ORDERED NANOPOROUS CARBONS (NCCR-56): SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

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Ordered nanoporous carbons having very high surface area are of great technological interest for the development of catalytic, electrocatalytic and hydrogen-storage systems. These carbons with various structures, e.g. CMK-1, CMK-3, NCCR-41, etc., have been synthesized by carbonization of sucrose, furfuryl alcohol and other suitable carbon containing precursors within the pores of nanoporous silicate molecular sieves. The inorganic templates were then removed by etching with HF, followed by filtration, washing and heat treatment to obtain the nanoporous carbons and nitrogen containing carbons. In the present study, ordered nanoporous carbon, designated as NCCR-56, was prepared using IITM-56 silica as the hard template and sucrose as the carbon source. This carbon was then used as a support for the preparation of mono dispersed gold nanoparticles (Au/NCCR-56), which shows promise for glycerol oxidation of reaction.

Keywords: mesoporous carbon, IITM-56, NCCR-56, gold nanoparticle.

INTRODUCTION

Porous carbon materials with high surface areas and pore volumes prepared from porous inorganic templates are of current interest for energy storage, separation, catalysis, and many other applications. One of the most successful examples is the synthesis of mesoporous carbons using surfactant-templated silica frameworks as templates (Ryoo et al., 1999). This approach is based on a multi-step process via polymerization/carbonization of carbon precursors diffused within inorganic matrix followed by removal of the inorganic framework by leaching so as to replicate the nanoporous structure of the inorganic templates, e.g. hexagonal SBA-15 and cubic MCM-48 (Figure 1). In this way, several nanoporous carbons with various structures have been prepared by carbonization of sucrose/furfuryl alcohol carbon precursors over mesoporous silica templates (Chang et al., 2007).

Figure 1. Schematic representation of formation of ordered nanoporous carbon
Several types of ordered nanostructured materials processed through templating approaches have been reported (Selvam et al., 2001; 2010a). In particular, nanoporous carbons, referred as CMK-1 and CMK-3, have been produced by carbonizing the organic precursor inside the pores of MCM-48 and SBA-15 silica, respectively (Ryoo et al., 1999). They are quite effective in dispersing metal nanoparticles, and as a consequence they show much higher catalytic activity. In this way, platinum supported nanoporous carbons show promise as electrode material for DMFC; gold supported nanoporous carbons exhibit excellent activity for the glycerol oxidation. Therefore, recently, we have also synthesized nanoporous carbons, designated as NCCR-1, employing MCM-41 silica as the structure directing agent (Selvam et al., 2008). In continuation of this work, in the present study, attempts has been made to synthesis and characterize a new type of carbon, designated as NCCR-56, using IITM-56 silica having a wall thickness like SBA-15 and a pore size similar to MCM-41 (Selvam et al., 2010b).

EXPERIMENTAL

Ordered nanoporous NCCR-56 carbon was prepared as the reported procedure (Ryoo et al., 1999). At first, IITM-56 (Selvam et al., 2010b) was added to an acidified sucrose solution obtained by dissolving suitable amount of sucrose and H2SO4 in water. The mixture was dried at 100°C for 6 h followed by drying at 160°C for 6 h. The impregnation step was repeated again. Prior to impregnating sucrose solution, the silica template was dried in vacuum at 100°C for 30 min. The dark brown/black sample obtained was carbonized at 900°C under nitrogen flow for 6 h with heating rate of 5°C/min. Finally, the silica template was removed by dissolving in dil. HF. The resulting carbon material was washed with ethanol and dried at 120°C for 6 h, systematically characterized by various analytical and spectroscopic techniques.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of IITM-56 and NCCR-56. The silica product exhibited well resolved reflections indicating the formation of highly ordered 2D-hexagonal nanoporous structure (Selvam et al., 2001; 2010a). The NCCR-56 carbon replica templated by IITM-56 exhibits a slight disorder as seen by a broad diffraction pattern. As expected, the broad reflection is systematically shifted towards higher angle suggesting a reduced unit cell constant for carbon replica (Table 1).
The \( \text{N}_2 \) adsorption isotherms of IITM-56 (not reproduced here) and NCCR-56 are shown in Figure 2. The textural parameters derived from them are listed in Table 1. Both these materials exhibit type-IV isotherms with H1 hysteresis loop indicating the mesoporous characteristics. The mean pore size of NCCR-56 found to be 2.5 nm, which indicates that the carbon is mostly nanoporous with quite narrow pore-size distribution. The pore size of NCCR-56 determined from \( \text{N}_2 \) sorption measurements is consistent with the high-resolution TEM images (Figure 5a). Further, the TEM image shows the structure of the NCCR-56 is exactly inverse replica of MCM-41.

