

The characteristics of copper containing SBA-15 prepared by impregnation and pH adjustment methods and their activities for N₂O decomposition

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ABSTRACT

Two types of Cu-SBA-15 catalysts were successfully prepared by impregnation and by pH adjustment methods. All synthesized materials have been characterized by XRD, Nitrogen adsorption-desorption, and TEM. After the impregnation of copper, the unit-cell, specific surface area and pore volume of SBA-15 were found to decrease, while the formation of CuO deposited on the framework was detected. On the contrary, the catalyst prepared by pH modification method indicated the increase of unit-cell, surface area, pore volume, and wall thickness after the incorporation of the copper ions on SBA-15 and copper atoms were substituted into the framework of the SBA-15. Series of N₂O decomposition experiments were carried out using the catalysts. Cu/SBA-15 samples prepared by pH adjustment method showed higher catalytic activity than Cu-SBA-15 samples prepared by impregnation method.

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INTRODUCTION

Due to the increasing concern over environmental issues, studies on N₂O have oriented towards the development of catalytic systems for its elimination. Various types of catalysts have been reported to be active for the decomposition of nitrous oxide. Cu-SBA-15 is one of those materials showing better prospects for application as catalyst for N₂O decomposition [1]. However, the catalytic performance of the metal depends on various parameters such as loading, dispersion, and method used for its deposition [2]. High copper dispersion in Cu-SBA-15 also shows interesting properties for the hydrogenation of dimethyl oxalate (DMO) to ethylene glycol [3]. Usually Cu-SBA-15 catalysts are prepared by wet impregnation methods in aqueous or organic medium. Even though, the impregnation methods were found to be effective, such an approach has been found to reduce the textural properties of the mesoporous framework as well as cause irregular distribution of active sites [4, 5].

Nevertheless, it is very difficult to introduce the metal ions into the framework of SBA-15 by direct synthesis route due to the difficulties in the formation of metal-O-Si bonds under the strong acidic conditions. However, some authors have reported successful direct methods to incorporate different heteroatom into SBA-15 structure. Chen *et al.* [6] reported a successful direct method to prepare Ti-SBA-15 by hydrothermal procedure at pH 1.8 and titanium chloride was added after prehydrolysis of tetraethyl orthosilicate. Li *et al.* [7] prepared highly ordered mesoporous Al/SBA-15 materials that were directly synthesized by a controlled hydrolysis approach in which the hydrolysis and condensation rates of silicon and aluminium precursors were finely controlled to match each other in the presence of fluoride. Shah *et al.* [8] also reported that incorporation of Sn in SBA-15 framework was successfully achieved by changes in the pH conditions through adjusting the molar ratio of H₂O/HCl within pH value of 1.0 – 1.5. Lou and co-worker [9] prepared Co/SBA-15 through direct synthesis under mild conditions (pH > 2.0) by a pH adjusting method using sodium hydroxide. The Co/SBA-15 sample obtained at pH 3.0 gave the best structure. Aguado *et al.* [10] combined the incorporation of aluminium and chromium on SBA-15 structure (Si/Al = 35 and Si/Cr = 66) by a direct route using aluminium

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isopropoxide and chromium nitrate at different pH values (0–3). Meanwhile Dai and co-worker [11] reported cerium incorporation into SBA-15 framework carried out by adjusting the pH. As observed, pH adjusting methods have been used by several authors to enable metal ions to substitute into mesoporous SBA-15 walls. Previously, Cu containing mesoporous silica SBA-15 was synthesized by internal pH-modification method using hexamethylenetetramine (HMTA) as a pH-modifier [12].

The objective of this study is to compare the characteristics of two Cu-SBA-15 catalysts prepared, by impregnation method and by pH adjustment method using HMTA. The synthesized materials were characterized by powder X-ray diffraction (XRD), N_2 adsorption-desorption, TPR, TEM and scanning electron microscopy (SEM) equipped with EDX to analyse the elemental composition. The activities of the Cu-SBA-15 samples for decomposition of N_2O were determined.

Experimental:

Materials:

All chemicals and reagents used in this study were commercially available and used as supplied without further purification. Tetraethyl orthosilicate (TEOS) as silicon source and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) as copper source were purchased from Aldrich and Merck, respectively. Triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (P123, EO_{20} - PO_{70} - EO_{20} ; $M_{AV} = 5800$) supplied by Aldrich was employed as template.

SBA-15 Preparation:

Four grams of P123 were dissolved in 100 mL of HCl solution of different molarity (2.0, 0.10 and 0.005 M) to obtain a clear solution. Then 9.2 mL TEOS was added drop-wise into this mixture while stirring continuously for 24 h at 35°C. The final mixture was transferred into a PP bottle and followed by hydrothermal treatment at 100°C for 2 days. The solid product was filtered, and then washed with distilled water, dried and calcined at 550 °C for 6 h.

