



Preparation and testing of cesium Brønsted ion-exchanged Al-SBA-15 supported heteropoly acid as heterogeneous catalyst in the fructose fragrance synthesis

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Abstract

Here we report a new cesium Brønsted ion-exchanged Al-SBA-15 (Cs/AS15) supported heteropoly acid (HPA) $H_3PW_{12}O_{40}$ (HPA-Cs/AS15) material which can be prepared and used as heterogeneous catalyst for the fructose fragrance synthesis. It was demonstrated that Cs^+ was more effective than NH_4^+ as counter cation of ion-exchanged AS15 support for preparing HPA/AS15 catalyst with higher acidity and HPA leaching stability. HPA-Cs/AS15 material showed high acidity with the maximum NH_3 desorption peak appeared at 759.6 °C in the NH_3 -TPD spectrum, stronger than pure HPA (635.7 °C) and the ammonium Brønsted ion-exchanged Al-SBA-15 supported HPA (HPA- NH_4 /AS15) (559.1 °C) materials. The HPA leaching stability test showed that the HPA content of HPA-Cs/AS15 catalyst reduced only by 2.55% after five washing times, much less than that of HPA- NH_4 /AS15 catalyst (49.22%).

The higher acidity helped improve the HPA-Cs/AS15 catalyst performance in the fructose fragrance synthesis. The ethyl acetoacetate conversion over this catalyst was 94.82%, better than those over HPA- NH_4 /AS15 (93.49%) and pure HPA (89.52%) catalysts, although HPA-Cs/AS15 catalyst had lower HPA content (23.16 wt%) than HPA- NH_4 /AS15 (24.28 wt%). In addition, it was shown that the reaction conditions such as ethyl acetoacetate:ethanediol reactant molar ratio of 1:1.5, ethanediol used as the diol reactant, and toluene used as the solvent, the fructose fragrance synthesis reaction over HPA-Cs/AS15 catalyst reached the highest ethyl acetoacetate conversion (95.58%). The toluene's boiling temperature of 110.6 °C can promote the dispersion and contact abilities of the reactants with HPA molecules presented inside the pores of HPA-Cs/AS15 catalyst.

Keywords Cesium counter cation · Heterogenised HPA · HPA/Al-SBA-15 · Fructose

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1 Introduction

Fructose (also known as 2,4-dimethyl-2-ethylacetoacetate-1,2-dioxolan) is a synthetic apple fragrance synthesised from the acetalisation reaction of ethyl acetoacetate (EAA)

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and diols substances using acid catalysts. Because of the commonly known disadvantages related to homogeneous acid catalysts such as difficulty to separate and recover from the products, not being able to be reused, highly corrosive, and expensive durable reactors required [1, 2], heterogeneous catalysts for fructose fragranciness synthesis such as SO₃H-functionalised carbon [3], copolymer of *p*-toluenesulfonic acid and *p*-formaldehyde [4], mesoporous Al-SBA-15 [5], and ultra-stable Y zeolite supported heteropoly acid [6], and a type of ionic liquid catalyst as SO₃H-functionalised BAILs [7] have been developed for easy recovery and reuse. Amongst these effective catalysts, the heteropoly acid (HPA) in α -Keggin form (H₃PW₁₂O₄₀) has been of great interest due to the high acidity of this catalyst and its potential to be heterogenised using various methods such as precipitation [8–12], hybridisation [13–16], dispersion [17–21], encapsulation [6, 22, 23], tethering [24–26], and grafting [27, 28].

It has been shown that precipitation of HPA with caesium metal cation can improve physical properties of the hybrid catalyst (i.e. Cs-HPA salt) including the increased specific surface area (130–135 m²/g compared to 3.1 m²/g in purely HPA) due to the formed microporous structure [2, 12]. However, it is noteworthy that this approach might lead to lowered acidity simply because of protons lost during the salt formation which is likely to hinder the activity of this catalyst. In addition, it is known that the size of an anion of HPA molecule in α -Keggin form is close to 1 nm [23] which is too negligible to Cs-HPA salt (with the size between 11.7 and 17.5 nm [8, 9, 12]). It has been shown that there was an unnecessary aggregation of the salt molecules, that might result in the reduction of HPA dispersibility. For this reason, immobilising the HPA catalyst on high specific surface area porous supported by tethering or grafting methods should be studied.

