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Study on the HPA immobilisation on Al-SBA-15 support over Brønsted groups

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Abstract

In this article, a significant aspect of Brønsted groups in the preparation of HPA/Al-SBA-15 catalyst by immobilising heteropoly acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPA) to mesoporous Al-SBA-15 support was studied. The crucial factors affected the preparation such as functional groups formed on the support, the use of HPA type for the immobilisation (commercial catalyst or *in-situ* synthetic HPA), and Si/Al molar ratio of Al-SBA-15 were systematically investigated. The prepared catalysts were tested their performance in polar reagent reactions (fructose synthesis was chosen as an example) to show the effect of HPA after the immobilisation. Here we tested the HPA content (by Energy-dispersive X-ray method),

acidity (by temperature-programmed desorption of ammonia method) and the ethyl acetoacetate conversion in fructose synthesis to prove this concept. The other characterisation methods such as small angle x-ray scattering, Fourier-transform infrared spectroscopy, specific surface area and pore volume also showed the properties change of materials before and after HPA immobilisation. It was shown that the HPA/Al-SBA-15 sample prepared by using HPA commercial catalyst and NH_4^+ ion-exchanged Brønsted groups of mesoporous Al-SBA-15 support (Si/Al molar ratio of 15) showed the highest acidity and catalytic activity (ethyl acetoacetate conversion of 93.49 wt%) in comparison to HPA commercial catalyst as well as to the other catalysts. In addition, this catalyst also showed good catalytic stability after five reaction cycles with slightly reduction of activity, suggesting the prospect of employing HPA/Al-SBA-15 catalyst for organic synthesis of polar compounds.

Keywords: Heteropoly acid catalyst, heterogenization, Al-SBA-15, Brønsted, fructose synthesis.

1. Introduction

HPA catalyst in α -Keggin form ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) is a very effective heterogeneous catalyst that has been commercialised for organic synthesis reactions such as hydration and polymerisation in non-polar media [1]. In polar reagents, however, this catalyst is not able to perform the same activity because of its high solubility in such compounds. Fructose, a flavouring material with apple scent, can be synthesised through the acetalisation reaction of polar reagents (*i.e.* ethyl acetoacetate and ethylene glycol), therefore, it is difficult for HPA to be used as a catalyst in this reaction. Recently, immobilising HPA on other solid supports has been demonstrated to be very promising to address this issue. Numerous types

of supports including silica [2-13], titania [14-16], zeolites (Y, USY) [17-19], mesoporous materials (SBA-15, MCM-41) [20-23], carbon [24-26] and graphene oxide [27] have been used to immobilise HPA by encapsulation, tethering and grafting routes. For example, Mukai *et. al.* presented research on a promising catalyst of HPA encapsulated in zeolite Y, thanks to its NH_4^+ or Cs^+ ion-exchanged Brønsted sites [18]. The results showed that if the compensated ions were NH_4^+ or Cs^+ , the process of "trapping" HPA was more effective than other ion types, such as Na^+ and K^+ . However, the pore direction and microporous structure are the mass transport limitation of this catalyst. More recently, it has been shown that SBA-15 materials with long-range ordered mesoporous structure can immobilize HPA inside its pore system [28-30]. In addition, Vinu *et. al.* demonstrated that Al-SBA-15 acidic mesoporous catalysts can dedicate both its acidic nature and mesoporous structure to improve the catalytic performance in fructose synthesis [31]. These results suggested an unreported significant aspect that Al-SBA-15 could immobilize HPA on its surface thanks to its ability to create a bonding between HPA and Brønsted groups. The other functional groups may be hydroxyl or amine (could be created by modification of hydroxyl groups of Al-SBA-15) groups [1].

In this research, the Al-SBA-15 mesoporous material was studied as a support for HPA catalyst. The method to synthesize this material was optimised to determine the role of functional groups and structural properties (Si/Al molar ratio) in HPA immobilisation. The prepared catalysts were applied in the fructose synthesis to confirm the relation between catalyst properties and the catalytic activity.