Cu-SBA-15 Preparations:

Cu-SBA-15 preparation by impregnation:

Exactly 5.0 g of the calcined SBA-15 was immersed in an aqueous copper nitrate solution at various Si/Cu molar ratio (10, 30, 50 and 70) under stirring for 3 h. After filtration, the solid product was dried at 80 °C overnight and calcined at 450 °C for 4 h.

Cu/SBA-15 Preparations by the pH adjustment using HMTA:

Cu/SBA-15 with different Si/Cu molar ratios were prepared as follows: 2.0 g of P123 was dissolved in 100 mL of 0.1 M HCl solution until a clear solution is obtained. The acidic solution of $Cu(NO_3)_2 \cdot 3H_2O$ (to obtain Si/Cu molar ratios of 10, 30, 50, and 70) and 9.2 mL of TEOS was added drop-wise into this mixture under continuous stirring. After 6 h, HMTA (HMTA/Si molar ratio 1:10) was added into the mixture. The final mixture was stirred for 24 h at 35°C and transferred into a PP bottle and then undergoes hydrothermal treatment at 100°C for 2 days. The resultant solid product was filtered, washed with distilled water, dried and calcined at 550°C for 6h.

Characterisation:

X-ray powder diffraction (XRD) pattern for the calcined samples were recorded with an X'Pert PRO XRD diffractometer using $CuK\alpha$ ($\lambda = 0.1541$ nm). The lower and wider scan ranges were 0.5 – 5° and 10 – 80°, respectively, and accumulated using 0.016° step size. N_2 absorption-desorption experiment was conducted at –196 °C using ASAP 2020. Prior to the experiment, the sample was outgassed at 200 °C for 6 h. Transmission electron microscopy (TEM) characterization of the samples was carried out using an FEI Tecnai G2 instrument.

N_2O decomposition:

The catalytic experiments for N_2O decomposition were carried out in an alumina tube (4.76 mm i.d.) micro-reactor. Amount of 500.0 mg sample of supported catalyst was filled into the reactor to form a catalyst bed. The reaction temperature was monitored by a K-type thermocouple inserted inside the catalyst bed. The reaction unit was equipped with mass flow controllers and product analysis was performed with on-line gas chromatograph (MicroGC 3000 series) equipped with two columns in series (molecular sieve 5A and OV-1 column) and TCD detector. The catalyst bed was heated to 400 °C in a 25 mL/min helium gas flow and held at that temperature for 1 hour. The reaction gas composed of 1% N_2O in helium at a total flow rate of 100 mL/min.

RESULT AND DISCUSSION

Elemental Analysis:

Table 1 summarizes elemental composition of Cu in SBA-15 samples prepared by the impregnation method and pH adjustment method. The amount of copper incorporated was higher for Cu-SBA-15 impregnation samples compared to Cu/SBA-15 pH adjustment method. This indicates that lesser copper species exist in SBA-15 under pH adjustment preparation condition. The addition of HMTA increased the pH value from 3.5 to 4.8 after hydrothermal process due to the decomposition of HMTA.

Table 1: Element analysis of Cu containing SBA-15 samples

No.	Samples Cu:SBA-15 (molar ratio)	pH _c value	Cu loading (wt. %)	EDX (% atomic)			Atomic ratio (Si/Cu)
				Cu	Si	O	
A. Impregnated method preparation							
1	Cu-SBA-15 (1:70)	-	1.44	0.58	32.54	66.88	56
2	Cu-SBA-15 (1:50)	-	1.96	0.85	32.31	66.84	38
3	Cu-SBA-15 (1:30)	-	3.51	1.12	31.91	66.97	28
4	Cu-SBA-15 (1:10)	-	9.53	3.46	30.82	65.72	9
B. pH adjustment method preparation							
5	Cu/SBA-15 (1:70)	3.5	0.89	0.39	30.54	69.07	78
6	Cu/SBA-15 (1:50)	3.9	1.31	0.55	30.51	68.94	55
7	Cu/SBA-15 (1:30)	4.3	2.48	1.01	30.04	68.95	30
8	Cu/SBA-15 (1:10)	4.8	4.06	2.46	29.82	67.72	12

XRD Analysis:

Small angle powder XRD patterns of Cu-SBA-15 impregnated samples exhibited three well-resolved diffraction peaks in the 2θ range of $0.5 - 5^\circ$, which correspond to the diffraction of (100), (110), and (200) planes, respectively as shown in Figure 1A. This indicates the good mesoscopic order and characteristic hexagonal features of SBA-15 are maintained in Cu-SBA-15 samples. However, when the amount of copper incorporation in SBA-15 was increased, the intensity of (100) reflection decreased. Beside that at Higher Cu/Si molar ratio the 2θ values of peak (100) slightly shifted to a higher value compared to that of pure SBA-15, indicating that the unit-cell decreased after the impregnation of the copper.