In our previous study, HPA was successfully immobilised on NH₄⁺ Brønsted ion-exchanged Al-SBA-15 mesoporous support. The prepared catalyst showed high catalytic activity in fructose fragranciness synthesis with high conversion of EAA (93.49%) [29]. Recently, Mukai et al. have shown that Cs⁺ cation was even more effective than NH₄⁺ as counter cation for the support of HPA immobilisation on zeolite Y microporous material in terms of HPA content and leaching stability [23]. However, the microporous structure of zeolite Y could limit the mass transfer of reactions and the contact between HPA molecules formed in the supercages of the support with reactants. Chamack et al. have reported the HPA immobilisation on mesoporous SBA-15 support which was prior impregnated on its surface with Cs₂CO₃ for oxidative desulfurisation processes [30]. The mesoporous structure of SBA-15 could solve the mentioned limitations of microporous structure of zeolite Y. In this reaction, the oxidative catalyst was more effective than acidic catalyst. Moreover, the

impregnation method has the disadvantage of low dispersibility of Cs₂CO₃ on SBA-15 support. The accumulation of Cs⁺ cations in support may conduct the loss of acidity of immobilised HPA as mentioned above. In order to disperse Cs⁺ uniformly on the support surface and remain the H⁺ of HPA molecule, the use of Al-SBA-15 support, which has Brønsted site locations ion-exchanged with Cs⁺ cations, expects to form the Al-SBA-15 supported HPA catalyst with high acidity.

In this study, HPA-Cs/AS15 material (the caesium Brønsted ion-exchanged Al-SBA-15 (Cs/AS15) supported heteropoly acid (HPA)) was prepared to be used as heterogeneous catalyst for the fructose fragranciness synthesis. The presence and content of immobilised HPA were characterised by Fourier-transform infrared spectroscopy (FTIR), small angle X-ray scattering (SAXS) and energy dispersive X-ray (EDX) methods. The effect of HPA immobilisation on the support physical properties was evaluated by nitrogen adsorption/desorption isotherms. Acidity comparison amongst samples was performed by using temperature-programmed desorption of ammonia (NH₃-TPD) method. The obtained products of the fructose fragranciness synthesis reaction were analysed by gas chromatography (GC).

2 Experimental

2.1 Catalyst preparation

2.1.1 Chemicals

The chemicals for HPA-Cs/AS15 preparation are listed in Table S1.

2.1.2 Synthesis of AS15 support

The AS15 support (denoted as AS15-OX) was synthesised by the typical process shown in the Sect. 1 (supporting information (SI) document) with the structural directing agent P123 removed by H₂O₂ oxidative agent.

2.1.3 Preparation of HPA-Cs/AS15 material

The HPA-Cs/AS15 material was prepared by the method shown in previous study [29] using two steps below.

Step 1- AS15-OX support was Brønsted ion-exchanged with Cs⁺ cation by using CsCl 1.5 M solution. The ion exchange procedure was shown in section 2 (SI document).

Step 2- HPA Brønsted immobilisation (Sect. 3 in the SI document).

2.1.4 Comparison of AS15 support treatment condition

AS15 support was P123 removed by another method of thermal decomposition to compare with the AS15-OX support that was P123 removed by H₂O₂ oxidative agent. The AS15 sample containing P123 was thermally treated at 550 °C for 6 h with ramp of 3 °C/min to get the AS15-CAL support.

The obtained support was Brønsted ion-exchanged with NH₄⁺ cation according to the ion exchange procedure (Sect. 2, SI document) using NH₄NO₃ 1.5 m solution, and then supported HPA according to the procedure of HPA-Cs/AS15 catalyst preparation to obtain the HPA-NH₄/AS15-CAL sample.

