

Synthesis, Characterization and Electrochemical Sensing Property of W-MCM-41

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Mesoporous tungsten incorporated MCM-41 (W-MCM-41) was prepared by direct hydrothermal method with different weight ratio of Si to W (Si/W = 25, 50, 100 and 150). The synthesized W-MCM-41 was characterized by low angle X-ray diffraction analysis, Fourier transform-infrared spectroscopy and UV-visible spectroscopy. From the XRD of W-MCM-41 it is observed that, when incorporation of tungsten into the MCM-41 matrix, the mesoporous structure is distorted slightly and hence the intensities are found to decrease with increase in tungsten concentration. The FT-IR spectrum of the samples showed that the tungsten was well incorporated within the MCM-41 framework. The morphological properties of the synthesized samples were characterized by scanning electron microscopy which showed that the synthesized samples comprise of highly agglomerated particles. The synthesized W-MCM-41 was used to modify glassy carbon electrode (W-MCM-41/GCE) and the modified electrode was used to detect 4-chlorophenol in a pH 7.4 phosphate buffer solution by cyclic voltammetry. At the W-MCM-41/GCE, 4-chlorophenol oxidized at less positive potential with larger current response than the bare GCE. The proposed sensor exhibits great potential in the electrochemical sensing of 4-chlorophenol and related pollutants.

Key Words: W-MCM-41, Mesoporous material, 4-Chlorophenol, Electrochemical sensor.

INTRODUCTION

Zeolites are very important catalytic materials and widely used in chemical industries for their crystalline aluminosilicate network. However, their application is still limited by the relatively small pore openings, particularly by the depletion of the light reserves of the fossil oil. Processing of the heavy crude requires large pores in the cracking catalysts, so that the reactants can reach the active sites in the internal surface of the catalysts. Therefore, in zeolite chemistry, a main aspect is pore enlargement. Large pores are present in porous glasses and porous gel, but their disordered pore systems with broad pore size distribution restrict their application severely. MCM-41 was the first synthetic mesoporous material with regularly ordered pore arrangement and a very narrow pore distribution, which was disclosed by the Mobil scientists in 1992¹. Since the discovery of MCM-41 by Mobil scientists numerous studies have been reported concerning, preparation conditions, characterization and application of these materials as catalysts and catalyst supports in various reactions²⁻⁴. Pure siliceous hexagonal MCM-41 cannot be directly used as catalysts. It may be due to the limited thermal stability and negligible catalytic activity of these MCM-41, because of the neutral framework and the lack of sufficient acidity. Mesoporous metallosilicates, developed by isomorphous substitution of Si with different

transition metal ions in a silicate structure, were used as catalysts in fine chemical industries to improve product yield⁵. In recent years, increasing attention has been directed towards the study of metal-containing mesoporous molecular sieves. These mesoporous materials with large pores (20-100 Å) are suitable for the transformation of bulky organic compounds⁶⁻¹⁰. Many researchers have reported the oxidation properties of metal ions such as Ti, V, Cr, Mn, Ce, Sn and Mo¹¹⁻¹⁷ incorporated into the MCM-41 framework. Ti-MCM-41¹⁸ has been investigated and are known to be effective catalysts with hydrogen peroxide and hydroperoxides as oxidants. Cationic vanadyl porphyrin-encapsulated mesoporous Al/V-MCM-41¹⁹ as heterogeneous catalysts for the oxidation of alkenes. Vapour phase oxidation of tetralin over Cr and Fe substituted MCM-41 molecular sieves²⁰ was investigated. In addition, there were material about tungsten incorporated, such as W-HMS²¹, W-SBA-15²² and W-MCM-41²³, which were synthesized easily. However, less attention was paid to the synthesis, characterization and electrochemical sensing property of tungsten incorporated MCM-41.

In this view, we have reported the preparation of W-MCM-41 using direct hydrothermal method. The synthesized W-MCM-41 were characterized by XRD, FT-IR, UV-visible and SEM. The prepared W-MCM-41 has been used to modify the glassy carbon electrode. The modified glassy carbon electrode

shows lower anodic peak potential with larger current response for the electrochemical oxidation of 4-chlorophenol when compared to the bare glassy carbon electrode.

