

ACTIVATED CARBON AS SUPPORT FOR Ni CATALYST FOR METHANE REFORMING WITH CARBON DIOXIDE

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Introduction

Because of its high surface area, relative inexpensive and inert nature, activated carbon has been increasingly used as support for catalysts. Other advantages include easy recovery of active metal species, pore and surface structure tailorability. Acid treatment is often used to modify the surface chemistry of the carbon supports for specific applications. In this work, we studied the effects of acidic treatments on the surface properties and interactions of Ni ions with the treated carbons as well as the active phase distribution in the support.

Experimental

A commercial activated carbon (Calgon, 4x6 mm) was treated with 2N HCl, 2N HNO₃, and 2N HF for 24 Hr. All samples were dried at 105 °C following washing to pH of 7.0. Ni(NO₃)₂·6H₂O was used to impregnate the carbon supports. 5 wt% of Ni loadings were maintained for all samples.

N₂ isotherms of all carbon supports were obtained using a automated surface area and porosimeter (NOVA 1200, Quantachrome) and used to determine the surface area and micro- and meso-porosities. TPD experiments were carried out to determine the surface C-O groups in a fixed bed tube reactor equipped with a GC (Shimadzu, GC 17A). XPS (PHI-560, Perkin Elmer) was used to determine surface Ni and carbon concentrations.

Results and Discussion

Acid treatment of activated carbons can remove most of inorganic components in the ash. It is found that Al, Si, Fe, Ti, K in carbons could be drastically removed by HF, whereas S and Ca can be effectively removed by HCl and HNO₃¹. From the analysis of the ash removal in this study, we found that the majority of the ash component removed is Al and Si compounds. As shown in Table 1, the removal of alumina and silica resulted in significant increase in microporosity. The micropore size distribution of the carbon support becomes more uniform after the acid treatment (Fig. 1).

The acidity of the supports are also increased due to

acid treatment, which results in the enhancement of Ni ion adsorption (Figure 2).

Table 1. Effects of acid treatment on pore structure

Sample	S _{BET} (m ² /g)	V _{mic} (cc/g)	V _{meso} (cc/g)
AC	972	0.495	0.033
AC-HCl	1015	0.513	0.035
AC-HNO ₃	987	0.498	0.036
AC-HF	1087	0.548	0.043

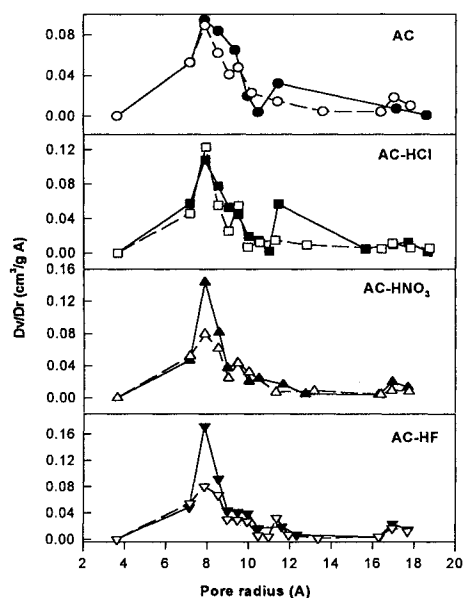


Figure 1. Micropore size distribution of the acid-treated carbons and impregnated catalysts

The increase in Ni²⁺ adsorption capacity is not only attributed to the increase in surface acidity, but also related to the surface hydroxyl groups. Our results and study by Noh and Schwartz² showed that more oxidized carbons adsorb more Ni ions at fixed pH and Ni concentration.

Figure 3 shows the TPD profiles of the raw carbon and acid-treated ones demonstrating the CO₂ complexes (acidic sites) are evolved at much lower temperatures than CO complexes. HNO₃ treatment results in an intense oxidation causing large amounts of CO₂ and CO releases. It is then deduced that more and stable carboxyl and anhydride groups formed on AC-HNO₃ and AC-HF.