2.1.5 Comparison of counter cation for AS15 support

AS15-OX support was Brønsted ion-exchanged with NH₄⁺ instead of Cs⁺ cation and then supported HPA according to the steps of HPA-Cs/AS15 catalyst preparation to obtain the HPA-NH₄/AS15 sample. The AS15 supported HPA (HPA/AS15) samples are listed in Table 1.

2.2 Characterisation

EDX spectroscopy, SAXS diffraction patterns, nitrogen adsorption and desorption isotherms, NH₃-TPD spectrums and FTIR spectrums of the samples were analysed as shown in the Sect. 4 (SI document).

2.3 Catalytic activity

Performance of the prepared HPA/AS15 samples was evaluated in the acetalisation reaction to synthesise fructose fragrance. The typical procedure was described in a previous study [29]. The reaction conditions were studied including solvent type (toluene, isooctane, cyclohexane) and catalyst weight (2, 3, 4 wt% to reactants total mass); molar ratio of acetoacetate:ethanediol (EAA:EG) reactants of 1:1, 1:1.25, 1:1.5 and 1:1.75.

The homogeneous catalysts such as *p*-toluenesulfonic acid monohydrate (PTSA), sulfuric acid (H₂SO₄) and pure HPA were used to make an activity comparison to the HPA-Cs/

AS15 catalyst. Weights of these catalysts were calculated to have the same H⁺ mole value.

The HPA/AS15 catalysts were reused for 4 cycles of the reaction to evaluate their catalytic stability by the procedure shown in the previous study [29].

3 Results and discussion

3.1 Catalyst characterisation

3.1.1 FTIR results

The presence of HPA on the AS15 support was detected by FTIR spectrums (see Fig. 1). Typical peaks attributed to the W-O-W, W-O and P-O linkages of HPA can be seen at 802.14 cm⁻¹, 892.97 cm⁻¹ and 983.54 cm⁻¹, and 1080.71 cm⁻¹, respectively (see Fig. 1f). These peaks were also observed in FTIR spectrums of the HPA-NH₄/AS15-CAL (Fig. 1a), HPA-Cs/AS15 (Fig. 1b) and HPA-NH₄/AS15 (Fig. 1c) samples. The higher intensity of the peak observed at 805.67 cm⁻¹ in the FTIR spectrums of HPA/AS15 samples compared to those in the AS15 supports indicates the presence of W-O-W linkages of HPA beside the Si-O-Si(Al) linkages of AS15 support.

3.1.2 SAXS results

SAXS patterns of the samples are shown in Fig. 2. There is a peak near 2-theta of 0.5–1° attributed to mesoporous structure of all the samples [29–31]. The presence of HPA is evidenced by the considerable decrease of those peaks in SAXS patterns of the HPA-NH₄/AS15-CAL (Fig. 2a), HPA-Cs/AS15 (Fig. 2b) and HPA-NH₄/AS15 (Fig. 2c) samples.

It can also be observed that these peaks in the SAXS patterns of HPA-NH₄/AS15-CAL and HPA-Cs/AS15 samples were shifted to the left. This shift may be due to the enlargement of mesopore size conducted by a part dissolution of framework Si and Al atoms in acidic HPA solution (pH ≈ 1.5) during the HPA Brønsted immobilisation.

3.1.3 Nitrogen adsorption and desorption isotherms

The presence of HPA in the HPA/AS15 samples can also be further confirmed by N₂ adsorption and desorption isotherms. The shape transformations of hysteresis loops in isotherms of the samples shown in Fig. 3 indicate a change of pore characteristic of the samples before and after supporting HPA. The data shown in Table 2 indicate a decrease of BET surface area (S_{BET}), average pore diameter (D_{pore}) and pore volume (V_{pore}) values of the HPA/AS15 samples compared with initial corresponding supports conducted by