2. Experimental

2.1. Preparation procedures

2.1.1. Chemicals

The chemicals for HPA/Al-SBA-15 preparation were phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, 99%, Sigma-Aldrich), ammonium nitrate (NH_4NO_3 , 99%, Sigma-Aldrich), ammonia solution (25%, Sigma-Aldrich), tetraethyl orthosilicate (TEOS, 99%, Merck), pluronic (P123, 99%, Sigma-Aldrich), aluminium sulfate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 99%, Sigma-Aldrich), aminopropyltriethoxysilane (APTES, 99%, Sigma-Aldrich), hydrogen peroxide (H_2O_2 , 30-32%, Sigma-Aldrich), phosphoric acid (H_3PO_4 , 85%, Sigma-Aldrich), hydrochloric acid (HCl, 36.5-38%, Sigma-Aldrich), absolute ethanol (99.7%, Sigma-Aldrich), ethyl acetoacetate (>99%, Sigma-Aldrich), ethylene glycol (anhydrous, 99.8%, Sigma-Aldrich), iso-octane (anhydrous, 99.8%, Sigma-Aldrich), and toluene (anhydrous, 99.8%, Sigma-Aldrich). Chemicals were directly used without further purification.

2.1.2. Preparation of Al-SBA-15 support

Al-SBA-15 support (Si/Al molar ratio = 15) was prepared by the typical process as follows: 1.75 g structural directing agent P123 was dissolved in 54 ml deionised water. After 3 h under stirring at room temperature, a clear solution was obtained. 0.48 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 4.5 g TEOS were added to the solution, stirring for 15 h at room temperature. The resulting gel was aged under stirring for another 24 h at 40 °C. The pH of the gel was adjusted to 5.5 by a solution of ammonia 25% and deionised water (1:1 volume ratio). The resulting gel was further aged at 90 °C for 48 h. After that, the solid was filtered, washed with deionised water until pH=7, and dried at 90 °C. P123 was removed from the product by H_2O_2 oxidation agent. 1 g dried solid was added to 50 ml H_2O_2 30% and this mixture was transferred to an autoclave with slow stirring at 100 °C for 24 h. The solid was filtered

and washed with deionised water and then with alcohol. After that, the solid was dried at 100 °C overnight to obtain Al-SBA-15-OH support.

2.1.3. Preparation of HPA/Al-SBA-15

The HPA/Al-SBA-15 preparation method was investigated using the procedures (proc) as described below.

Proc 1- Al-SBA-15-OH support was functionalised with NH_4^+ : 1 g Al-SBA-15-OH was added to 50 ml NH_4NO_3 solution (1.5 M), stirring for 1.5 h at 70 °C. The product was filtered and washed with deionised water until pH 7 was attained. This process was repeated three times. Then, the solid was dried at 100 °C overnight to obtain the sample (Al-SBA-15- NH_4^+).

Proc 2- Al-SBA-15-OH support was functionalised with NH_2 : 3 ml APTES was dispersed in 75 ml anhydrous toluene in a round-bottom flask. The reactor was aerated with argon for 30 min (100 ml/min) to expel the air and moisture. Then the APTES/Toluene mixture was sonicated for 15 min at room temperature. 0.5 g Al-SBA-15-OH support was added to the mixture and refluxed for 24 h at 90 °C under stirring with argon flow. The solid was washed with 20 ml toluene, and then with deionised water until pH 7 was attained. After that, the solid was dried at 70 °C overnight to obtain the sample (Al-SBA-15- NH_2).

Proc 3- HPA commercial catalyst immobilisation: 0.5 g functionalised Al-SBA-15 material was dispersed in a solution containing 0.5 g HPA commercial catalyst dissolved in 20 ml H_2O . The mixture was stirred for 24 h at room temperature. The solid was filtered, washed with a mixture of deionised water and ethanol (50 ml; 1:1 volume ratio), and dried at 110 °C overnight to obtain the sample.

Proc 4- *In-situ* synthetic HPA immobilisation: 0.5 g functionalised Al-SBA-15 material was dispersed in 20 ml H₂O. 0.69 g Na₂WO₄ was slowly added to the mixture. After being stirred for 24 h at room temperature, 0.069 ml H₃PO₄ 85% was added to the mixture. The pH of mixture was adjusted to 2 by adding HCl 0.2 M solution. The mixture was stirred at 95 °C for 3 h in a reflux system. The product was filtered and washed with deionised water until pH 7 was attained, and then the solid was dried at 110 °C overnight.