Meanwhile Figure 1B shows the small angle XRD patterns of Cu/SBA-15 prepared using pH adjustment by addition of HMTA for different Cu/Si molar ratio. All the Cu/SBA-15 samples also have typical highly ordered hexagonal structure, indicating that the preparation method does not destroy the characteristic structure of SBA-15. With higher Cu/Si molar ratio loading, the 2θ values of peak (100) shift to a lower value compared with that of pure SBA-15, indicating that the unit-cell increased after the incorporation of the copper ions. Previous reports stated that the lengths of Cu–O bonds are larger than that of Si–O bond, thus their incorporation into the framework of SBA-15 may increase the unit-cell parameter a_0 [13, 14]. However, the long-range ordering of Cu/SBA-15 is gradually lost with an increase in Cu/Si molar ratios. This may be due to an increasing number of defect sites and bond strain of these materials that is evidenced by the decreasing intensities of the (100) peak, and the destruction of the 110 and 200 peak index as observed on samples Cu/SBA-15-(1:10) in Figure 1B(e).

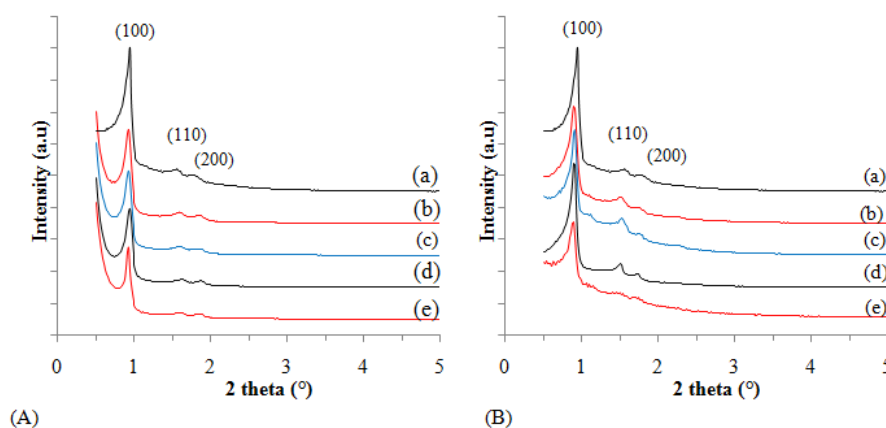


Fig. 1: The small-angle XRD pattern of Cu/SBA-15 samples prepared by impregnation (A) and pH adjustment (B) method at different Cu:Si molar ratio: (a) SBA-15, (b) Cu/SBA-15-(1:70), (c) Cu/SBA-15-(1:50), (d) Cu/SBA-15-(1:30) and (e) Cu/SBA-15-(1:10).

Figure 2A shows the wide-angle XRD patterns Cu-SBA-15 samples prepared by impregnation method at different Cu:Si molar ratio (1:70, 1:50, 1:30 and 1:10) compared to pure SBA-15. Diffraction peaks were

detected for the samples that were synthesized in the impregnation method. The existence of a peak in the XRD pattern refers to the presence of CuO formation in SBA-15. The intensity for each sample is significantly related with the composition of Cu as detected using elemental analysis. This indicates that copper deposits on the framework of SBA-15 samples. For Cu/SBA-15 samples prepared by pH adjustment method in Figure 2B shows the results that are slightly different compared to samples that were produced using the impregnation technique. The diffraction peaks formed has low intensity for a sample of low copper metal loading. This may be due to the formation of non-crystalline CuO on the surface, or the substitution of copper atom in the framework of the SBA-15. However, the crystallinity of copper increased proportionally with the increase of metal loading in the synthesis solution as clearly seen for Cu/SBA-15 1:10. This is likely due to the formation of CuO particles on the surface and within the framework of SBA-15.

Textural properties:

The textural properties of pure SBA-15 with the copper supported SBA-15 catalysts prepared by impregnation and pH adjustment techniques are summarized in Table 2. It was clearly found that when SBA-15 silica was impregnated with Cu, the surface area and pore volume were gradually decreased compared that of pure SBA-15. This could also be due to pore blockage by copper species [8], suggesting that copper particles were formed in the channel of SBA-15 and occupied pore space. The wall thickness also decreased significantly compared to pure SBA-15, probable caused by the placement of CuO on the surface which allows the reduction of the thickness of the wall. However the pore diameter increased compared to pure SBA-15. Increase in the diameter of the pore size may be due to the placement of Cu particles in the pores causes the width of the pore itself.