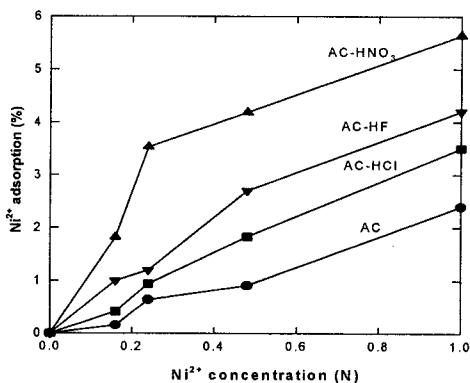


Figure 2. Adsorption isotherms of Ni^{2+} on various carbon supports

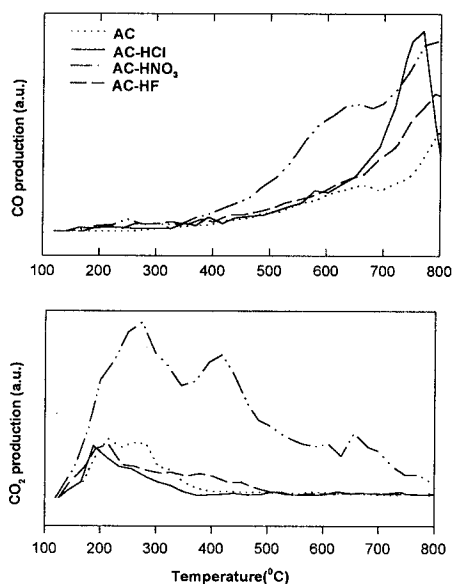


Figure 3. TPD profiles of carbon supports

XPS analysis of the treated and untreated carbons also shows that HCl and HNO_3 treatment generally increase the surface oxygen content, whilst HF decreases surface oxygen. The XPS spectra of acid-treated samples show strong evidence of acidic functional groups such as carboxylic, which is consistent with the pH and adsorption capacity measurements

Table 2 summarizes the XPS and gravimetric analysis of the Ni/C ratios. It is seen that large amount of nickel is on the surface of the carbon supports. This is clearly due to the large crystallite sizes (d) of Ni. With acid treatment, particularly HNO_3 , the ratio $(\text{Ni}/\text{C})_{\text{XPS}}/(\text{Ni}/\text{C})_{\text{g}}$ is reduced indicating that acid treatment improves the Ni ion distribution in activated carbon pores. This is also illustrated in Figure 1.

Table 2. Ni/C ratios and crystallite size of Ni catalysts

Catalyst	$(\text{Ni}/\text{C})_{\text{XPS}}$	$(\text{Ni}/\text{C})_{\text{g}}$	d (nm)
Ni/AC	0.040	0.010	10.4
Ni/AC-HCl	0.021	0.0093	21.8
Ni/AC- HNO_3	0.0089	0.0092	9.0
Ni/AC-HF	0.018	0.0090	12.7

TGA curves of Ni catalysts supported on various carbons, as shown in Figure 4, demonstrate that $\text{Ni}(\text{NO}_3)_2$ decomposes to NiO at about 200-300 °C being lower than the temperature for its corresponding unsupported salt (335 °C). The peaks appeared at about 500-700 °C indicate NiO reduction to Ni on the carbon supports. The crystallite state and size are confirmed by XRD analysis. The acid treatment is seen to have little effect on the nickel nitrate decomposition temperature, but it does affect the NiO-C reduction reaction. Acid treatment generally decreases the reaction rates for both reactions³.

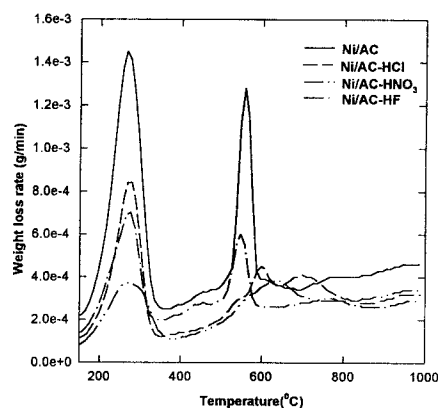


Figure 4. Thermal decomposition of Ni catalysts supported on various acid-treated carbons

Conclusion

In this work, it has been shown that acid treatment (HF in particular) enhances the microporosity of the carbon support. Acidity of the carbon supports and adsorption capacity for Ni^{2+} are increased by acid treatment because of the formation of more acidic surface functional groups. Impregnation of Ni catalyst reduces the accessibility of micropores. On acid-treated carbons, the distribution of the active phase is more uniform and more into the inner pores.

References

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