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Comparative synthesis of mesoporous MgO-MoO₃ catalyst for potential industrial application

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The elevated interest in new materials as porous catalyst supports demands alternative strategies to improve yield of these systems through simple synthesis methodologies. In this work, different porous materials of MgO-MoO₃/SBA-15 were synthesised at air, oven and microwave conditions to investigate and identify the best method for producing high surface area MgO-MoO₃/SBA-15 catalyst. The results showed successful synthesis of mesoporous SBA-15 with homogenous dispersion of MgO-MoO₃ nanocatalyst within the SBA-15 framework. The extent of crystallisation, the pore distribution and surface area was dependent on the crystallisation conditions adopted. The channels of the porous MgO-MoO₃/SBA-15 network from the oven dry module were highly ordered, distinct and parallel. The oven drying crystallisation process module also yielded catalyst with surface area about ten folds higher than that of the air dry processes indicating that a given process module can be tailored for specific industrial application. The results also suggest that longer crystallisation time at temperatures in the range of 100 °C favours the formation of uniform pore structure with high surface area.

Key words: Catalyst, SBA-15, Mesoporous, Crystallisation, XRD, MgO, MoO₃, TEM.

Introduction

Mesoporous molecular sieves have received widespread interest in research because of their vast application in catalysis, adsorption, encapsulation for drug delivery, photonics [1-6]. The use of several porous catalyst systems, either homogenous or heterogeneous has been proposed, investigated and found to provide effective surface area for speeding and improving process yield [3,7,8]. Some heterogeneous catalysts include alkaline earth oxides, metal oxides supported alkali or alkaline earth metals, basic zeolites and hydrotalcites and their catalytic activity have been shown to depend on the alkalinity including several variables such as temperature and catalyst type [9, 10].

SBA-15 a mesoporous material, has high ordered pores with thicker pore walls and two dimensional hexagonal structure and is usually synthesised using triblock-copolymer structure directing agent in an acidic medium [11]. The porous medium of SBA-15 however is deficient in active sites necessary for reactive reaction and they are usually functionalised by doping or incorporation of heteroatoms such as Ti, Zn, Al into the mesoporous silica framework [11]. It is suggested that there is a leverage among the catalytic

The surfactant template effectiveness as a catalyst support has been shown to be affected by several variables including the crystallisation methods and time [16-19]. In this work three methods (room temperature conditions, oven and microwave heating) were used to prepare novel MgO-MoO/SBA-15 catalyst systems and we show that the crystallisation conditions (temperature and time) has a tremendous effect on the surface area and pore distribution of the composite catalyst. The morphology and texture of the bare SBA-15 template and the MgO-MoO₃/SBA-15 solid catalyst will be characterised and compared using powdered X-ray diffraction (XRD), optical microscope, transmission electron microscopy (TEM), Nitrogen porosimeter and Fourier transform infrared spectroscopy (FTIR). Elemental analysis of the bulk weight percentages of the compounds presents were measured from the ICP-AES.

Experimental

Materials

All the chemicals: pluronic copolymer (P123) and tetraethyl orthosilicate, 2M HCL solution, ammonium

properties of the metal oxides, the high surface area of the surfactant template, the high mechanical and temperature stability of the surfactant template leading to better activity as observed by Sharma and coworkers using SBA-15 support [11-15].

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heptamolybdate, magnesium nitrate of analytical grade were obtained from Sigma Aldrich, London, United Kingdom (UK). The SBA-15 template was prepared following previously reported procedures [20, 21]. 8g of pluronic copolymer was dissolved in 60 ml of deionised water in a 500 ml beaker and 250 ml of 2 M HCl solution was added. This mixture was stirred at a temperature of 40 °C until a homogenous mixture was formed. Under continuous stirring, 18.6 ml of tetraethylorthosilicate was added to the pluronic copolymer solution. The resultant gel was stirred at 40 °C for 24 hrs followed by the three different crystallisation procedures: batch samples were air dried at room temperature for 48hrs, oven dried in a Binder electrical oven at 100 °C and microwave dried in a Samsung ME731 microwave at 500 W for two minutes in order to observed the effect of temperature on the physico-

chemical properties of the template and the catalyst systems. After each of the crystallisation process, the solid product was filtered and washed with deionised water. The solid filtrate from all the three different process routes were then dried in air at room temperature and calcined at 550 °C for 6 hrs to achieve the SBA-15 support.