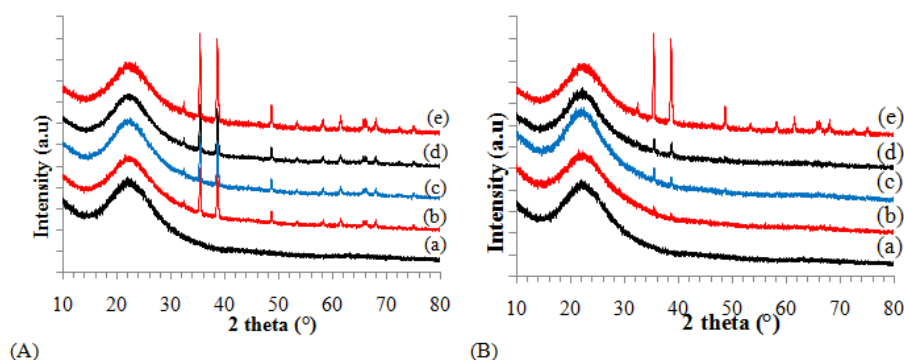


Fig. 2: The wide-angle XRD pattern of Cu/SBA-15 samples prepared by impregnation (A) and pH adjustment (B) at different Cu:Si molar ratio: (a) SBA-15, (b) Cu/SBA-15-(1:70), (c) Cu/SBA-15-(1:50), (d) Cu/SBA-15-(1:30) and (e) Cu/SBA-15-(1:10).

Table 2: Texture properties of Cu containing SBA-15 samples different method preparation

No.	Samples Cu/SBA-15 (molar ratio)	Unit Cell a_0 (nm)*	Surface area (m^2/g)	Pore volume (cm^3/g)	Average Pore size (nm)	Wall thickness (nm)
	SBA-15	10.81	660	0.86	4.69	6.12
A. Impregnated method preparation						
1	Cu-SBA-15 (1:70)	10.67	611	0.55	5.18	5.50
2	Cu-SBA-15 (1:50)	10.67	595	0.54	5.38	5.30
3	Cu-SBA-15 (1:30)	10.60	598	0.54	5.34	5.26
4	Cu-SBA-15 (1:10)	10.56	573	0.54	5.50	5.06
B. pH adjustment method preparation						
5	Cu/SBA-15 (1:70)	11.06	621	0.68	4.52	6.54
6	Cu/SBA-15 (1:50)	11.26	625	0.77	4.43	6.83
7	Cu/SBA-15 (1:30)	11.48	685	0.86	4.67	6.81
8	Cu/SBA-15 (1:10)	11.47	588	0.91	4.95	6.52

* $a_0 = 2d_{100}/\sqrt{3}$

Meanwhile, Cu/SBA-15 prepared by pH adjustment has shown differences in surface area, pore volume and wall thickness, which is generally of higher value. The average pore size was reduced compared to that of pure SBA-15. This is probably due to the substitution of Cu particles in the framework of SBA-15 structure. However, the addition of more Cu in sample preparation materials for Cu/SBA-15 (1:10) resulted in the formation of CuO on the surface, this shows the limitation of substitution and formation of CuO. CuO forms on the surface of SBA-15 and its effects on surface area and wall thickness decreased dramatically. While the

average pore size increased, this clearly shows the sample look a lot like the physical condition of the samples were prepared by impregnation method.

The N_2 adsorption–desorption isotherms for pure SBA-15 and copper supported SBA-15 catalysts prepared by impregnation are shown in Figure 3A. All of the N_2 adsorption–desorption isotherms are type IV in nature according to the IUPAC classification and exhibited an H1 hysteresis loop which is a characteristic of mesoporous solids. The adsorption branch of each isotherm showed a sharp inflection at $P/P_0 = 0.40 - 0.80$, which means a typical capillary condensation within uniform pores. The similar isotherm shape between Cu-SBA-15 and the pure SBA-15 suggests that the uniform mesoporous structure was mostly retained after copper impregnating. The capillary condensation step of the isotherm occurred at a higher relative pressure for Cu-SBA-15 as compared to the pure silica SBA-15, indicating an increase of the average pore sizes after copper loading. The pore size of pure silica SBA-15 was 4.69 nm, obtained from N_2 physisorption, while the pore size of Cu-SBA-15 was 5.18 nm to 5.55 nm. This can be ensured in the pore size distribution diagram (Figure 3B), that show an increase in pore size of a sample of metal impregnated SBA 15 compared to pure SBA 15. The increase of the pore diameter after copper was loaded resulted from the additional layer of copper oxide formed on the SBA-15.