![Figure 2. \( \text{N}_2 \) sorption isotherms and pore size distribution of NCCR-56](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit cell constant (nm)</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IITM-56</td>
<td>5.94</td>
<td>772</td>
<td>0.98</td>
<td>38</td>
</tr>
<tr>
<td>NCCR-56</td>
<td>5.10</td>
<td>1367</td>
<td>1.40</td>
<td>27</td>
</tr>
</tbody>
</table>

Table 1. Structural and textural properties of nanoporous materials

Figure 3 depicts the FT-IR spectra of IITM-56 and NCCR-56. The spectra reveal the signatures of several functional groups distributed at the surface of the nanoporous carbon. The broad band at 3400 cm\(^{-1}\) is attributed to O–H stretching vibration of the adsorbed water; the corresponding bending vibration is seen at 1633 cm\(^{-1}\). The IR bands at 2983 and 2879 cm\(^{-1}\) corresponds to asymmetric and symmetric C–H stretching vibrations of \( \text{sp}^2 \)-type carbon whereas the bands at 2946 and 2828 cm\(^{-1}\) to asymmetric and symmetric stretching vibrations of \( \text{sp}^3 \)-type carbon; their respective bending vibrations are seen at 1280 and 1470 cm\(^{-1}\). The presence of C=C and C–C bonds is supported by the bands at 1568 and 1440 cm\(^{-1}\), respectively. The broad band in the range 1150-1300 cm\(^{-1}\) is assigned to C–O stretching and O–H bending modes of alcoholic, phenolic, and carboxylic groups. Stretching band due to C=O vibrations of
carbonyl functional groups is seen at 1730 cm\(^{-1}\). Furthermore, the absence of band
\(~1100 \text{ cm}^{-1}\) is due to Si–O–Si asymmetric stretching vibration confirms almost
complete removal of the silica from the nanoporous carbon.

Gold supported carbon catalyst (Au/NCCR-56) was prepared via the formation of a
gold sol followed by deposition of the sol onto the nanoporous carbon support
according to the procedure described earlier (Prati et al., 2004). Figure 4 depicts the
XRD patterns of the gold deposited carbon. The formation of gold metallic particles on
NCCR-56 was confirmed as strong reflections corresponding to planes of face-centered
cubic lattice. Further, gold loading has no remarkable effect on the surface area, as it
decreases only marginally from 1367 to 1305 m\(^2\) g\(^{-1}\) for Au/NCCR-56.
TEM bright field images of the samples NCCR-56 and Au/NCCR-56 are given in Figure 5. It can be seen that NCCR-56 show the presence of ordered channels, typical of periodic nanoporous materials. Further, the micrograph (Figure 5b) also indicates good dispersion of gold nanoparticles with a narrow particle size distribution which is ably supported by the histogram (Figure 5c). The average crystallite size obtained by TEM is in close agreement with the values calculated from the XRD data. The catalytic activity of the supported Au/NCCR-56 catalyst was tested for the glycerol oxidation reaction and the results are presented in Table 2.

![TEM images of NCCR-56 and Au/NCCR-56](image)

**Figure 5. TEM images of: (a) NCCR-56; (b) Au/NCCR-56; (c) Particle size distribution of 1wt % Au/NCCR-56**

**Table 2. Conversion and selectivity of glycerol oxidation reaction***

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Glycerol Conversion (%)</th>
<th>Glyceric acid</th>
<th>Selectivity (%)</th>
<th>Oxalic acid</th>
<th>Tartaric acid</th>
<th>Glycolic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/NCCR-56</td>
<td>95</td>
<td>40</td>
<td>5</td>
<td>21</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>

*Reaction conditions: glycerol = 0.3 M; glycerol/Au = 500 mol/mol; glycerol/NaOH = 4 mol/mol; T = 60°C; time = 5 h, pO$_2$ = 7 atm.

**CONCLUSION**

In summary, nanoporous NCCR-56 carbon material was successfully synthesized using IITM-56 silica as template, and systematically characterized employing various analytical and spectroscopic techniques. Further, NCCR-56 carbon was also used as support for the dispersion of uniform shape and size gold nanoparticles (Au/NCCR-56). This supported catalyst is tested for the oxidation of glycerol.

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