Effects of Activated Carbon Surface Property on Structure and Activity of Ru/AC Catalysts

S K Xu\textsuperscript{a, b}, L M Li\textsuperscript{b} and N N Guo\textsuperscript{b}

\textsuperscript{a} College of Material Engineering, Henan University of Technology, Zhengzhou 450001, China
\textsuperscript{b} Department of Chemistry, Zhengzhou University, Zhengzhou 450001, China

E-mail: sankui_xu@haut.edu.cn

Abstract. The activated carbon (AC) was modified by supercritical (SC) methanol, HNO\textsubscript{3} oxidation, or HNO\textsubscript{3} oxidation plus SC methanol, respectively. Then, the original and the modified AC were used as supports for Ru/AC catalysts prepared via the impregnation method. The results showed that the SC methanol modification decreased the content of surface acidic groups of AC. While HNO\textsubscript{3} oxidation displayed the opposite behavior. Furthermore, the dispersion of ruthenium and the activity of catalysts were highly dependent on the content of surface acidic groups, and the SC methanol modified sample exhibited the highest activity for hydrogenation of glucose.

1. Introduction

Activated carbon (AC) is a material that has all the required characteristics to be used as a catalyst support. Additionally, the unique properties such as the stability in both acidic and basic media, the possibility of tailoring both its textural and surface chemical properties according to the targeted aims of the catalyst producers also make AC an ideal candidate as catalyst support [1-3]. It was known that catalytic properties are determined both by the texture and surface chemistry of support. Despite a lot of literatures have been published on it, the effect of AC texture and surface groups on the metal dispersion and activity is still under controversy. It has been well established in the literature that the surface groups, which form anchoring sites for metallic precursors, dominantly determine the properties of AC as a catalyst support [1-3]. The acidic groups on the surface decrease the hydrophobicity of AC, leading to the accessibility of the surface to aqueous metal precursors, while the less acidic groups increase the interaction of the metal precursor or the metal particle with the support and consequently minimize the sintering propensity of metal on carbon [3-4]. On the other hand, the nature and concentration of surface functional groups may be modified by suitable thermal or chemical post-treatments such as gas oxidation, liquid oxidation and microwave treatment [5-10]. The supercritical fluid (SCF) is being explored as potential replacement for conventional solvents in various extractive processes, chemical reaction and the preparation of new materials [11]. However, the literature on SCF modified AC was rarely reported. On the other hand, the hydrogenation of glucose to sorbitol is of great industrial importance. The frequently used catalyst for this process is Raney-Ni owning to its excellent settling properties and low cost. However, dissolution of Ni occurs during the hydrogenation of glucose. As a consequence, purification of sorbitol is necessary and renders this process economically less attractive. Thus, great efforts have been made to develop the new efficient and environment-friendly catalysts. Recently, the use of ruthenium-based catalysts could overcome this problem since ruthenium is stable against leaching and has exceptional activity [12-13].
2. Experimental

2.1 Chemicals. Coconut AC was purchased from Fuzhou Carbon Material Company. Glucose, HNO₃ and methanol were supplied by Tianjin Fine Chemical Incorporated Company. RuCl₃ (37wt.%) was provided by Guiyan Rare Metal Material Company. All of the chemicals were used as received.

2.2 Activated carbon modification. The typical procedure for the modification of the original AC (size 0.25-0.38 mm) was as follows:

(i) For SC CH₃OH treated sample (marked as ACS): Firstly, 56mL of CH₃OH was placed into a stainless-steel autoclave of 150 mL. Secondly, 2.0g of AC was placed in a cage fixed at the upper part of the autoclave. The autoclave temperature was adjusted up to 573 K and maintained for 4h. Then, the autoclave was cooled to below 353 K. Finally, the AC was removed and dried at 383 K.

(ii) For HNO₃ oxidized sample (marked as ACH): 2.0g of AC sample was oxidized in 30wt.% HNO₃ solution at 333 K for 4 h and washed with distilled water till the pH of the rinsed solution reached 7.0. The ACH sample was then dried at 383 K.

(iii) For the sample of HNO₃ oxidation plus SC CH₃OH treatment (marked as ACHS): 2.0g of ACH sample was modified with the method described in section 2.2(i).

2.3 Ru catalysts preparation. Ru/AC catalysts were prepared by impregnation of aqueous solution of RuCl₃ with AC, ACS, ACH and ACSH as supports. In a typical experiment, 0.6g of AC was added to 6.0 ml RuCl₃ solution and impregnated for 6 h. The mixture was then dried at 393 K for 8 h. The solid products were reduced with H₂ at 573 K for 3 h.