Meanwhile Figure 4A shows the N_2 adsorption–desorption isotherms of the samples of Cu/SBA-15 prepared by pH adjustment. The isotherm of various Cu/SBA-15 samples shows a type IV isotherm with capillary condensation occurring at P/P_0 is 0.4, with H1 hysteresis loops virtually like to that of pure SBA-15. This demonstrates that the mesoporosity of materials is preserved after Cu incorporated into mesoporous SBA-15. Figure 4B indicates the pore sizes distribution of Cu/SBA-15 samples remain narrowly distributed, which in turn shows that the incorporated Cu is well dispersed throughout the SBA-15. In addition, there is another narrow pore size distribution in all samples that was absence in the samples prepared by impregnation method. This feature highlights the differences in the preparation method. It indicate the samples prepared by pH adjustment method possesses microporous amorphous nanoparticles (plugs) in the uniform mesoporous structure.

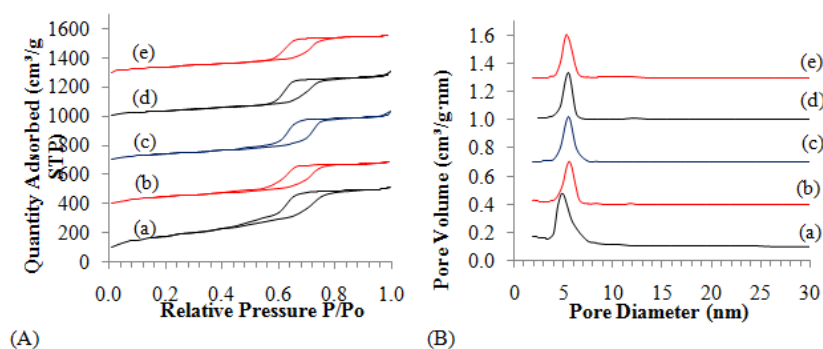


Fig. 3: The isotherm (A) and pore size distribution (B) of Cu/SBA-15 samples prepared by impregnated at differences Cu:Si molar ratio: (a) SBA-15, (b) Cu/SBA-15-(1:70), (c) Cu/SBA-15-(1:50), (d) Cu/SBA-15-(1:30) and (e) Cu/SBA-15-(1:10).

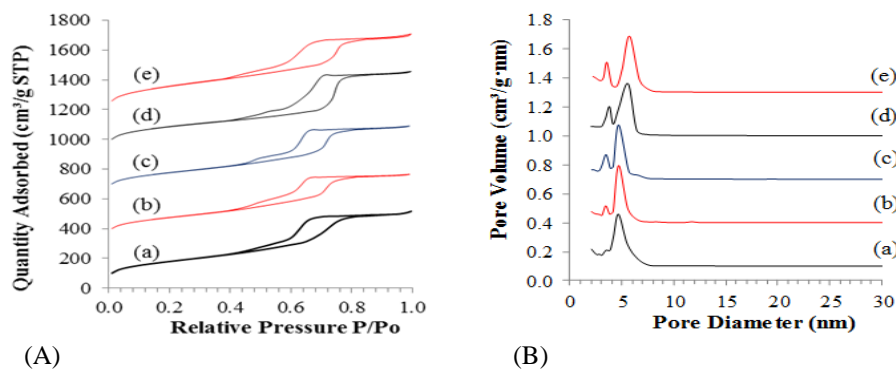


Fig. 4: The isotherm (A) and pore size distribution (B) of Cu/SBA-15 samples prepared by pH adjustment method at different Cu:Si molar ratio: (a) SBA-15, (b) Cu/SBA-15-(1:70), (c) Cu/SBA-15-(1:50), (d) Cu/SBA-15-(1:30) and (e) Cu/SBA-15-(1:10).

TEM image:

Figure 5 presented the TEM image of the different Cu/SBA-15 impregnated with different Cu:Si molar ratio. The micrographs show CuO particles as dark spots on the external surface of SBA-15 being very dispersed and confined to the channels of SBA-15. Large copper particles observed on the impregnated sample Cu/SBA-15 occur as a result of sintering during heat treatment [15]. In contrast, for Cu/SBA-15 samples with pH adjustment method, fewer Cu particles on the external surface of SBA-15 formed compared to that of Cu/SBA-15 samples, as indicated by Figure 6. Meanwhile, it should be pointed out that no observation was made on small particles confined in the channels of SBA-15 on that samples based on dark area spot on the samples. This remarkable difference in particle distribution of the two methods indicates that the pH adjustment method is superior to the impregnation method for obtaining the better dispersed Cu particles.