Table 1 The prepared HPA/AS15 samples

Sample	P123 degradation method		Counter cation	
	Thermal treatment	Oxidation	NH ₄ ⁺	Cs ⁺
HPA-NH ₄ /AS15-CAL	x		x	
HPA-NH ₄ /AS15		x	x	
HPA-Cs/AS15		x		x

Fig. 1 Fourier-transform infrared spectroscopy (FTIR) spectrums of the samples: **a** HPA-NH₄/AS15-CAL; **b** HPA-Cs/AS15; **c** HPA-NH₄/AS15; **d** AS15-CAL; **e** AS15-OX; **f** heteropoly acid (HPA)

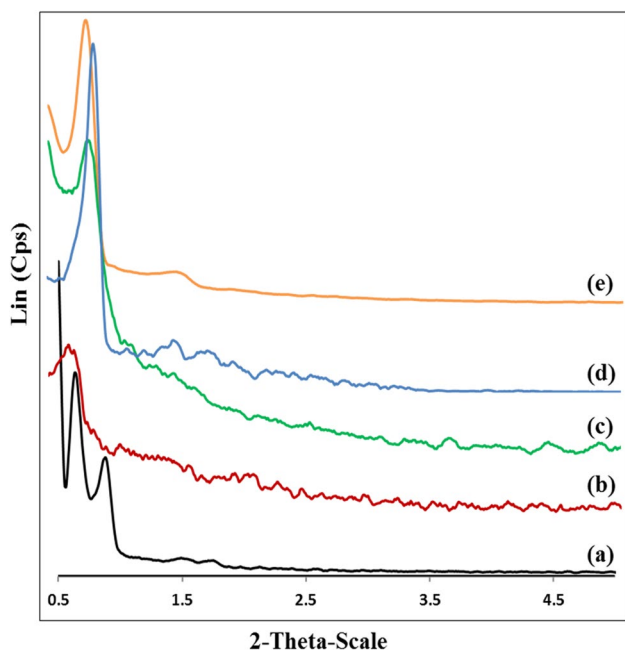
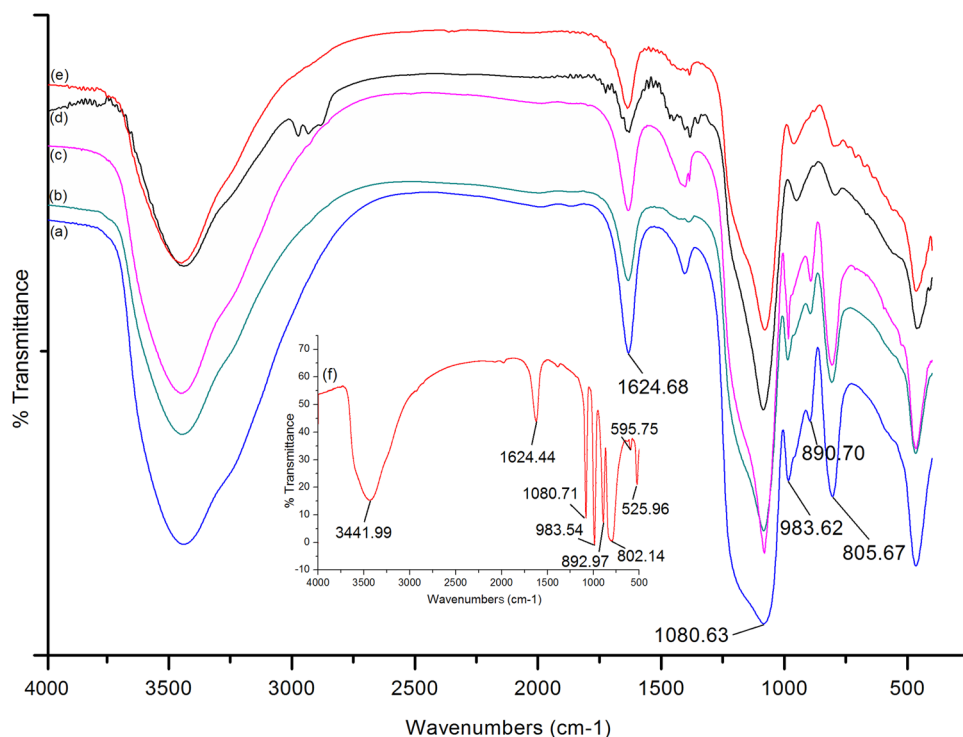