In this study, eight HPA/Al-SBA-15 samples with different functional groups (OH, NH₂, NH₄⁺) were systematically prepared by using a combination of the above procedures (see Table 1). The HPAS-1, HPAS-2, HPAS-3 samples were prepared with the immobilisation of the *in-situ* synthetic HPA over OH, NH₄⁺ and NH₂ groups of Al-SBA-15 support, respectively. The HPAS-4, HPAS-5, HPAS-6 samples were prepared with the immobilisation of HPA commercial catalyst over NH₄⁺, NH₂ and OH groups of Al-SBA-15 support, respectively. The HPA commercial catalyst was immobilised to the Al-SBA-15 support that has both NH₄⁺ and NH₂ groups on its surface to prepare the HPAS-7 sample. This type of Al-SBA-15 support was also used to immobilize both *in-situ* synthetic HPA and HPA commercial catalyst to prepare the HPAS-8 sample.

2.2. Characterisation

The energy-dispersive X-ray (EDX) spectroscopy was recorded on a JEOL JSM equipment with spectral resolution of 0.126 keV and accelerating voltage of 20 kV. The small angle X-ray scattering (SAXS) diffraction patterns were recorded on a HUT-PCM-Bruker D8 Advance instrument diffractometer system equipped with Ni-filtered Cu Ka radiation (operating at 40 kV, 40 mA, wavelength $\lambda = 0.154$ nm). The specific surface area and pore volume (BET) analysis were measured by an ASAP2010 equipment (Micrometrics-USA).

The sample was degassed under dynamic vacuum at 120 °C for 4 h and then at 350 °C for 9 h before carrying out nitrogen sorption at 77 K. The temperature-programmed desorption of ammonia (TPD-NH₃) spectrums were recorded on an AutoChem II 2920 with temperature varying from 100 to 600 °C, temperature ramp of 10 °C/min and NH₃ flow rate of 30.14 cm³ STP/min. The Fourier-transform infrared spectroscopy (FTIR) spectrums were recorded using an IMPACT-410 (Germany) Infrared Spectrophotometer at room temperature in a range of 4000-400 cm⁻¹ on a thin KBr wafer in which 1% (w/w) of sample was dispersed.

2.3. Catalytic activity

In this study, catalytic activities of prepared HPA/Al-SBA-15 samples were tested in fructose synthesis. In the typical procedure, 3.90 g ethyl acetoacetate, 2.79 g ethylene glycol, 40 ml iso-octane (solvent), 0.1 g tetradecane (internal standard) and 0.20 g HPA/Al-SBA-15 catalyst were mixed in a two necked round-bottomed flask equipped with a magnetic stirrer and a thermometer. A Dean-Stark apparatus with a reflux condenser was used to continuously remove water from the reaction mixture. A small amount of samples were taken at regular time periods to analyse the reaction conversion by an Agilent 7890B gas chromatography equipment with a 25 m x 0.22 mm x 0.25 m capillary column and FID detector. Tetradecane was chosen as an internal standard in the analysis to avoid the effect of solvent evaporation during the reaction process. Ethyl acetoacetate concentration was calculated by establishing a ratio of ethyl acetoacetate and the internal standard (see Formula S1 in research data file).

The best HPA/Al-SBA-15 catalyst sample was reused for 4 reaction cycles and evaluated its catalytic stability. After each cycle, the catalyst was separated from the product by

centrifuged and washed with a mixture of water and ethanol (50 ml; 1:1 volume ratio) under stirring for 30 min. Then, the catalyst was filtered, dried at 110 °C overnight, and charged into the next reaction without further regeneration.

3. Results and discussion

3.1. Characterisation results

3.1.1. EDX results

HPA catalyst can be immobilised on to Al-SBA-15 material by creating linkage with OH, NH₂ and NH₄⁺ functional groups. In addition, HPA catalyst synthesised using HPA commercial catalyst and *in-situ* synthetic HPA will be discussed.