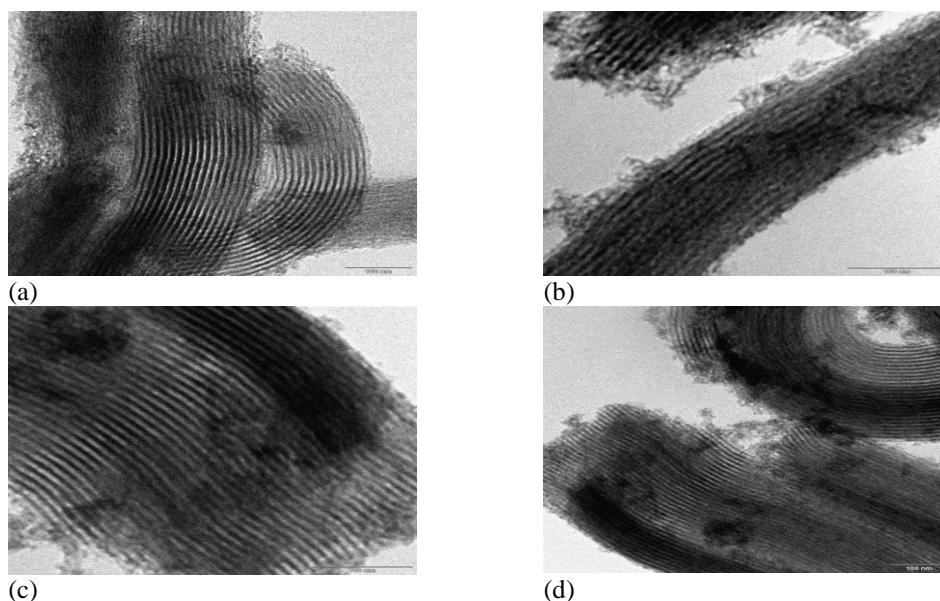


Fig. 5: The TEM image of Cu/SBA-15 samples prepared by impregnation with different Cu:Si molar ratio: (a) Cu/SBA-15-(1:70), (b) Cu/SBA-15-(1:50), (c) Cu/SBA-15-(1:30) and (d) Cu/SBA-15-(1:10).

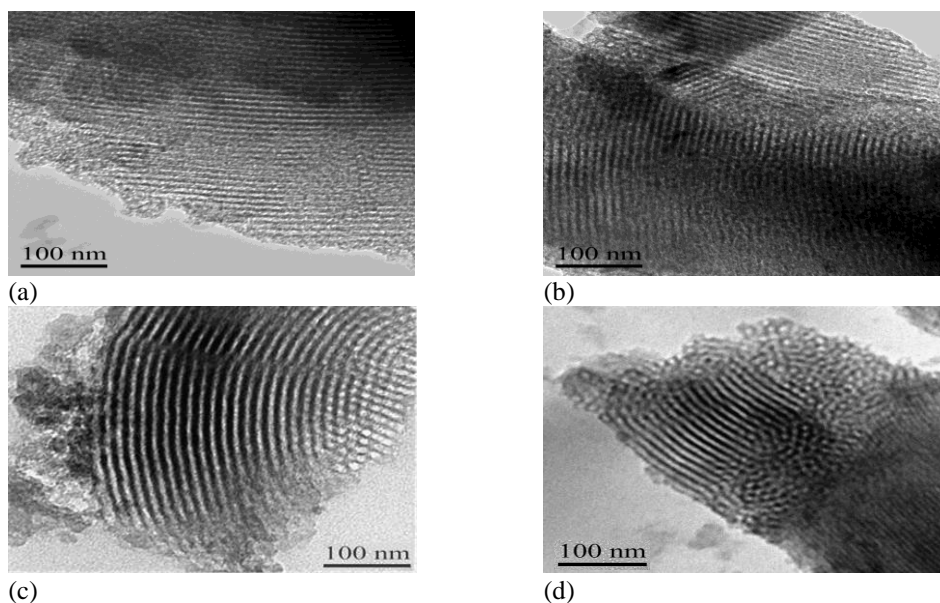


Fig. 6: The TEM image of Cu/SBA-15 samples prepared by pH adjustment method with different Cu:Si molar ratio: (a) Cu/SBA-15-(1:70), (b) Cu/SBA-15-(1:50), (c) Cu/SBA-15-(1:30) and (d) Cu/SBA-15-(1:10).

