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SYNTHESIS AND CHARACTERISATION OF CESIUM-BASED MCM-41 ALUMINOSILICATE MESOPOROUS NANOSPHERICAL MATERIAL (CSAL-MCM-41)

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Abstract
Cesium based Mesoporous aluminosilicate materials (CsAl-MCM-41) with an atomic Si/Al ratio of 20 have been synthesized at temperature of 100 º C using aluminium Isoproxide, hexadecyltrimethylammonium bromide (CTAB), LUDOX AS-40, Caesium hydroxide and distilled water as starting materials. The products were characterized by powder X-ray diffraction (XRD), Fourier transform Infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), nitrogen adsorption-desorption isotherm and Thermal Gravimetric Analysis (TGA). The product obtained made up of a range of mesoporous nanospheres lies between 25 to 30 nm. The d100 spacing was found to be 28.6 nm which corresponds to the average value obtained from the TEM measurement (28.9 nm) and the Nitrogen adsorption (28.7 nm). The product also revealed large surface area of 425.04 m^2g^{-1} with pore volume 0.909 cm^3g^{-1}. The absorption bands at 2921 and 2853 cm^{-1} were assigned due to C-H bond from the surfactant molecule, while, the vibration bands at 1232, 1065 and 788 cm^{-1} assigned to the asymmetric and symmetric stretching of Si-O-Si bonds. Vibrational peak at 952 cm^{-1} is attributed to the stretching of the bond Si-O-Cs, which explain the incorporation of Caesium into the framework of the mesoporous silica materials. The bands at 453 cm^{-1} refer to tetrahedral Si-O and Al-O bending modes. The material experiences weight loss up to 20 % at 139 º C and 430 º C due to desorption of water and surfactant material. The product also shows high thermal stability at higher temperatures up to 900 º C without further structural collapse.

Keywords: *Mesoporous, Nanosphere, surfactant, Aluminium Isoproxide, Cesium Hydroxide*

Introduction

Porous materials has been discovered and largely used as catalysts, adsorbents, molecular sieves, ion exchangers and chromatographic agents in fine chemicals industry, this happened due of their unique nature and properties such as uniform pore size, large surface area and flexible frameworks (Jian *et al.,* 2000). Considering the definition accepted by IUPAC, porous materials can be grouped into three classes based on their pore diameter: microporous, < 2.0 nm; mesoporous, 2.0 < Ø < 50 nm; and macroporous, > 50 nm (Bouhadjar *et al.,* 2017). Among the porous solids, microporous zeolites and mesoporous molecular sieves are mostly used as acid and base catalysts, especially in the petrochemical industry. They possess numerous desirable catalytic properties including high surface area, adjustable pore size, acidity and high thermal stability (Eng-Poh *et al*., 2016).

The discovery of new family called mesoporous materials, chosen and named as MCM-41 (Mobile composite of matter No 41), has been attracting worldwide interest since their first synthesis in 1992 (Jian *et al.,* 2000). Their vital applications as catalysts, adsorbents and host matrixes are due to their exceptional and unique structure, which exhibits a regular range of uniform pore openings. However, the MCM-41 materials made up with pure-silica framework are of limited use for various applications because of the lack of acidic or basic sites and ion-exchange capacity (Leen *et al.,* 2003). as a result, much attention has therefore been devoted to isomorphous substitution of Al as well as Mn, V, Cr, and Ti, in the silicate framework. However, these have improved the catalytic properties of the material. Most of the reported syntheses of these materials were performed under hydrothermal conditions (100-150 º C), but few were made using solvothermal synthesis (Leen *et al.*, 2003; Peter and Thomas, 1996). Kresge *et al.* (1992) discovered that the acid-side synthesis of purely siliceous MCM-41 material can be achieved at room temperature. This have the advantage to operate in a shorter synthetic time and required lower surfactant concentrations as compared with the basic-side catalyst which require high-temperature and longer synthetic time (Miao *et al.,* 2005).