EXPERIMENTAL

Sodium metasilicate, sodium tungstate, cetyltrimethylammonium bromide (CTAB) and sulphuric acid were purchased from Qualigens and used as received. Deionized water was used throughout the experiment.

The prepared sample was studied by FT-IR spectroscopy using a Shimadzu FT-IR 8300 series instrument. The crystalline structure of the samples were analyzed by a Rich Siefert 3000 diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). In order to have an elemental composition in W-MCM-41 samples, energy dispersive spectroscopy (EDS) was carried out with EDAX Prime equipment coupled to a JEOL 5800 LV scanning electron microscope. The analyses were randomly taken in several sample zones to have a representative value of the elemental composition at low magnification. Morphological characterization was carried out using a HITACHI SU6600 scanning electron microscopy. SEM specimens were prepared by dispersing the sample in ethanol with ultrasound for 5 min. A drop of the suspension was placed into an aluminum foil and was allowed to dry. The UV-visible spectra were recorded on UV-1601OC, Shimadzu instrument using distilled water as a solvent.

Electrochemical experiment: The modifying process of the electrode was followed by literature method²⁴ as follows: Electrochemical measurements were carried out by cyclic voltammetry (CV) in a conventional three-electrode cell. A glassy carbon electrode with a surface area of 0.07 cm^2 was used as working electrode. The W-MCM-41 suspension were prepared by dispersing 1 mg of sample in 5 mL of acetone using ultrasonication for 10 min. The $5 \mu\text{L}$ of the above suspension was spread on the highly polished glassy carbon electrode surface from the aliquots and dried at room temperature. Electrochemical measurements were performed at 298 K using a CHI 600A. A three-electrode cell was used with a saturated calomel electrode (SCE: $\text{Ag}/\text{AgCl}/\text{sat. KCl}$) as reference electrode, platinum wire as counter electrode and the modified glassy carbon electrode as the working electrode. The cyclic voltammetry studies were performed in 0.1 M PBS electrolyte solution saturated with nitrogen at potential range of 0 to +1 V at the scan rate of 10 mVs^{-1} .

Synthesis of W-MCM-41: The mesoporous W-MCM-41 with variable Si/W ratios were synthesized by the following procedure: 18.94 g of sodium metasilicate was dissolved in deionized water under mechanical stirring. To this, the required amount of sodium tungstate solution was slowly added. The pH of the solution was adjusted to 10.5 with 2 M sulphuric acid and the obtained gel was stirred for 1 h. To this, an aqueous solution of cetyltrimethylammonium bromide was added very slowly and the mixture was continuously stirred for another 1 h at room temperature. The gel was transferred into Teflon-lined stainless steel autoclave and kept at $170 \text{ }^\circ\text{C}$ for 12 h. The obtained solid product was cooled to room temperature, filtered, washed with de-ionized water and dried at $100 \text{ }^\circ\text{C}$. The sample was then calcined in air at $550 \text{ }^\circ\text{C}$ for 6 h. The

molar composition of the gel was subjected to hydrothermal synthesis as follows:

$\text{SiO}_2 : n \text{ WO}_3 : 0.2 \text{ CTAB} : 0.89 \text{ H}_2\text{SO}_4 : 120 \text{ H}_2\text{O}$. Here, $n = 0.007\text{-}0.04$.

The samples are designated as W-MCM-41 (X) where X is the Si/W ratio in the gel: 25, 50, 100 and 150.

RESULTS AND DISCUSSION

FT-IR analysis: The FT-IR bands of W-MCM-41 samples are listed in Table-1. Fig. 1 shows the absorption bands at 1639, 1077, 967, 802 and 475 cm^{-1} . The strong absorption band at 1639 cm^{-1} is ascribed to bending vibration of hydroxyl group of water molecule, which shows that a large number of surface hydroxyl groups and H_2O exist on the surface of W-MCM-41, which play a key role for bonding metal ions from the impregnating sol. The bands observed at 1077, 802 and 475 cm^{-1} are due to symmetric stretching, asymmetric stretching and bending vibration of Si-O-Si^{25,26}. In addition, these bands are narrow and more intense due to free vibration of Si-O-Si and Si-O-W bonds in W-MCM-41. The band at 967 cm^{-1} can be attributed to the vibration of hydroxyl groups shared by Si and W atoms in the W-MCM-41 framework²⁷. It can be seen that, the intensity of the Si-O-W peak at 967 cm^{-1} increases with increasing tungsten content (Fig. 1), which is in agreement with the XRD results. This is the evidence of tungsten incorporating into the silica framework.