In the case of using *in-situ* synthetic HPA, the HPAS-1, HPAS-2 and HPAS-3 samples were prepared. Their HPA contents are shown in Table 2. The HPA content of HPAS-1 is only 0.12 wt%. It shows that *in-situ* synthetic HPA cannot be immobilised over OH groups of Al-SBA-15-OH support in this experiment condition. By using ion exchange to form NH₄⁺ functional groups on Al-SBA-15-OH support (HPAS-2 sample), the HPA content reaches 13.64 wt%. In comparison to the HPA-1 sample, it is shown that NH₄⁺ can promote the formation of HPA catalyst from precursor substances on the surface of Al-SBA-15-NH₄⁺ material. This result agrees with the result published by S. R. Mukai et. al. that studies the preparation of *in-situ* synthetic HPA immobilised on NH₄⁺ ion-exchanged zeolite Y [18]. In addition, HPA content of the HPAS-3 sample prepared by immobilising HPA over NH₂ functional groups is 31.19 wt%. This result is in a good agreement with the paper published by H. Liu et. al. [20], in which HPA can be effectively immobilised by creating the linkage to NH₂ groups. Therefore, the methods that prepare the HPAS-2 and HPAS-3 samples are suitable for the HPA/Al-SBA-15 preparation using *in-situ* synthetic

HPA. This result shows the role of NH_4^+ and NH_2 functional groups in the formation of HPA/SBA-15 catalysts.

HPA contents of the HPA/Al-SBA-15 samples prepared by using the HPA commercial catalyst are listed in Table 2 (HPAS-4, HPAS-5, HPAS-6, HPAS-7 samples). The HPA content of HPAS-6 is only 0.82 wt%. This sample was prepared by immobilising HPA commercial catalyst over OH groups of Al-SBA-15-OH support. This shows that HPA commercial catalyst, as well as *in-situ* synthetic HPA (HPAS-1 sample), cannot be immobilised over OH groups of Al-SBA-15-OH support. The difference between the HPAS-4 and HPAS-6 samples is the NH_4^+ ion-exchange to form NH_4^+ groups at Brønsted sites of Al-SBA-15-OH support. The HPA content of HPAS-4 is 24.28 wt%. It can be shown that HPA commercial catalyst can be immobilised on Al-SBA-15 by the interaction with NH_4^+ functional groups. These results indicate that both *in-situ* synthetic HPA and HPA commercial catalyst can be immobilised on Al-SBA-15 by the interaction between HPA with NH_4^+ sites (HPAS-2 and HPAS-4 samples).

The HPAS-5 and HPAS-7 samples were prepared by immobilising HPA commercial catalyst on Al-SBA-15 support over NH_2 groups and (NH_2 , NH_4^+) groups. The interesting result is the high and unremarkable change of HPA contents of these samples (35.24 wt% over the HPAS-5 sample and 36.59 wt% over the HPAS-7 sample), showing that NH_4^+ groups cannot immobilize the HPA commercial catalyst in the presence of NH_2 groups. To overcome this limitation, a further procedure of adding *in-situ* synthetic HPA into the HPAS-7 sample to get the HPAS-8 sample was performed, resulting in the HPA content increases from 36.59 wt% (HPAS-7 sample) to 47.12 wt% (HPAS-8 sample) (see Table 2). This may be due to the blockage of APTES molecules inside the mesoporous system of Al-

SBA-15 support, hence HPA commercial catalyst molecules with 1 nm in diameter [17] are unable to go through the space between APTES molecules to contact with NH_4^+ sites. In contrast, by adding precursor substances (to form *in-situ* synthetic HPA) into the HPAS-7 sample, the ions of precursor substances (WO_4^{2-} , PO_4^{3-} and H^+) with much smaller size can diffuse in APTES molecules and interact with NH_4^+ sites to form the linkages, leading to the increase of HPA content in the HPAS-8 sample. Note that the Si/Al molar ratio can affect the aluminium content of Al-SBA-15 support and therefore affect the number of NH_4^+ groups, as well as HPA content of the HPA/Al-SBA-15 material. Table 3 shows the HPA contents of the HPA/Al-SBA-15 samples prepared by the same method to prepare HPAS-4 sample but with different Si/Al molar ratios of Al-SBA-15-OH support.