Varying amounts of MgO-MoO₃ (2.6 wt%, 10 wt %) was prepared by loading the SBA-5 template with precursor solutions of both Mg(NO₃)₂ and (NH₄)₆Mo₇O₂₄. After impregnation (loading), the samples were dried overnight at 100 °C and calcined at 550 °C for 6 hrs to enable the Mg(NO₃)₂ and (NH₄)₆Mo₇O₂₄ compounds to decompose to their metal oxides within the porous framework of SBA-15.

Characterization

Powder X-ray diffraction (XRD) patterns were collected on a XPERT-PRO diffractometer (PANalytical BV, Netherlands) using CuK_{α} (35 kV and 50 mA) and scans in the 2 θ range 30 ° \leq 2 θ \leq 90 ° with 0.04 step size 1.00 seg/step at room temperature. The phases in the samples were identified with the help of X'Pert Highscore Plus database software.

The morphology of the batch samples were analysed with Meiji MT8100 optical microscope at magnifications 50x under the different experimental conditions.

The texture and morphology of the bare SBA-15 and the MgO-MoO₃-SBA-15 catalyst systems were observed with the Philips CM 100 transmission electron microscope operated at 100 KV. Before the imaging, the samples were dispersed in H_20 using sonication and subsequently deposited on carbon-coated copper gold.

Porosity and surface area were measured using Quantochrome NOVA 4200e instrument by N_2 adsorption using Novawin v11.0 analysis software. Samples were degassed under vacuum at 120 °C for 24 hours prior to analysis. Adsorption and desorption isotherms were recorded at -196 °C. BET surface areas were calculated over the relative pressure range 0.05-0.5 where a linear

relationship was observed. Mesopore diameters were calculated applying the BJH method to the desorption branch.

The surface chemistry of the porous silica supports were investigated with Magna-R 750 Fourier Infra-red absorption spectrometer manufactured by Nicolet Instrument Co. of USA. Elemental analysis was performed using a Thermo-Fisher iCAP 7000 inductively-coupled plasma atomic emission spectrometer (ICP-AES), calibrated to a magnesium standard (1000 ppm, Sigma Aldrich) diluted to give a calibration curve of 1, 5, 10, 50, 100 ppm and an R^2 value of 0.9998. The magnesium content was directly measured from the inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Results and Discussion

XRD patterns of the bare SBA-15 support template and MgO-MoO₃ doped SBA-15 catalyst systems with 2.6 wt% Mg(NO₃)₂ and 10 wt% (NH₄)₆Mo₇O₂₄ under varying crystallisation conditions are shown in Fig. 1 and Fig. 2 respectively. In Fig. 1, the low angle X-ray diffraction pattern shows the characteristic pattern of SBA-15 and confirms the presence of the hexagonal pore structure with the presence of the d_{10} reflection representing the 2D symmetry of the structure.

The differences in peak intensities as observed in Fig.



Fig. 1. Low angle XRD patterns for SBA-15 silica for oven dried, air dried and microwaved crystallisation process.



Fig. 2. XRD patterns of MgO-MoO₃/SBA-15 catalyst support: for oven dried, air dried, microwaved sample.

1 is indicative that the three process schemes results in different morphologies with resultant differences in crystallinity, particle and particle sizes. Fig. 2, shows the wide angle XRD diffractograms of bare SBA-15 loaded with 2.6 wt% Mg(NO₃)₂ and 10 wt% (NH₄)₆Mo₇O₂₄. Characteristic XRD peaks are observed, indicating the presence of crystalline nanoparticle of MgO and MoO₃ within the pore structure of SBA-15 network. The characteristic XRD peaks at 20 angles of 34.3° and 49.2 ° were observed for all the three crystallisation condition (air, oven and microwave drying) and were ascribed to MoO₃. The peaks at 20 angles of 47.3° and 54.1° were assigned to MgO. The appearance of these peaks suggests that the MgO and MoO₃ nanocrystallites were formed after thermal decomposition of the magnesium and molybdenum precursor solutions, confirming successful impregnation of nanocrystals of the catalyst compounds into the channels of the SBA-15. In addition to the characteristic peak of MgO and MoO₃, there were characteristic XRD peaks at 20 equal to 31.4°, 57.9°, 59.5° which is assigned to MgMoO₄ perovskite. The MgMoO₄ complex formation compound is due to the reaction of MgO with Mo within the SBA-15 network and on the surface during the crystallisation processes [22-26]. The solid reaction between MgO and MoO₃ is reported to enhance stability of the solid catalyst by preventing leaching of the catalyst components [27-29]. It is also observed that, the characteristic peaks of the catalyst compounds are much intense for the air dry processing method in comparison to the 'oven and microwave dry processing methods. This is an indication that the catalyst mixed compounds of MgO-MoO₃ are homogeneously and well dispersed in the SBA-15 pore network of the air dried samples after encapsulation. The higher peak

intensity at 2θ equal to 39° of the air dried samples in Fig. 2, also indicates that the process temperature and time impacts on the morphology, pore structure, dispersion of the catalyst compounds and their crystallinity [30, 31].