Fig. 2 Small angle X-ray scattering (SAXS) patterns of the samples: **a** HPA-NH₄/AS15-CAL; **b** HPA-Cs/AS15; **c** HPA-NH₄/AS15; **d** AS15-CAL; **e** AS15-OX

the influence of HPA molecules presented inside the pores of AS15 support.

The enlargements of pore diameter of the samples after the HPA Brønsted immobilisation can be observed in Fig. 4.

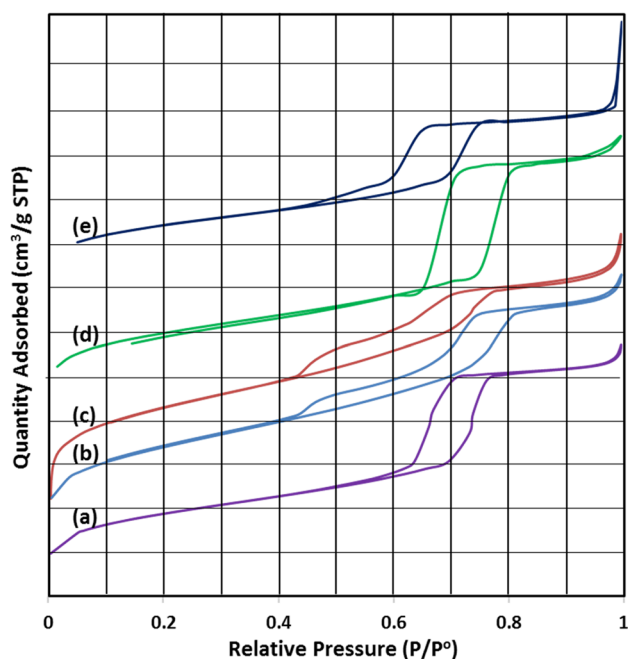
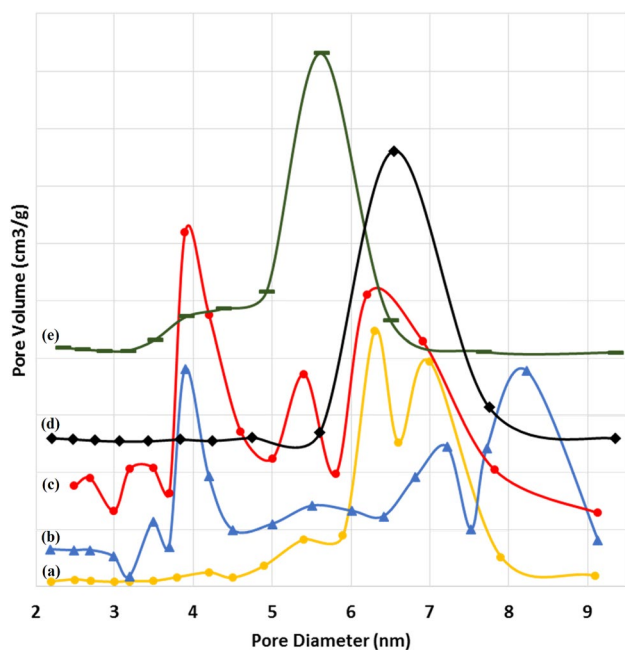


Fig. 3 Nitrogen adsorption and desorption isotherms of the samples: **a** HPA-NH₄/AS15-CAL; **b** HPA-Cs/AS15; **c** HPA-NH₄/AS15; **d** AS15-CAL; **e** AS15-OX