TABLE-1
BAND ASSIGNMENTS IN THE FT-IR
SPECTRUM OF (25) W-MCM-41

Band assignments	Wavenumber (cm^{-1})
δ_b (Si-O-Si)	475
δ_s (Si-O-Si)	816-600
δ_{as} (Si-O-W)	967
δ_{as} (Si-O-Si)	1077
$\delta \text{ OH}$ (H_2O)	1639

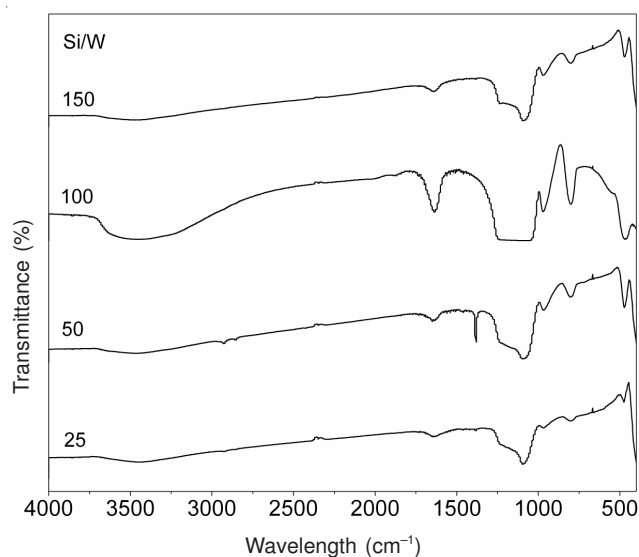


Fig. 1. FT-IR spectrum of W-MCM-41 with different Si/W ratios

XRD analysis: The mesostructural and ordered characteristics of the samples were determined by XRD measurements.

The low-angle XRD patterns of W-MCM-41 were shown in the Fig. 2. All the samples exhibit well-defined (1 0 0), (1 1 0) and (2 0 0) reflections (indexed on the hexagonal lattice) in their XRD patterns²⁸, suggesting the formation of the long-range ordered MCM-41 nanopores. The diffraction peaks were broadened and slightly shifted to higher angle with increasing tungsten content. The ionic radius of W (0.62 Å) is higher than that of Si (0.42 Å). Hence, upon incorporation of W into the MCM-41 matrix, the mesoporous structure is distorted slightly and hence the intensities were found to decrease with increase in W concentration.