We describe here the synthesis and characterization of high-quality Cesium aluminosilicate CsAl-MCM-41 with Si/Al ratio of 20 at temperature of 100 º C by adjusting the pH of the reaction gel from highly basic (pH 14-15) to moderately basic (pH 8-9) conditions. Surfactants play a key role in nanoparticle synthesis by adsorbing to the surface of the forming nanoparticle and lowering its surface energy, hexadecyltrimethylammonium bromide (CTAB) used as surfactant, however, this also serve as structure directing agent.

Materials and Methods

Materials

Important synthetic recipe for CsAl-MCM-41 outlined as follows: 250 ml polypropylene bottle was used to dissolve 0.21744 g of CTAB in 4.03708 g distilled water (H_2O) under vigorous stirring and levelled as solution-1. Yellow cap bottle was used to dissolve 0.1981 g $CsOH.H_2O$ into 0.504 LUDOX AS-40 which was levelled as solution-2. Then Solution-2 was added into solution-1 drop wise under continuous stirring. Therefore, 0.0328 g of Aluminium Isopoxide (Al) is added into the polypropylene bottle containing the hydro gel solution under vigorous stirring. The molar composition of the mixture gel is CTAB: Cs_2O: Al: SiO: H_2O and the ratio is 1: 1: 0.2: 4: 400 respectably. The Si/Al ratio is 20. The sample was placed in an oven for 24 hours. The pH of the mixture was maintained at 10.0 with 5wt.% acetic acid. The pH adjustment was repeated twice. The product was filtered, washed and dried at 60 º C for 10 hours (Martins *et al.,* 1999).

Characterisation

The XRD patterns of the calcine samples were collected on an X-ray diffractometer (X_PERT SW) operated at 40 kV and 10 mA with nickel filtered CuKa radiation (k = 1.54060 A˚). The structure and morphologies of the sample were observed by means of TEM (JEOL, JEM-2010) equipped with an energy dispersive X-ray spectrometer (EDS) at an accelerating voltage of 200 kV, respectively. The nitrogen sorption and desorption analysis was conducted on an ASAP-2405N instrument at liquid nitrogen temperature. Prior to the adsorption, the sample was degassed at 300 º C for 12 h at 10 135 Torr. FT-IR spectra of samples were recorded with a TEN-SOR27 (BRUKER) spectrometer in KBr pellet. Thermogravimetric analysis (TG) of the sample was carried out in a Rheometric scientific (NETZSCH4) thermo balance (Mokhonoana and Coville*,* 2009).

Results and Discussion

Following the above recipe, high quality Cesium aluminosilicate mesoporous (CsAl-MCM-41) material has been synthesized. The Powder XRD result of the sample was made known in Fig. 1. The XRD pattern of the calcine sample consists of one strong peak at 2.41 º. However, the peak usually corresponds to the d spacing of 28.6 nm as calculated from the scherrer equation (Mokhonoana and Coville*,* 2009).