S. R. Mukai *et. al.* show that in the case of zeolite Y support, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 20-100 (Si/Al=10-50) were suitable for *in-situ* synthetic HPA formation [18]. It was also stated that when the Si/Al molar ratio was lower than this range, the support was likely to be destroyed during catalyst preparation due to the low stability of aluminosilicate supports in acidic solutions. Moreover, it was difficult to encapsulate HPA to supports with extremely low aluminium content. In our study, the Si/Al molar ratios were studied in the range of 10-25. The maximum HPA content of 24.28 wt% is obtained with Si/Al molar ratio of 15 (HPAS-415 sample). When Si/Al molar ratio value increases from 15 to 20 or higher, the HPA content slightly decreases to 21.53 wt% (HPAS-420 sample) and to 19.14 wt% (HPAS-425 sample). In addition, when Si/Al molar ratio value decreases from 15 to 10, the HPA content also slightly decreases to 21.82 wt% (HPAS-410 sample). These results show that Si/Al molar ratio of 15 is suitable for Al-SBA-15 to be used as HPA support.

The HPAS-2, HPAS-4 (also known as the HPAS-415 sample), HPAS-5 and HPAS-8 samples, therefore, are chosen as typical HPA to be immobilised on Al-SBA-15-OH support. These samples will be further characterised by FTIR, SAXS, BET and TPD-NH₃ methods.

3.1.2. SAXS results

The SAXS method was used to demonstrate presence of HPA on the Al-SBA-15 support. The SAXS patterns of samples before and after HPA immobilisation are shown in Figure 1. The functionalisation of Al-SBA-15 with NH₄NO₃ and APTES to form Al-SBA-15-NH₄⁺ and Al-SBA-15-NH₂ samples can be seen by the decrease of diffraction peak near 2-theta of 0.5-1°. The uniform hexagonal structure of Al-SBA-15 support was affected by APTES more than it was by NH₄NO₃ salt. In addition, the dramatic decrease of the peaks near 0.5-1° 2-theta in the SAXS patterns of HPA/Al-SBA-15 samples in comparison to those of Al-SBA-15-NH₄⁺ and Al-SBA-15-NH₂ samples clearly show the presence of HPA on the Al-SBA-15 support. The more HPA molecules are immobilised, the lower peak intensity is observed. This result can be further illustrated by looking at the HPA content of the HPA/Al-SBA-15 samples showed in Table 2.

3.1.3. TPD-NH₃ results

The HPAS-4, HPAS-5 and HPAS-8 samples were immobilised over NH₄⁺ groups (HPAS-4 sample), NH₂ groups (HPAS-5 sample), and a mixture of NH₄⁺ and NH₂ groups (HPAS-8 sample). The TPD-NH₃ results show that the HPAS-5 and HPAS-8 samples have higher acidities than Al-SBA-15-OH support (see Table 4). In Figure 2, it can be seen that there is a strong desorption peak around 400 °C in both these samples, which is evidenced by the presence of strong acidic sites. In the TPD-NH₃ curve of HPAS-4 sample, there is a

desorption peak that appears at 559.6 °C. This peak attributed to the stronger acidic sites of HPAS-4 compared to HPAS-5 and HPAS-8 samples.

The different acidity of HPAS-4 and HPAS-5 samples can be explained by the HPA immobilisability and the proton preservation of immobilised HPA molecules of the samples.

The Bronsted site numbers of HPAS-4 and HPAS-5 samples were expected to be the same because they used the same Al-SBA-15-OH support. However, the Bronsted sites of Al-SBA-15-OH support in HPAS-4 sample were modified with NH_4^+ by the ion-exchange procedure ($\text{Proc1}/\text{NH}_4^+$) while those in HPAS-5 were unmodified. In the case of HPAS-5 sample, the unmodified Bronsted sites of this sample could not immobilise HPA. This result can be seen from the HPA content of HPAS-6 sample, it was only 0.82 wt%. The unmodified Bronsted sites of Al-SBA-15-OH support in HPAS-6 sample were directly used to immobilise HPA without NH_4^+ ion-exchange ($\text{Proc1}/\text{NH}_4^+$). In addition, the OH groups of HPAS-5 were modified with APTES to form NH_2 groups on its surface. By these modifications, we obtained HPAS-4 with NH_4^+ groups and HPAS-5 with NH_2 groups. After the HPA immobilisation, we obtained different HPA contents of HPAS-4 and HPAS-5 sample due to the different HPA immobilisability of NH_4^+ and NH_2 groups. This HPA immobilisability result partly conducted the different NH_3 -TPD curves of the samples. The main factor affected the NH_3 -TPD result is acid strength. It is interesting that the acid strength of HPAS-4 sample is better than that of HPAS-5 sample even the HPA content of HPAS-4 sample is lower (HPAS-4: 24.28 wt%, HPAS-5: 35.24 wt%). It may be due to the proton preservation ability of the samples.

