment destroys active groups such as carboxyl, lactone, and increases inactive groups such as carbonyl, phenol. This does not only decrease the catalyst dispersion thus weakening N_2O dissociative chemisorption, but also slows down the oxygen transfer and release.

Based upon the above analysis, the roles of acidic treatments can be examined from the following angles: (1) More active acidic groups are useful for a more uniform catalyst dispersion or more catalyst active sites, resulting in stronger N_2O dissociative chemisorption. This is why N_2O dissociative chemisorption over Ni/AC or Ni/AC–HNO_3 is stronger than over Ni/AC–HCl. Actually, Ni/AC–HNO_3 should also show stronger N_2O dissociative chemisorption than Ni/AC, but our GC is not sensitive enough to distinguish such a small difference. (2) More uniform catalyst dispersion provides more catalyst–carbon contact, making oxygen transfer easier. (3) Active acidic groups are especially useful for the release of carbon–oxygen surface complexes. At the same time quick decomposition of surface complexes can also greatly promote the oxygen transfer from Ni to carbon and N_2O dissociative chemisorption as well. To some degree, the third role is the most important one because the stronger N_2O dissociative chemisorption and oxygen transfer will be slowed down or even stopped without the quick release of surface complexes.

It is also easy to understand the different activities caused by different heat treatments. Heat treatment at higher temperature removes more oxygen from Ni catalysts, resulting in a high N_2O dissociative chemisorption initially. This is why we observed a much higher N_2O conversion at the beginning of the reaction. At the same time, too much active surface groups are also removed by the severe heat treatment, making the surface of carbon more inactive. As reaction proceeds, oxygen can not be transferred from Ni to carbon and released timely, resulting in the quick deactivation. The higher the temperature of the heat treatment, the more the active surface groups are removed. This is why the stable level of N_2O conversion caused by the heat treatment at 773 K was even lower than that by the treatment at 573 K over Ni/AC and Ni/AC–HNO_3. For Ni/AC–HCl, due to the strengthened stable surface complexes caused by HCl, little difference in activities at the stable level is observed after different heat treatments.

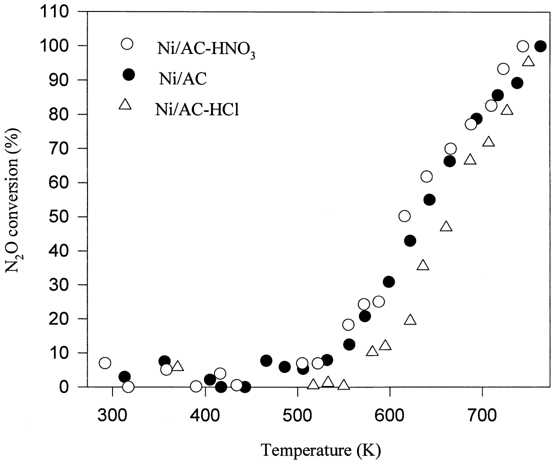

Fig. 7. N_2O conversion during TPR (Other conditions: $P = 1$ atm, GHSV = 22 500 cm^3/g h, $N_2O/He = 3000$ ppm).

Therefore, heat treatment at 573 K provided higher activities of Ni catalysts, but heat treatment at 773 K showed us a clearer reaction mechanism.

In a study of NO-carbon reaction catalysed by transition, Illán-Gómez et al. [11] provided a good insight into the mechanism by using TPR. Following Illán-Gómez et al's work, we carried out similar TPR experiments but our samples can not be heated to 1173 K (as achieved by Illán-Gómez [11]) as such a severe treatment may destroy all the active groups. According to the isothermal reaction, we just treated our samples at 773 K before reaction so that there were still enough acidic groups left for our investigation. 773 K proves to be suitable for heat treatment according to the results in Fig. 7. 100% of N_2O conversion is reached below this temperature and the order of activity during TPR keeps the same as that in the isothermal reactions: Ni/AC–HNO_3 > Ni/AC > Ni/AC–HCl. A detailed analysis of product evolution during TPR is presented in Fig. 8 and three regions can be observed over all three catalysts.