The crystallinity of the MgO-MoO₃/SBA-15 catalyst system after loading was determined using the X'Pert High Score Plus Database Software. It was observed that the air dried crystallization process had a high crystallinity of 63.40% followed by the microwaved method of 15.12% and the oven dried process of crystallinity of 11.47% indicating the approximate differences in the amount of the catalyst species confined with the pore structures of the SBA-15. This underpins the differences in the morphological and pore structures of the various processing procedures. The impregnation of the catalyst compounds into the SBA-15 pore network under various batch process methods were also observed with optical microscopy as seen in Fig. 3. The SBA-15 network is observed in Fig. 3(a-c). The optical microscope shows the presence of visible texture due to the alignment of molecules with different mesophases thereby showing difference in textures. In Fig. 3(a), a highly homogenous dispersion of the nanocrystallites is seen attached to the SBA-15 framework and this is ascribed to the loaded 2.6 wt% MgO-10 wt% MoO catalyst. The pores within the SBA-15 network are however dispersed suggesting bigger and wider channels within the framework. The SBA-15 support network was seen with large voids/ cavities between them. This is an indication of the formation of wider channels in comparison to the air and microwave dry processes.

Fig. 4 presents TEM images of bare SBA-15 for the different porous structures consisting of a parallel array



Fig. 3. Optical Micrograph of MgO-MoO₃-SBA-15 catalyst support (a) air dried (b) oven dried (c) microwave dried.



Fig. 4. TEM Micrograph of bare SBA-15 support (a) air dried (b) oven dried (c) microwave dried.



Fig. 5. TEM Micrograph of SBA-15 template loaded with MgO-MoO₃ nanocrystals using oven dried procedures (a) 1D parallel Channels (b) 2D Hexagonal Structure.



Fig. 6. N_2 adsorption desorption isotherm for the oven and microwaved dried process.



Fig. 7. BJH plots showing the pore size distribution of the various crystallisation process.

of straight channel as seen in Fig. 4(a-c). Well crystallised and defined channel morphology is also seen in Fig. 4(b) (oven dried) suggesting a wider pore channel structure than that of the air and microwave batch process. Fig. 5 shows TEM images of the MgO-MoO₃-SBA-15 catalyst surfactant support. The absence of dark spots in Fig. 5(a) indicates that the catalyst compounds are well dispersed over the support surface. The absence of dark spot in Fig. 5(b) indicates the absence of large agglomerates of the catalyst samples.

 Table 1. Structural analysis data for SBA-15 air crystallisation process.

	Average surface area	Average pore volume	Average pore diameter
Before Loading	2557 m ² /g	3.3 cc/g	3.4 nm
After Loading	39 m ² /g	0.3 cc/g	9.8 nm

Table 2. Structural analysis data for oven dried process.

	Average surface area	Average pore volume	Average pore diameter
Before Loading	$263 \text{ m}^2/\text{g}$ $8313 \text{ m}^2/\text{g}$	0.370 cc/g	3.93 nm
After Loading	8313 m/g	44.0 CC/g	5.00 mm

Table 3. Structural analysis data for microwaved process.

	Average surface area	Average pore volume	Average pore diameter
Before Loading	334 m²/g	0.5 nm	3.9 nm
After Loading	263 m ² /g	0.4 nm	9.8 nm

The N_2 adsorption desorption isotherms of the oven and microwave dried materials before loading are observed in Fig. 6. Both the oven and microwaved dried processes show the H1 hysteresis loop with the characteristic type IV isotherm typical of mesoporous materials. There is however, a constriction in the hysteresis loop of the oven dried process as compared to the microwaved process. This could be associated with a decrease in the pore size of the oven dried process compared to the microwaved [32].

The mesoporous pore size distributions for the various crystallisation processes before loading the precursor solution are evaluated from the BJH plots in Fig. 7. From the graph, it is observed that there is no increase in the pore size for the oven dried and the microwaved processes. However, a sharp increase in the pore size distribution of the air dried process is observed. This could be attributed to the lower temperature at which the air dried process was done (25C room temperature).