In the case of HPAS-5 sample, hydroxyls (OH) are the main groups of Al-SBA-15-OH support, resulting in the high APTES concentration because of the linkage formation between OH groups of APTES and those of Al-SBA-15-OH support during the functionalisation (proc 2). During the HPA immobilisation, one proton of HPA molecule will form a linkage to one NH_2 site of APTES molecule to form NH_3^+ -HPA [33]. An HPA molecule has three protons ($\text{H}_3\text{PW}_{12}\text{O}_{40}$). The one or two left protons of HPA molecule may be occupied by one or two NH_2 sites of the neighbouring APTES molecules. This occupation conducts the loss of proton of HPA in HPAS-5 sample.

In the case of the linkage formation between HPA and NH_4^+ groups of Al-SBA-15- NH_4^+ functionalised support to form the HPAS-4 sample, because of the much lower number of aluminium atoms in comparison to silicon atoms (Si/Al molar ratio=15), the two left protons of HPA molecule can be preserved. This leads to the higher catalytic activities of HPAS-2 and HPAS-4 samples (HPA molecules are immobilised over NH_4^+ groups) compared with those of HPAS-3 and HPAS-5 samples (HPA molecules are immobilised via NH_2 groups), respectively.

The TPD- NH_3 of HPA sample with three protons in each HPA molecule shows the NH_3 desorption peak at high temperature of 635.7 °C. HPAS-4 sample with two protons of each HPA molecule (one proton was replaced by NH_4^+ ion) shows the peak at 559.6 °C. The loss of protons in HPAS-5 and HPAS-8 shows the NH_3 desorption peak at 400 °C. This result shows that the loss of protons number conducts the change of NH_3 desorption peaks to lower temperature.

The data in Table 4 shows the detail of acidities of samples via chemisorbed NH_3 quantities at different desorption temperatures. Chemisorbed NH_3 quantities at around 400 °C of

HPAS-5 and HPAS-8 samples are 11.66 cm³/g STP and 14.25 cm³/g STP respectively. The dominant acidity of HPAS-4 sample can be seen over the chemisorbed NH₃ quantity of 169.42 cm³/g STP at high desorption temperature (559.6 °C). This shows the **higher** acidity of HPAS-4 in comparison to HPAS-5 and HPAS-8 samples. The properties of the samples before and after HPA immobilisation will be further evaluated by FTIR and BET methods.

3.1.4. FTIR results

The presence of HPA on Al-SBA-15 support can be illustrated in FTIR spectrums in Figure 3. The peaks attributed to Si-O-Si linkages of Al-SBA-15-OH support can be observed at 1084.79, 950.21, 806.30 cm⁻¹. There is an appearance of HPA typical peaks at 525.96 cm⁻¹ (W-O-P linkage), 802.14 cm⁻¹ (W-O-W linkage), 892.97 cm⁻¹ and 983.54 cm⁻¹ (W-O linkage), and a peak at 1080.71 cm⁻¹ (P-O linkage) in the FTIR spectrums of both HPAS-4 and HPAS-5 samples. This appearance clearly shows the presence of HPA on Al-SBA-15-OH support.

3.1.5. BET results

The structural change of samples before and after HPA immobilisation is further characterised by BET method. The N₂ adsorption/desorption isotherms of HPAS-4 and Al-SBA-15-OH samples are shown in Figure 4. It can be seen that the wide hysteresis loops in the p/p^o range of 0.45-0.75 of the isotherms assigned to mesoporous structure [32] are identical in both samples, indicating that HPA immobilisation does not break the mesoporous structure of Al-SBA-15-OH support. The different shape of hysteresis loops shows the change in properties of the samples.