The pore sizes of AS15-OX (Fig. 4e) and AS15-CAL (Fig. 4d) samples were mainly 5.5 and 6.5 nm in diameter, respectively. After the HPA Brønsted immobilisation, HPA molecules entered the pores of AS15 support and created

Table 2 BET data of the samples

Sample	S_{BET} , m^2/g	Average D_{pore} , nm	V_{pore} , cm^3/g
AS15-CAL	786	6.54	0.96
AS15-OX	750	5.10	0.93
HPA-NH ₄ /AS15-CAL	628	5.28	0.86
HPA-NH ₄ /AS15	603	5.05	0.59
HPA-Cs/AS15	591	5.57	1.22

**Fig. 4** Pore size distribution (BJH desorption) of the samples: **a** HPA-NH₄/AS15-CAL; **b** HPA-Cs/AS15; **c** HPA-NH₄/AS15; **d** AS15-CAL; **e** AS15-OX

the smaller pore systems with 4.0 and 6.25 nm in diameter for the samples using AS15-OX support [HPA-NH₄/AS15 (Fig. 4c) and HPA-Cs/AS15 samples (Fig. 4b)] and AS15-CAL support [HPA-NH₄/AS15-CAL sample (Fig. 4a)], respectively.

Beside the smaller pore systems, the bigger pore systems were also observed with 6.5 nm for HPA-NH₄/AS15 samples (Fig. 4c) and 7.0 nm for HPA-NH₄/AS15-CAL sample (Fig. 4a) compared to the pore systems of the corresponding supports. The formation of these bigger pores systems agrees with the obtained XRD result. It helps to improve the specific surface area of the supports and be the reason of the slightly decreased S_{BET} values even with high immobilised HPA contents of the HPA/AS15 samples.

Especially, the observed bigger pore system of HPA-Cs/AS15 sample of 8.2 nm in diameter (Fig. 4b), even larger than that of HPA-NH₄/AS15 sample (6.5 nm) (Fig. 4c). The

pore-size enlargement of HPA-Cs/AS15 sample may be due to the interaction between the strong base support (Cs⁺ Brønsted ion-exchanged AS15) and the strong acid (HPA), conducting the D_{pore} and V_{pore} increases of this sample compared to HPA-NH₄/AS15-CAL sample.

3.2 Catalytic activity

3.2.1 Effect of support treatment condition

The AS15 support was synthesised by using structural directing agent (Pluronic-P123). This agent needs to be removed after the structure formation of AS15. The removal methods, such as thermal treatment or using strong oxidation agent (H₂O₂), lead to material changes in the properties. BET results of the samples shown in Table 2; Fig. 4 indicate that HPA-NH₄/AS15-CAL sample (prepared using AS15-CAL support) had slightly higher S_{BET} , D_{pore} and V_{pore} values than HPA-NH₄/AS15 sample (prepared using AS15-OX support). However, EDX results shown in Table 3 indicate that HPA content of HPA-NH₄/AS15-CAL sample was only 17.81 wt%, lower than that of HPA-NH₄/AS15 sample (24.28 wt%). This results in the lower catalytic activity of HPA-NH₄/AS15-CAL sample compared to that of HPA-NH₄/AS15 sample in the fructose fragranciness synthesis. Figure 5 and the data shown in Table S2 indicate that ethylacetoacetate conversion (EAA conv.) over HPA-NH₄/