2.4 Characterizations. The contents of surface acidic groups on AC were titrated by the Boehm method [14]. The chemical constituent difference between methanol mother solution which was used to treat AC and pure methanol was analyzed by GC-MS (DSQ II). The textural properties of AC samples were measured by N₂ adsorption at 77 K. The adsorption capacities of Ru³⁺ on ACs were analyzed by ICAT6000 SERIES. The surface morphologies of Ru catalysts were determined by TEM (HRTEM, JEM-2010).

2.5 Activity test. The activity was performed in a 150 ml stainless-autoclave containing 0.3g of Ru-based catalyst and 50ml of glucose aqueous solution. The H₂ pressure was in the range of 4.0-2.0 MPa with a reaction temperature at 393 K and a stirring rate at 1000 rpm. The activity of the hydrogenation was obtained by recording the decrease of H₂ pressure with time, which was then converted to the hydrogen uptake rate per gram of Ru according to the ideal gas equation.

3. Results and discussion

3.1 Textural properties of AC. The textural properties of AC samples are given in Table 1. Although the ACS sample displayed larger pore volume than the othersamples, all samples have quite similar total surface area and pore volume, which indicates that the AC has a relatively stable physical structure during treatment. We think that the increase in pore volume after SC methanol treatment can be attributed to the extraction of SCF. Because the experimental material is coconut AC, it surely contains some organic ingredients. Thus the extraction process must take place in SC CH₃OH. Some organic ingredients on the surface of AC were leached.

3.2 Boehm titration. The acidic properties of AC may be resulted from the presence of carboxylic groups, lactones or lactols, and hydroxyl groups of phenolic character. These groups differ in their acidities and can be differentiated by neutralization with solutions of NaHCO₃, Na₂CO₃ and NaOH, respectively. Table 2 shows the concentration of the surface acidic groups of AC samples. It can be seen that SC CH₃OH treatment can decrease the content of acidic groups on AC. It can be explained that the SCF extracts some surface acidic groups of AC. Meanwhile, some surface acidic groups, for example carboxylic etc., may react with CH₃OH in supercritical state. To further prove the SC
extraction and reaction, the different chemical composition of methanol mother solutions and pure methanol was analyzed by GC-MS. The results show that the methanol mother solution contains certain amount of organic chemical compositions such as dimethyl ether and methyl propionate etc.

| Sample | Surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) |
|--------|---------------------|--------------------|---------------------|
| AC     | 1430.7              | 1.040              | 1.440               |
| ACS    | 1413.1              | 1.038              | 1.4689              |
| ACH    | 1430.7              | 1.030              | 1.440               |
| ACHS   | 1489.2              | 1.075              | 1.444               |

| Sample | Total acidic (µmol/g) | Carboxylic (µmol/g) | Lactones (µmol/g) | Phenol (µmol/g) |
|--------|-----------------------|---------------------|-------------------|-----------------|
| AC     | 225.1                 | 11.6                | 14.5              | 199.1           |
| ACS    | 33.9                  | —                   | —                 | —               |
| ACH    | 1012.5                | 458.0               | 80.3              | 474.2           |
| ACHS   | 358.0                 | 68.1                | 87.2              | 202.7           |

AC was oxidized by HNO₃ in order to examine the surface chemical characterization. The results indicate that the HNO₃ oxidation significantly increases the content of acidic groups, evidenced by forty times higher of carboxylic group content. It is proposed that the HNO₃ oxidation could lead to the formation of surface acidic groups. And the ACHS sample has lower content of acidic groups, obviously one seventh of carboxylic group content in comparison with ACH sample. The results suggest that the SC methanol has the potential of extraction and/or chemical reaction with acidic surface groups, which would result in a decrease in the content of acidic surface groups.

![Fig. 1 TEM images of the Ru based catalysts](image)

3.3 TEM of catalysts. Fig. 1 shows the TEM morphologies of these supported Ru catalysts. It can be seen from Fig. 1 that the order of Ru particle size is ACH > ACHS > AC > ACS. The ACS supported catalyst exhibits uniformly dispersed Ru nano-particles at a narrow particle size distribution (1.2-3.7 nm). And the ACH supported sample had the largest particle Ru size (2.6-25.8 nm) with the broadest particle size distribution. The results consistent with reference [4], which reported that metal dispersion was highly dependent on the degree of carbon support oxidation, being lower for the support containing higher amount of surface acidic groups. This is attributed to the decomposition of surface complexes, which act as anchoring centers for the metal precursor upon the catalysts reduction. It can be concluded that SC CH₃OH modification could increase the Ru dispersion as it extracts the surface acidic groups of AC and reduces Ru gathering chance. HNO₃ oxidation greatly
increases the surface acidic groups, and enhanced the adsorption of Ru\(^{3+}\). However, some of these groups have a limited thermal stability at temperatures which the catalyst is treated for achieving the reduction of the metal precursor. The decomposition of the less stable surface complexes could result in metal gathering on the surface of support, thus would affect the final dispersion of the metal.