In Table 5, it can be seen that the specific surface area (S) decreased from 750.7 m²/g (Al-SBA-15-OH support) to 584.6 m²/g after the immobilisation (HPAS-4 sample). The

decrease of specific surface area shows the presence of HPA molecules on Al-SBA-15-OH support. The decrease of pore volume (V) from 0.93 cm³/g to 0.59 cm³/g and the unchanged average pore width may show that there might be a presence of HPA molecules immobilised inside the mesopore system of Al-SBA-15-OH support.

3.2. Catalytic activity of the prepared catalysts in the synthesis of fructose

3.2.1. Catalytic activity of the samples prepared by different methods

The catalytic activities of different HPA/Al-SBA-15 samples, Al-SBA-15-OH support, HPA commercial catalyst as well as the reaction without catalyst in the Fructose synthesis were shown in Figure 5, data in Table S1 and Table S2 (research data file). It can be seen that the HPAS-4 sample performed the highest catalytic activity with the dominant EAA conversion of 93.49%, followed by the HPA commercial catalyst (EAA conversion of 88.94%). All the other catalysts show lower catalytic activities with EAA conversions ranging between 60 and 70% which is not too far different from the reaction without catalyst (EAA conversion is 59.49%). These results show that, the method used for HPAS-4 sample is the best method to synthesise HPA/Al-SBA-15 materials, even the HPA content of the HPAS-4 sample is not highest. In addition, because of the lower catalytic activities of the other prepared HPA/Al-SBA-15 samples even some of them have higher HPA content than the HPAS-4 sample, there are some discussions can be given here. Firstly, The HPA/Al-SBA-15 catalysts, in which HPA molecules are immobilised over NH₄⁺ groups, have better catalytic activity than those where HPA molecules are immobilised over NH₂ groups. This discussion is illustrated by the catalytic activity comparison between the HPAS-4 and HPAS-5 samples. The lower catalytic activity of HPAS-5 sample compared to that of HPAS-4 caused by the the loss of protons of HPA

molecules during the linkage formation with NH_2 groups of APTES molecules on the HPAS-5 sample as discussed in NH_3 -TPD result, conducting the low acidity and activity of HPAS-5 sample compared to that of HPAS-4.

Secondly, the *in-situ* synthetic HPA is not suitable to prepare the HPA/Al-SBA-15 catalyst (HPAS-2 and HPAS-3 samples) in this preparation condition. This may be caused by the fact that during the formation of HPA molecules from precursors, HPA molecules may fully fill the mesopore system of Al-SBA-15 support as shown in the case of zeolite Y [18], and this leads to the activity loss of this catalyst.

Thirdly, the presence of both NH_2 and NH_4^+ groups in HPAS-8 sample did not help this catalyst to obtain any catalytic activity improvement even it can immobilize the HPA molecules with the highest content of 47.12 wt% among the HPA/Al-SBA-15 samples. This aspect may be caused by the fact that the protons of further immobilised *in-situ* synthetic HPA of HPAS-8 sample by proc 4 in the preparation method still may be occupied by free NH_2 groups of neighbouring APTES molecules or the formed *in-situ* synthetic HPA molecules may fully fill the mesopore system of Al-SBA-15 support. This once again shows the important role of NH_4^+ groups in preserving the two left protons of HPA molecule on HPA/Al-SBA-15 material and therefore improving the acidity and catalytic activity of sample. This is a major result of this research.

In addition, the better catalytic activity of HPAS-4 compared to that of HPA commercial catalyst in the fructose synthesis shows that HPAS-4 is a promised catalyst for the heterogenisation of HPA catalyst for the catalytic applications in polar media.

3.2.2. Catalytic activity of the samples prepared by different Si/Al molar ratio

The method that prepared the HPAS-4 sample is selected to immobilize HPA catalyst on Al-SBA-15 support. The aluminium content of Al-SBA-15 affects the HPA immobilisation because the NH_4^+ ion-exchanged Brønsted sites are formed by framework aluminium of Al-SBA-15 material. In order to find the suitable aluminium content, the HPA/Al-SBA-15 samples with Si/Al molar ratios of 10, 15, 20, 25 were prepared by the same method to prepare HPAS-4 sample. These sample were respectively denoted as HPAS-410, HPAS-415, HPAS-420 and HPAS-425. The catalytic activities of these samples are shown in Figure 6 and Table S3 (research data file). The HPAS-425, HPAS-420, HPAS-410 samples have lower catalytic activities than the HPAS-415 sample. This result is reasonable because of the HPA contents of these samples (see Table 3). By using the same selected preparation method, the higher the HPA content, the better the catalytic activity is.