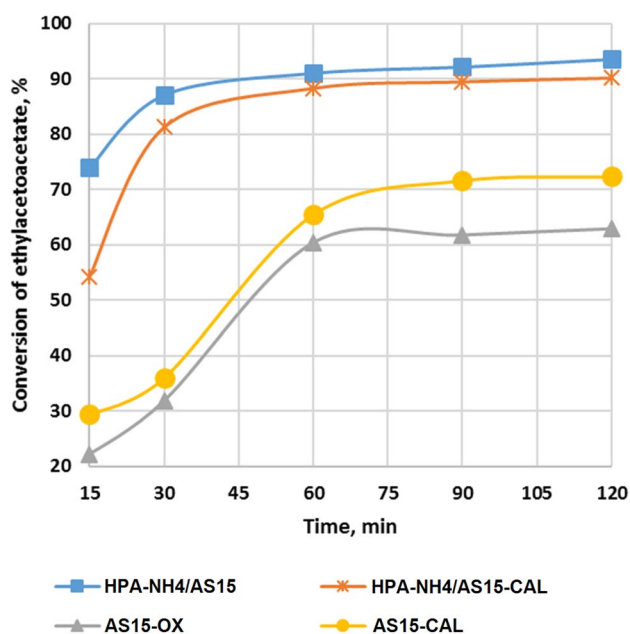
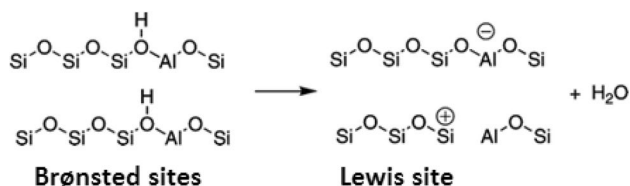
**Fig. 5** Catalytic activities of the catalysts in fructose fragranciness synthesis under different support treatment conditions (other reaction conditions - catalyst weight: 3 wt%, solvent: isooctane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

Table 3 Heteropoly acid (HPA) contents of HPA/AS15 catalysts by EDX

Sample	HPA content, wt%
HPA-NH ₄ /AS15-CAL	17.81
HPA-NH ₄ /AS15	24.28
HPA-Cs/AS15	23.16

**Fig. 6** The decomposition of Brønsted sites

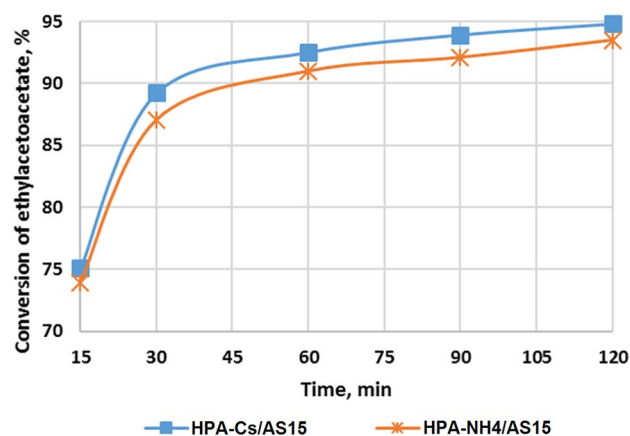
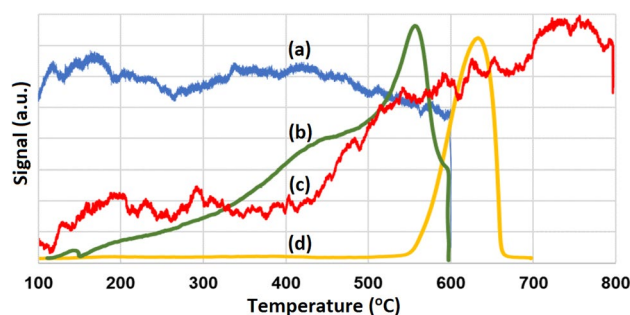
AS15-CAL sample was 90.14%, lower than that over HPA-NH₄/AS15 sample (EAA conv. is 93.49%).

The different HPA contents of the samples with different support treatment conditions may be explained by the fact that Si/Al molar ratio of AS15 support was 15. During the thermal treatment at 550 °C to remove P123, two neighbouring Brønsted sites can react to each other to form one Lewis site by the reaction shown in Fig. 6 [32]. This reaction decomposes the Brønsted sites and made them malfunction. In this case, HPA cannot be immobilised on these malfunctioned Brønsted sites, leading to the lower HPA content and therefore lower catalytic activity of HPA-NH₄/AS15-CAL sample compared to that of HPA-NH₄/AS15 sample. This result shows that P123 structural agent removed by oxidation method using H₂O₂ agent is more suitable than that by thermal treatment method to synthesise AS15 support for HPA Brønsted immobilisation.