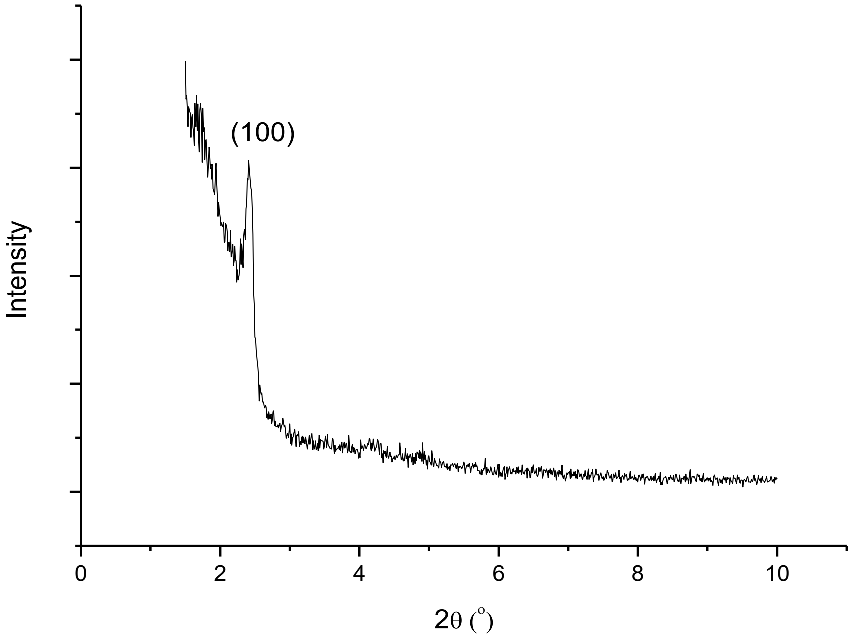

Figure 1: XRD patterns of CsAl-MCM-41 samples obtained using a CuKa X-ray source.

Fig.2. shows FTIR spectral curve of **(a)** uncalcine and (b) calcine samples of CsAl-MCM-41.

Both uncalcine and calcine FTIR spectrum data was analyzed. The vibrational frequencies at 1232, 1065, 788 and 456 cm^{-1} were attributed to the characteristic of silica framework in CeAl-MCM-41. Uncalcined (a) exhibits absorption bands around 2921 and 2853 cm^{-1} assign to C–H vibrations of the surfactant molecule (Structure directing group), while the surfactant molecule disappear in Calcined sample (b) due to calcinations process. There for, this indicated that the calcinations process was effective in removing surfactant material completely from the catalyst. The broad bands around 3500 cm^{-1} attributed to surface silanols and adsorbed water molecules, while deformational vibrations of the adsorbed water molecules cause the absorption bands at 1643 cm^{-1}.

Vibrational peak at 952 cm^{-1} is attributed to the stretching of the bond Si-O-Cs, which explain the incorporation of Cesium element into the framework of the mesoporous silica materials. The band at 453 cm^{-1} is attributed to tetrahedral Si-O bending modes.

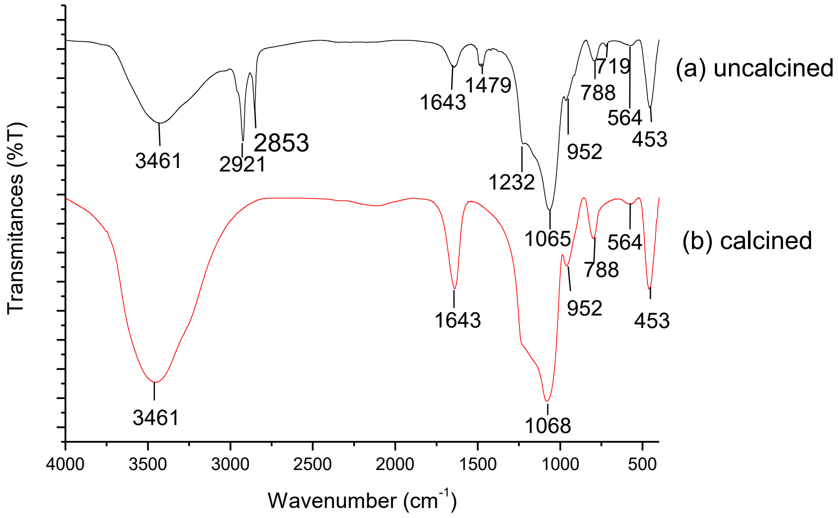

Figure 2: FTIR spectra of CsAl-MCM 41 (a) Uncalcined (b) Calcined

Table 1: **Vibrational frequencies of uncalcined and calcine samples of CsAl-MCM 41**

Samples	OH	C-H	Si-O-Si	Si-O-Cs	Si-O-Al
Uncalcine	3461	2921-2853	1232-788	952	453
Calcine	3461	-	1232-788	952	453

The vibrational band at 1232, 1065 and 788 cm^{-1} refers to the asymmetric and symmetric stretching of Si-O-Si bond. Table 1 shows the FTIR spectral bands of both uncalcine and calcine sample.