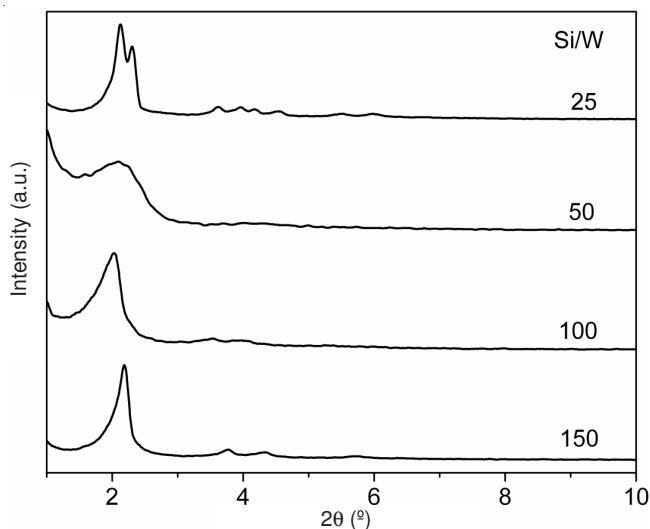


Fig. 2. Low-angle XRD patterns of W-MCM-41 with different Si/W ratios

UV-visible analysis: UV-visible diffuse reflectance spectroscopy is an effective technique for determining local molecular coordination and bonding information for inorganic compounds like mixed oxides²⁹. To obtain the chemical nature and coordination state of tungsten oxide species in MCM-41 matrix, the diffuse reflectance spectra in the UV-visible region of W-MCM-41 samples with different Si/W ratios were recorded (Fig. 3). Fig. 3 showed two characteristic absorption bands for W-MCM-41 in the UV region. The intense band at 229 nm was attributed to an isolated $[WO_4]$ tetrahedral species³⁰ depending on the ligand field symmetry surrounding the W center³¹. This band is generally regarded as the direct proof that transition metal atoms have been incorporated into the framework of a molecular sieve. Therefore, it should be considered as the direct proof for the presence of the framework tungsten species in tetrahedral coordination. The band at 273 nm may be attributed to a distorted tetrahedral coordination environment or the existence of some tungsten species in an octahedral coordination environment³¹. The intensity of the two bands is found to increase with the increase of tungsten content, which suggests that the amount of framework tungsten oxide species increased.

SEM analysis: Typical SEM images of W-MCM-41 were shown in Fig. 4. The images indicated that the particles are agglomerated and the size of the particles is in the nanometer range. The encapsulated materials possess the same morphology with that of W-MCM-41 and hence the solid supports were structurally unchanged upon encapsulation.

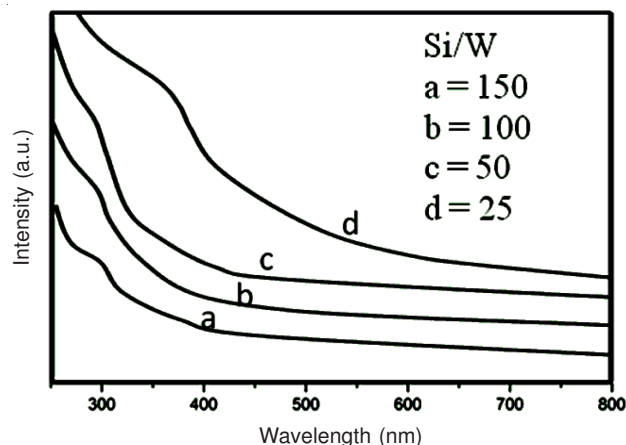


Fig. 3. UV-VIS diffuse reflectance spectra of W-MCM-41 with different Si/W ratios

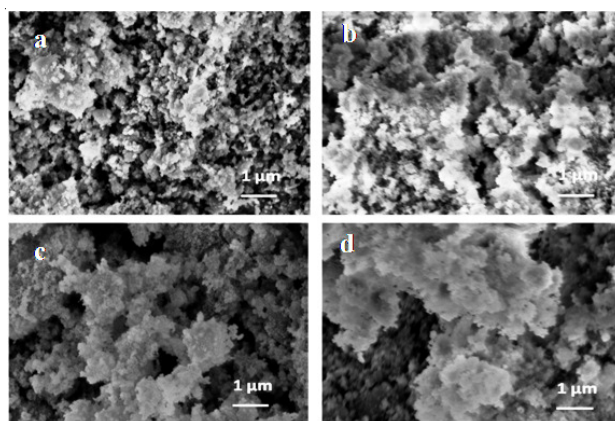


Fig. 4. SEM images of W-MCM-41 with different Si/W ratios (a = 150, b = 100, c = 50, d = 25)

Electrochemical sensing property: Cyclic voltammograms (CVs) were recorded to evaluate the electrochemical sensing property of the modified electrode towards the oxidation of 4-chlorophenol in the potential range of 0 to +1 V. The cyclic voltammograms of bare and W-MCM-41/GCE in the absence of 1 mM 4-CP in 0.1 M PBS show no redox peak for W-MCM-41/GCE in blank 0.1 M PBS indicates that the W-MCM-41/GCE (figure not shown) is not electroactive in the selected potential range. In addition, the W-MCM-41/GCE shows enhanced peak current than the bare glassy carbon electrode indicates the electrocatalytic ability of the modified electrode. This electrocatalytic effect was attributed to the larger available surface area of the modified layer³². Fig. 5 displays the cyclic voltammograms of bare and W-MCM-41/GCE in the presence of 1 mM 4-chlorophenol in 0.1 M PBS at a scan rate of 10 mV/s. The cyclic voltammogram of 4-chlorophenol (Fig. 5a) at bare glassy carbon electrode shows a very broad peak at about 0.68 V. The 4-chlorophenol voltammogram obtained for MCM-41/GCE showed a broad oxidation peak potential at 0.67 V. However, the 4-chlorophenol voltammogram obtained for W-MCM-41/GCE showed well defined oxidation wave of 4-chlorophenol with shift in potential and increase of the oxidation peak current than the bare and pure MCM-41/GCE, indicating the electrocatalytic ability of the modified electrode. From the Fig. 5, it can be seen that the oxidation potential and current response of 4-chlorophenol varied with