3.4 Activity. The catalytic behaviors of the Ru catalysts during the glucose hydrogenation are summarized in Fig. 2. It can be seen from Fig. 2 that the activity of catalysts follows the order of Ru/ACS > Ru/AC > Ru/ACHS > Ru/ACH, which is the same order as Ru dispersion. The Ru/ACS catalyst shows the highest activity, which is 1.56 times as large as that of Ru/AC catalyst. It shows that SC methanol treatment can increase the activity, whereas HNO\(_3\) oxidation would greatly decrease the activity. The extraction and some chemical reaction may take place on the surface of AC in SC CH\(_3\)OH as mentioned above, and therefore result in leaching of some surface groups on AC. This could be confirmed by the previous Bohem titration and GC-MS results. It was known that the surface groups on the support have profound influence during the catalyst preparation step, acting as anchoring centers for the metal precursor [4]. However, some of these groups have low thermal stability when the catalyst is reduced. The decomposition of the less stable surface complexes could result in metal gathering on the surface of support, thus affect the final dispersion of the metal phase. The SC methanol treatment can decrease the surface acidic groups of AC, reduce metal gathering and finally increase Ru dispersion. The higher metal dispersion could increase the electron interaction between Ru and support. And the interaction results in Ru lacking electron benefiting chemisorb hydrogen. Therefore, the higher Ru dispersion increases the activity of catalysts. HNO\(_3\) oxidation can increase the content of surface acidic groups of AC. But some of these groups have a limited thermal stability when the catalyst is reduced. This results in lower Ru dispersion and decreases the activity of catalysts. This is consistent with reference [15] which reported HNO\(_3\) treatment could increase the surface acidic groups of AC, leading to lower Ru dispersion and decrease the activity of Ru/AC ammonia synthesis catalysts.

4 Conclusions

Three modifications of AC would have great effects on the content of surface acidic groups and the adsorption capacity of AC, whereas their effects on textural properties are rather limited. The dispersion of Ru and activity of catalysts are found to be highly dependent on the content of surface groups of AC, which is higher for the ACS support containing lower amount of surface acidic groups. HNO\(_3\) oxidation could lead to the formation of surface groups that decomposes at a relatively higher temperature or reduction which results in metal gathering on the surface of AC support. SC methanol modification could greatly decrease the surface acidic groups, obviously carboxylic group.
minimizes the gathering propensity of metal, leads to higher dispersion of Ru. Thus obviously increased the activity of the corresponding Ru/ACS catalyst.

Acknowledgments

This work was supported by the School high-level talent fund (No. 2013BS065).

References

[1] Rodriguez R F 1998 *Carbon*. 36 159-175.
[2] Auer E, Freund A, Pietsch J and Tacke T 1998 Appl. *Catal. A Gen*.173259-271.
[3] HagenS, BarfodR and FehrmannR 2003 *Catal. 214* (2) 327-335.
[4] ColomaF, Sepulveda-EscribanoA, FierroJ LG 1997 Appl. *Catal. A Gen*.150 165-183.
[5] AksoyluA E, FreitasM A, FigueiredoJ L 2000 Appl. *Catal. A Gen*. 192 29-42.
[6] SongW, LiY, GuoXH, LiJ, HuangXM and ShenWJ 2010 *Mol. Catal. A Chem*. 328 53-59.
[7] ZhengXL, ZhangSJ, XuJ X and WeiK M 2002 *Carbon*. 40 2597-2603.
[8] HoweJY, DadmunMD, BrittP F 2007 *Carbon*. 45 1072-1080.
[9] HanW F, LiuH Z and ZhuH 2007 *Catal. Commun.* 8 351-354.
[10] TakaokaM, YokokawaH and TakedaN 2007 Appl. *Catal. B. Environ.* 74179-186.
[11] UshikiI, TakahashiN 2017 *J. Supercritical Fluids*, 120, 240-248.
[12] HofferB W, CrezeeE, MooijmanP R M, LangeveldA D, KapteijnF and MoulijnJ A 2003 *Catal. Today* 79-80:35-41.
[13] KusserowB, SchimpfS and ClausP 2003 Adv. Synth. Catal. 345:289-299.
[14] BoehmH P 1994 *Carbon*. 32:759-769.
[15] HanWF, ZhaoB, HuoC and LiuH Z 2004 *Chinese J. Catal.* 25194-198.