The structural morphology and the shapes of the synthesized material were observed by transmission electron microscope (TEM) and the TEM images are shown in Fig. 3. The TEM result of Cesium Alminosilicate (CsAl-MCM-41) sample was observed to have spherical shapes with average particle size of about 28.9 nm, which is consistent with the XRD results calculated. The results, however, is in agreement with the TEM image observation by co-worker for MCM-41 which has slighted pH adjustment. The sample has also shows regular spherical arrangement of uniform pore size distribution (Kunio 1997).

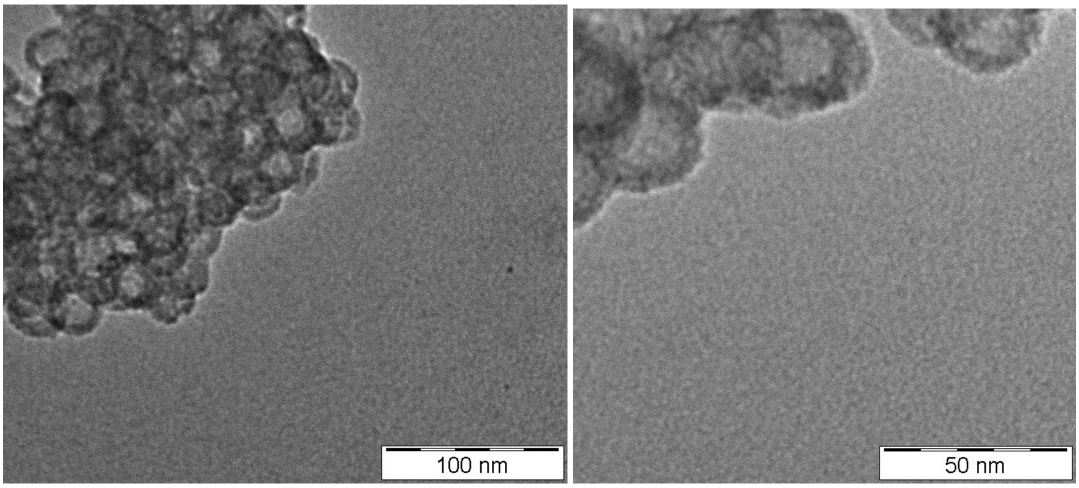

Figure 3: Transmission electron Microscope (TEM) image of CsAl-MCM-41

The surface area, pore volumes and pore size distribution of the porous material can be measure by N_2 adsorption-desorption isotherm analysis (Möller and Bein, 2017)

. The calcined Sample CsAl-MCM-41 was further characterized by N_2 adsorption isotherm which is shown in (Fig. 4).

Table 2: Physical Characteristic of CsAl-MCM-41

Si/Al ratio	**BET surface Area (m^2g^{-1})**	**Pore Volume (cm^3g^{-1})**	**Pore size (nm)**	**d-spacing (nm)**	**TEM (nm)**
20	425.04	0.909	28.7	28.6	28.9

The isotherm exhibited a type IV adsorption isotherm (Yongju *et al.*, 2017). The adsorbed N_2 volume at relative pressure 0.2-0.3 indicates the existence of mesoporosity of the calcined CsAl-MCM-41 material. The pore size distribution, which was calculated from the adsorption curve using BJH model shows an average pore size of about 28.7 nm and pore volume 0.909 cm^3g^{-1}. However, this material exhibit high surface area up to 425.04 $cm^{-2}g^{-1}$ as shown in Table 2. Though, the silicon to aluminium ratio is 20.