the amount of the added tungsten. For better clarification, we plotted the concentration of tungsten against the oxidation potential and current response for the oxidation of 4-chlorophenol which is shown in Fig. 6. Especially (Si/W = 25) W-MCM-41/GCE showed higher oxidation peak current with lower oxidation potential at +0.60 V. The overpotential had thus decreased by +80 mV indicating the strong electrocatalytic effect of W-MCM-41/GCE modified layer.

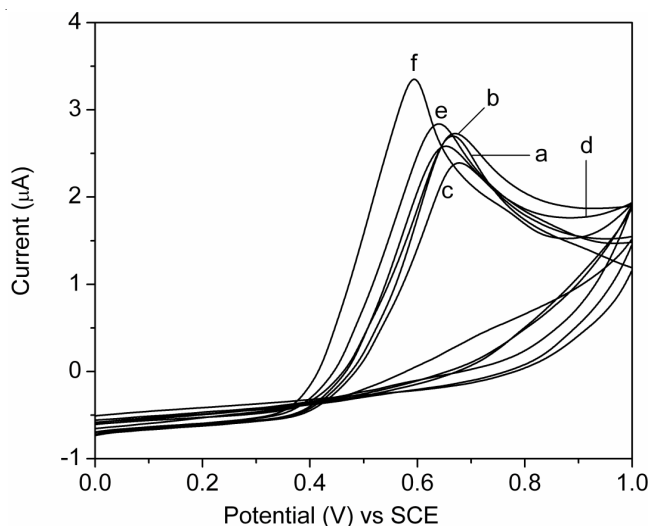


Fig. 5. Cyclic voltammetric response of 1 mM 4-chlorophenol at W-MCM-41/GCE with different Si/W ratios (a = bare, b = 150, c = 100, d = 50, e = 25)

The above results indicate that catalytic reaction occurred between the W-MCM-41/GCE with 4-chlorophenol. The catalytic reaction facilitates electron transfer between 4-chlorophenol and the modified electrode, as a result the electrochemical oxidation of 4-chlorophenol becomes easier. The reason for this is that the W-MCM-41 can act as a promoter to increase the rate of electron transfer, lower the overpotential of 4-chlorophenol at the bare electrode and the anodic peak shifts less positive potential. Thus, it is clear that W-MCM-41/GCE can be successfully used as a sensor for the determination of organic pollutant.

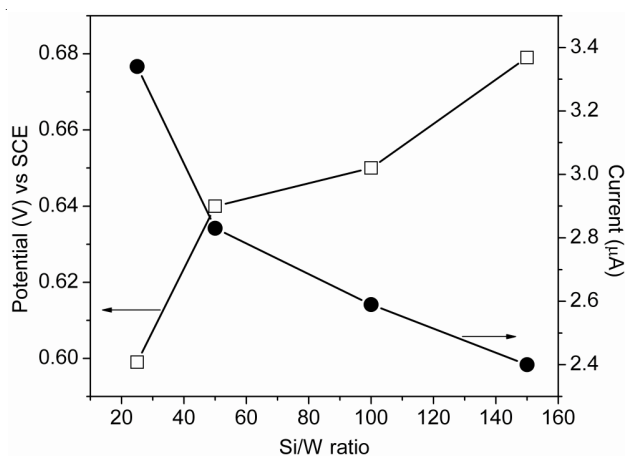


Fig. 6. Plot of concentration of W vs. peak potential and current response

Conclusion

W-MCM-41 was synthesized by direct hydrothermal method. The synthesized W-MCM-41 was characterized by XRD, FT-IR, SEM and UV-Visible. XRD reveals the formation of the W-MCM-41. FT-IR shows the incorporation of tungsten into the Si frame work. SEM analysis indicates that the sample was found to be aggregated in nature. The electrochemical sensing property of 4-CP by W-MCM-41 was investigated by cyclic voltammetry. The results suggest that the W-MCM-41 have higher electrocatalytic activity.

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