TPR analysis:

TPR profiles of the Cu-SBA-15 impregnated samples at different Cu:Si molar ratio are shown in Figure 7A. For Cu-SBA-15, two reduction peaks are observed: the first peak corresponds to the first reduction step of CuO ($\text{CuO} \rightarrow \text{CuO}_2$) at temperature range 200–250 °C. Meanwhile at the temperature 300–350 °C, the second peak was detected for attributed to the reduction of intermediate CuO phase ($\text{CuO}_2 \rightarrow \text{Cu}^0$). The high temperature H_2 consumption peak at 345 °C observed for the Cu-SBA-15-(1:10) may result from the direct reduction of aggregated CuO particles to Cu metal and at 255 °C before, shows the reduction of highly dispersed Cu^{2+} in CuO particles to Cu^+ in CuO_2 which is intermediate of CuO. While the rest sample of Cu-SBA-15, an abroad H_2 consumption peak is observed in the temperature range of 150–250 °C, shows the reduction of highly dispersed Cu^{2+} in CuO particles to CuO_2 , then followed by another reduction of intermediate CuO phase (CuO_2) to Cu^0 at 330 °C for the samples. Cu/SBA-15-(1:10) was more difficult to reduce than other preparing sample loading, and required higher temperatures for reduction. This might be cause of contains bulk or aggregate CuO particles that are larger was formed in the catalyst prepared with high Cu loading.

Meanwhile for the Cu/SBA-15 by pH adjustment method at different Cu:Si molar ratio, the TPR profiles are shown in Figure 7B. For Cu/SBA-15-(1:70) and Cu/SBA-15-(1:50), two reduction peaks are observed: the first peak corresponds to the first reduction step of CuO ($\text{CuO} \rightarrow \text{CuO}_2$) at temperature 210°C. Meanwhile at 310 °C, the second peak was detected for attributed to the reduction of intermediate CuO phase ($\text{CuO}_2 \rightarrow \text{Cu}^0$). For high Cu loading in Cu/SBA-15-(1:10), the high temperature H_2 consumption broad peak at 310 °C observed may result from the direct reduction of aggregated CuO particles to Cu metal. But, for Cu/SBA-15-(1:30) shows slightly differences when there was four peaks in observation. The initial peak observed at low temperature (140 °C) corresponds to of small copper clusters on surface reducible, it also can be observed in the sample ratio of 1:50 and 1:70 there are small broad peaks at same temperature. It is happen due to that small copper clusters much easier to reduce compared to aggregate CuO. The second peak was detected corresponds to the first reduction step of CuO aggregated ($\text{CuO} \rightarrow \text{CuO}_2$) at 250°C. Meanwhile at 285 °C, the third peak was detected for attributed to the reduction of intermediate CuO phase ($\text{CuO}_2 \rightarrow \text{Cu}^0$). The final peaks was obtain at 340 °C the reduction peak is attributed to reduction of the barely reducible copper silicates (CuSiO_3) formed by the strong interaction between cooper and the siliceous support.

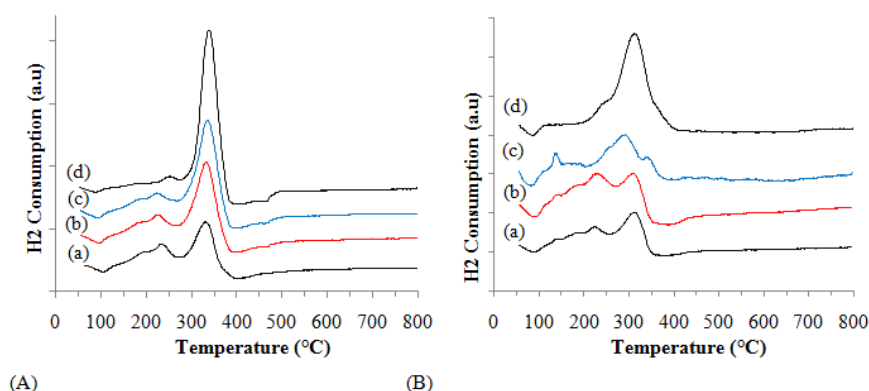


Fig. 7: The TPR profile of Cu/SBA-15 samples prepared by impregnation (A) and pH adjustment (B) method at different Cu:Si molar ratio: (a) Cu/SBA-15-(1:70), (b) Cu/SBA-15-(1:50), (c) Cu/SBA-15-(1:30) and (d) Cu/SBA-15-(1:10).

It is observed that for Cu/SBA-15 prepared by pH adjustment method, the peak position of the first reduction of CuO has significantly shifted to lower temperature, meaning that CuO particles in SBA-15 are more easily reduced to Cu species; opposite to that Cu-SBA-15 impregnated sample in the supported catalysts. Taking into account of the general dependence of the reduction temperature, for Cu substitution in SBA-15, the copper-silica support interaction improving the reduction of CuO to Cu and most likely due to the weakening of copper - silica support interaction. This suggests that the copper particles in impregnated method in SBA-15 was big aggregates of formation CuO with less reducible that contributes to the lower catalytic activity.