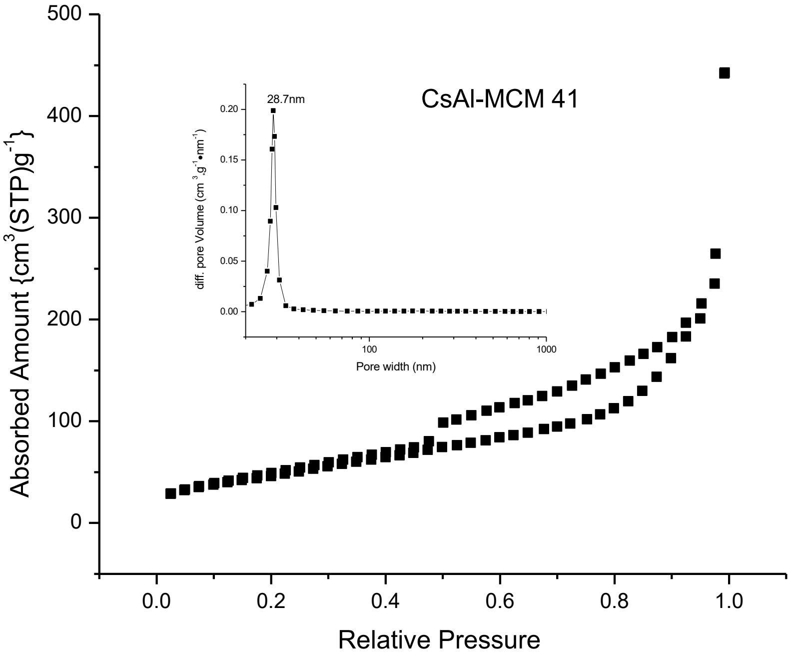

Figure 4: Nitrogen adsorption-absorption Isotherms

The TG curve of mesoporous (CsAl-MCM-41) material shown in the figure 5; the TG curve revealed approximately 20% loss of weight at > 465 ° C, with broad and intense endothermic signal at 134 ° C and 465 ° C. These signals were assigned due to desorption of water and organic surfactant respectively. However, above 465 – 900 ° C indicating no further structural collapse. Based on these data above, a temperature up to 550 ° C was chosen for calcination of the sample. This help in the removal of the surfactant particles from the synthesized catalyst (Yongju *et al.,* 2017).

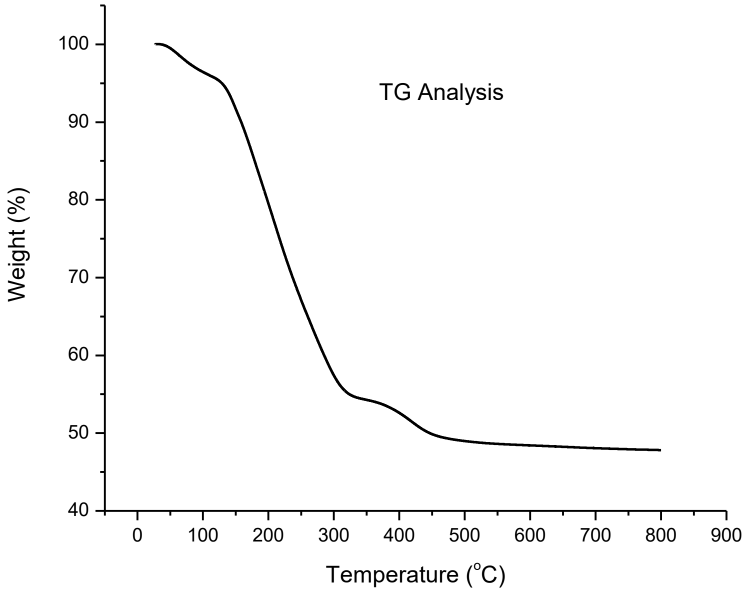

Figure 5: Thermal Gravimetric analysis of CsAl-MCM-41

Conclusion

This shows that high quality Cesium aluminosilicate mesostructured (CsAl-MCM-41) materials, having spherical pores shapes have been synthesized at 100 ° C using hydrothermal process. The pore obtained lies between 25-30nm, however, this could be effective in molecule sieving process. The incorporation of Aluminium (Al) and Cesium (Cs) in the framework has adequately improved its catalytic application. The material also exhibited high thermal stability with free structural collapse as indicated by thermal gravimetric analysis. This important property would help to catalyze reactions under extreme conditions.

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