3.2.3. Catalytic stability

The reusability of the best HPA/Al-SBA-15 catalyst (HPAS-4 sample) was evaluated by further testing in four reaction cycles. In figure 7, it can be shown that that after four further reaction cycles, catalytic activities of the reused samples just slightly reduced, showing that HPAS-4 sample has good catalytic stability. The catalytic reduction of reused samples may be due to the weight loss of sample during the recovery procedure of catalyst from the ended reaction for the next cycle.

4. Conclusions

The preparation methods of HPA/Al-SBA-15 heterogeneous catalysts were studied by using different types of HPA (commercial catalyst and *in-situ* synthetic HPA), different modification agents to form group types (NH_4^+ , NH_2 , OH), and different properties of Al-SBA-15 support (Si/Al molar ratio). The fructose synthesis model reaction was used to

more clearly proved the results obtained from the catalyst preparation methods evaluation. The results showed that HPA commercial catalyst is suitable to be immobilised on the Al-SBA-15 support that was modified to form NH_4^+ groups in terms of HPA content, acidity and the ethyl acetoacetate conversion in fructose synthesis. In addition, Si/Al molar ratio was an important factor that affected the immobilised HPA quantity. The suitable Si/Al molar ratio value for Al-SBA-15 support is 15. The higher catalytic activity of the best HPA/Al-SBA-15 sample (HPAS-4) in comparison to that of HPA commercial catalyst, and the good catalytic stability of HPAS-4 after five reaction cycles showed that HPA/Al-SBA-15 was a very promising catalyst for the organic synthesis in polar media.

Figure Captions

Figure 1. SAXS patterns.

Figure 2. TPD-NH₃ curves.

Figure 3. FTIR spectra.

Figure 4. N₂ adsorption/desorption isotherms.

Figure 5. Catalytic activity of HPA/Al-SBA-15 samples in fructose synthesis.

Figure 6. Catalytic activities of HPA/Al-SBA-15 samples by Si/Al molar ratio in fructose synthesis.

Figure 7. Catalytic stability of catalyst after 4 reaction recycles.

Conflicts of interest

There are no conflicts to declare.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1. HPA/Al-SBA-15 preparation methods.

Sample	HPAS-1	HPAS-2	HPAS-3	HPAS-4	HPAS-5	HPAS-6	HPAS-7	HPAS-8
Proc 1/ NH_4^+		x		x			x	x
Proc 2/ NH_2			x		x		x	x
Proc 3/comm. HPA				x	x	x	x	x
Proc 4/in-situ HPA	x	x	x					x

Table 2. HPA content of the HPA/Al-SBA-15 samples prepared by different methods

Sample	HPAS-1	HPAS-2	HPAS-3	HPAS-4	HPAS-5	HPAS-6	HPAS-7	HPAS-8
HPA content, wt%	0.12	13.64	31.19	24.28	35.24	0.82	36.59	47.12

Table 3. HPA content by Si/Al molar ratio of HPA/Al-SBA-15 samples.

Sample	HPA-410	HPA-415	HPA-420	HPA-425
HPA content, wt%	21.82	24.28	21.53	19.14

Table 4. TPD-NH₃ data.

Sample	Peak	Temperature at	NH ₃ quantity, cm ³ /g
	number	maximum, °C	STP
Al-SBA-15-OH	1	131.7	0.17
	2	264.2	1.01
	3	391.5	0.10
HPA	1	635.7	5.79
HPAS-4	1	149.6	0.63
	2	559.6	169.42
	3	600.1	0.12
HPAS-5	1	122.9	0.28
	2	163.9	0.46
	3	412.0	11.66
HPAS-8	1	126.9	0.13
	2	187.2	0.25
	3	409.6	14.25

Table 5. BET data.

Sample	BET data		
	S, m ² /g	V, cm ³ /g	D, nm
Al-SBA-15-OH	750.70	0.93	5.10
HPAS-4	584.60	0.59	5.05