Table 1, Table 2 and Table 3 shows the structural analysis data obtained from the porosimetry for the air, oven, and microwave crystallisation before and after loading the precursor solution, respectively. Comparatively from Tables 1, 2 and 3, it is observe that the air dried process gives a higher surface area before loading followed by microwaved process then the oven dried process. After loading and calcination of the precursor solutions for the formation of nanocrystallites MgO·MoO₃, the oven dried process shows the highest surface area followed by the microwaved process then the air dried process. This suggests that the bare SBA-15 of the air dried crystallisation before loading had smaller particle sizes comparatively while the oven dried process after





Fig. 9. FTIR spectra for MgO-MoO₃-SBA-5 catalyst under the various crystallisation processes.

loading and calcination had smaller particles as observed also in the XRD pattern in Fig. 1. This results suggest that a specific synthesis route can be used for specific industrial application that fits the pore characteristics measured.

Fig. 8 illustrates the FTIR spectra of the different crystallisation process for bare SBA-15 support. In all the methods the bare SBA-15 spectra exhibited similar features. The strong bands at 1,100 and the small bands around 800 cm⁻¹, represent the characteristics of the asymmetric and symmetric modes of Si-O-Si groups respectively confirming that the SBA-15 is made of silica groups [33, 34]. The band at 960 cm^{-1} is assigned to Si-OH stretching modes of non-condensed Si-OH groups and the band at 465 cm⁻¹ is due to bending of the O-Si-O groups. Weak absorption band is observed for all the process methods around $1625-1750 \text{ cm}^{-1}$. This is ascribed to traces of the organic pluronic copolymer used as template directing agent that results in the overlap of the C = O and O-H bands as observed [35]. The broadband of absorption between 3000 and 3,750 cm⁻¹ corresponds to molecular water hydrogens bonded to each other and to Si-OH groups and are assigned to stretching vibrations of O-H and Si-OH

Table 4. Elemental	analysis	of various	crystallisation	processes
using ICP-AES.				

	%Mg	%Mo
Oven dried	0.404	8.806
Air dried	0.141	7.853
Microwaved	0.006	6.292

bands [33, 34].

The spectra for the impregnated SBA-15 are depicted in Fig. 9. It is observed that only one distinct IR band occurs at 1630 cm^{-1} , which is due to H-O-H bending vibration of water absorbed in the pores and on the surface of SBA-15 network [33-36]. This suggest that the traces of the copolymer is completely eliminated during calcination process for the formation of the nano-catalyst.

The absence of any visible additional band apart from those associated with bare SBA-15 is an indication that there was no significant chemical interaction between the nano-catalyst and silica matrix [33-35].

The elemental bulk weight percentages for the compounds present are determined for the oven dried, air dried and microwaved process after loading 2.6 wt% $Mg(NO_3)_2$ and 10 wt% $(NH_4)_6Mo_7O_{24}$ precursor solutions as shown in Table 4. From the table 4, it is evident that there is a considerable decrease in the weight percentages of Mg species and Mo species per the varying crystallisation processes. However, the microwave process shows a huge decrease in the Mg weight percentage. This suggest the evaporation of more Mg species at that crystallisation method.

Conclusions

The feasibility of using room temperature, oven and microwave drying conditions to synthesis mesoporous MgO-MoO₃/SBA-15 catalyst has been successfully investigated for possible industrial applications. XRD diffraction peaks confirmed the presence of hexagonal structure with the presence of d_{10} reflections representing the 2D symmetry of the SBA-15 support and the presence of crystallites of MgO-MoO₃ mixed catalyst within the SBA-15 support framework.

Optical micrograph images suggest higher amount of crystalline catalyst species embedded within the pore framework of the air dried process. This suggest that the pore size influences the distribution of the MgO- MoO_3 catalyst compound which is also influenced by the process method and process temperature used. The TEM images revealed ordered parallel channels of bare SBA-15 support. FTIR analysis confirmed that the SBA-15 network is made of silica based compounds.

The extent of crystallisation, the pore distribution and surface area was dependent on the crystallisation conditions adopted. The channels of the porous MgO- MoO₃/SBA-15 network from the oven dry module were highly ordered, distinct and parallel. The oven drying crystallisation process module also yielded catalyst with surface area about ten folds higher than that of the air dry processes indicating that a given process module can be tailored for specific industrial application. The results also suggest that longer crystallisation time at temperatures in the range of 100 °C favours the formation of uniform pore structure with high surface area. Porosimetry structural data suggest that the different synthesis route can be tailored for specific industrial applications.

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