Catalytic Activity for N_2O decomposition:

The activity of SBA-15 and Cu-SBA-15 impregnated with different Cu:Si molar ratio was tested for decomposing 1% N_2O in helium through direct decomposition as shown in Figure 8A. The Cu containing samples were found to be significantly more active for the decomposition of N_2O compared to pure SBA-15. In case of Cu-SBA-15 impregnated sample the reaction starts around 400 °C and reaches more than 80 % conversion at 650 °C. For pure SBA-15 sample the reaction only starts around 550 °C, and at a 650 °C only

15% conversion was achieved. At 600 °C, the high loading copper on SBA-15 achieved more than 80 % conversion compared with low Cu loading that show only 40% conversion. This suggests that the catalytic activity is strongly dependent copper loading.

The conversion of N₂O as a function of temperature for Cu/SBA-15 prepared by pH adjustment method at different Cu:Si molar ratio and that for pure SBA-15 are shown in Figure 8B. The Cu containing samples were found to be significantly more active for the decomposition of N₂O compared to pure SBA-15 and compared to equivalent Cu-SBA-15 samples prepared by impregnation method. The Cu/SBA-15 with Cu:Si molar ratio 1:50, 1:30 and 1:10 samples prepared by pH adjustment method shows more than 80 % conversion at 550 °C for. This indicates that these samples are more active than that of Cu-SBA-15 impregnation method samples. As shown in Figure 8B for the Cu/SBA-15 catalysts, the catalyst activity increased as the Cu loading increased from Cu:Si molar ratio of 1:70 to 1:30 and then decreased as the Cu loading increased further from molar ratio 1:30 to 1:10. The result shows that there is a maximum Cu loading (molar ratio 1:30) on Cu/SBA-15 catalysts for the maximum conversion of N₂O. This may occur due the aggregation of the metal into bigger particles, which may then block the openings of the pores and affect the mass transport of reactants to the catalytic sites inside the pores.

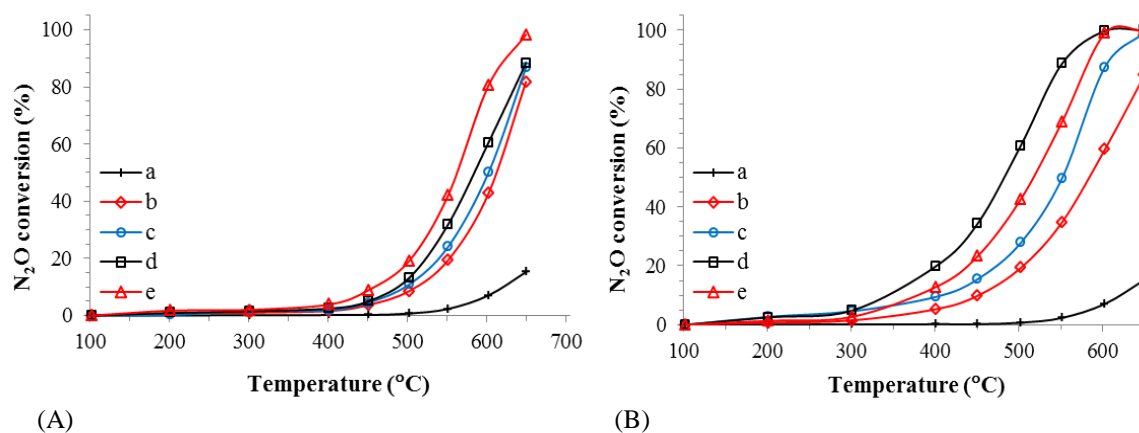


Fig. 8: The catalytic activity for N₂O decomposition on Cu-SBA-15 samples prepared by impregnation (A) and pH adjustment (B) method at different Cu:Si molar ratio: (a) SBA-15, (b) Cu/SBA-15-(1:70), (c) Cu/SBA-15-(1:50), (d) Cu/SBA-15-(1:30) and (e) Cu/SBA-15-(1:10).

Conclusion:

Cu-SBA-15 catalysts were prepared by impregnation and the pH modification using HMTA method under different Cu/Si molar ratio. The Cu/SBA-15 samples prepared by pH adjustment method has lower Cu loading compared to sample prepared by impregnation method using same starting Cu:Si molar ratio. Characterisation results show that unit-cell, specific surface area and pore volume of SBA-15 decreased after the impregnation of the copper and formation of CuO deposited on the framework was detected. Compared to pH adjustment method preparation, the unit-cell, surface area, pore volume and wall thickness increased after the incorporation of the copper ions on SBA-15 and copper atom substituted in the framework of the SBA-15. However, the crystallinity of copper oxide increased proportionally with the increase of metal loading, indicating that CuO formation on the surface happen after the limitation of substitution of SBA-15 framework. Cu/SBA-15 samples prepared by pH adjustment method were found to shows higher activity for N₂O decomposition than Cu-SBA-15 samples prepared by impregnate method.

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