1. At low temperatures, the conversion is negligible. Neither N_2 nor oxygen-containing product other

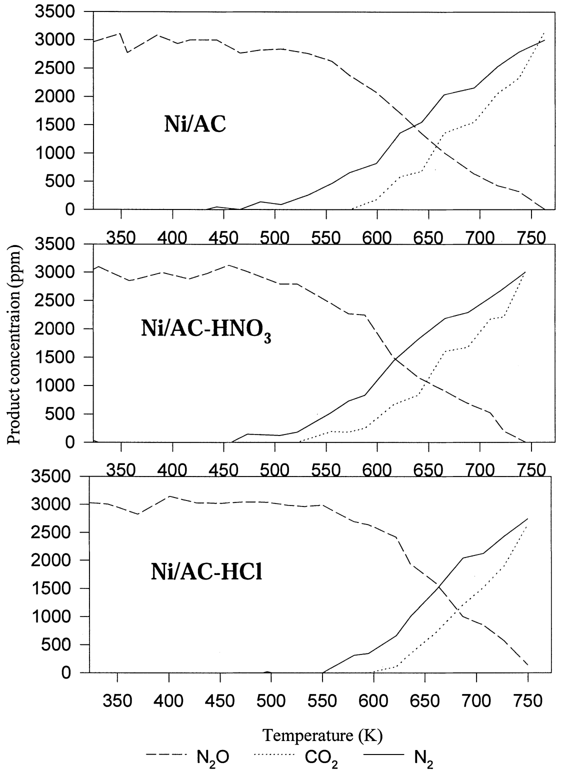

Fig. 8. Evolution of products during TPR.

than N_2O was detected by the GC, and the N_2O conversion is close to zero.

2. The second region is characterized by the appearance of N_2, but yet no CO_2 in the products. The negative oxygen balance is obviously due to N_2O dissociative chemisorption and oxygen retention on Ni catalysts. The temperature for the detectable N_2 is influenced by acidic treatment. N_2 began to evolve over Ni/AC below 473 K, the temperature for N_2 appearance over Ni/AC–HNO_3 was close to that over Ni/AC, but there was no N_2 over Ni/AC–HCl until above 548 K. This means that Ni/AC and Ni/AC–HNO_3 have similar abilities for N_2O dissociative chemisorption, but Ni/AC–HCl possesses a much poorer one. This is in good agreement with the results obtained from the isothermal reactions.
3. As temperature increased further, CO_2 began to evolve, and thus greatly promoting the N_2 evolution as well as N_2O conversion. For Ni/AC, CO_2 appeared at 573 K, but over Ni/AC–HNO_3, this temperature decreased to 523 K, and over Ni/AC–HCl it increased to over 598 K. This is also consistent with the analysis of isothermal reaction above. HNO_3 treatment improves the ability of Ni catalyst in oxygen transfer and release, while, substantially delayed by HCl treatment. Based upon the above analysis, it can be seen that TPR can show the mechanism more directly, while the activity difference can be more clearly shown by isothermal reactions. Therefore, two modes of experiments can indeed give complementary information important to elucidation of the reaction mechanisms and the role of surface chemistry.

5. Conclusions

The influences of acidic treatments on N_2O reduction over Ni catalysts supported on activated carbon was systematically studied. It was found that HNO_3 treatment produces more active acidic surface groups such as carboxyl, lactone etc., which are not only beneficial to the initial dispersion of nickel catalyst during the loading stage, but also help maintain the uniform dispersion during reduction stage. Although HCl treatment can slightly improve the Ni^{2+} adsorption the catalyst dispersion can not be maintained during heat treatment resulting in much poorer catalyst dispersion. More uniform dispersion facilitates both N_2O chemisorption and oxygen transfer from the catalyst active phase to the carbon surface. This is an important reason why HNO_3 treatment improves the catalytic activity of catalyst while HCl treatment plays the opposite role in N_2O reduction. Another reason is that acidic groups produced by HNO_3 can be more easily released from the carbon surface thus promoting the redox cycle while HCl treatment produces acidic groups depressing the release of surface complexes.

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