3.2.2 Effect of counter cation of AS15 support

Cs⁺ and NH₄⁺ are well known as effective counter cations for HPA encapsulation in zeolites [2, 22, 23]. Mukai et al. showed that Cs⁺ cation was even better than NH₄⁺ for HPA Brønsted immobilisation on zeolite Y support [23] with higher HPA content and better leaching stability in polar media. This result once again can be seen in the case of AS15 support. Mesoporous system of the AS15 support promotes the easy ion exchanges between counter cations (NH₄⁺ and Cs⁺) and Brønsted sites, resulting in the similar HPA contents of HPA-NH₄/AS15 (24.28 wt%) and HPA-Cs/AS15 (23.16 wt%) samples, as can be seen in Table 3.

The fructose fragrant synthesis efficiency shown in Fig. 7 and Table S3 indicates that HPA-Cs/AS15 sample had slightly better EAA conversion (94.82%) than HPA-NH₄/

**Fig. 7** Effect of counter cation type on the catalytic activities of the samples in fructose fragrant synthesis (other reaction conditions - catalyst weight: 3 wt%, solvent: isooctane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)**Fig. 8** NH₃-TPD spectrums of the samples: **a** AS15-OX; **b** HPA-NH₄/AS15; **c** HPA-Cs/AS15; **d** pure HPA

AS15 sample (93.49%) even with slightly lower HPA content. This result indicates that HPA-Cs/AS15 sample may have a higher acidity than the HPA-NH₄/AS15 sample (Fig. 8).

In comparison to the AS15-OX support with low acidity, the NH₃-TPD spectrums of HPA-NH₄/AS15 and HPA-Cs/AS15 samples show a much higher acidity by the appearance of NH₃ desorption peaks attributed to strong acid sites at high temperatures. In comparison to HPA sample (which has NH₃ desorption peak in the NH₃-TPD spectrum observed at 635.7 °C), HPA-NH₄/AS15 sample shows lower acidity (with the peak observed at 559.1 °C), HPA-Cs/AS15 shows even higher acidity (with the peak appeared at 759.6 °C). The different acidity of the samples shows that there was a counter cation effect. Cs⁺ cation can promote the acidity of the HPA formed in HPA-Cs/AS15. Reversely, NH₄⁺ counter cation leads to the weakened HPA acidity in the HPA-NH₄/AS15 sample. The obtained result shows that Cs⁺ is more suitable than NH₄⁺ as counter cation of AS15 support's Brønsted site to prepare HPA/AS15 material.

The priority of Cs^+ counter cation is also proved by the HPA leaching and catalytic stabilities. Figure 9 and the data shown in Table S4 indicate that after five washing cycles times with ethanol-water mixture, the HPA content of HPA-Cs/AS15 sample changed inconsiderably (23.16 wt% at 1st and 22.57 wt% at 5th washing time). The HPA contents of HPA- NH_4 /AS15 sample after 1st and 5th washing times were 24.28 wt% and 12.33 wt%, respectively. These results show that HPA-Cs/AS15 sample has better HPA leaching stability than HPA- NH_4 /AS15 sample. Figure 10 and the data shown in Table S5 indicate that the catalytic activity of HPA- NH_4 /AS15 and HPA-Cs/AS15 decreased because the loss of HPA after each reaction cycle. The HPA loss conducts the decrease of ratio of active site number to the reactants, leading to the decrease of EAA conversion in the fructose fragrance synthesis over catalysts. By the more stable HPA Brønsted immobilisation, HPA-Cs/AS15 sample shows a better catalytic stability at fifth reaction cycle compared with HPA- NH_4 /AS15 sample. The EAA conversion over HPA-Cs/AS15 catalyst reduce 5.52% (from 94.82% at the first reaction cycle to 89.59% at the fifth reaction cycle), lower than that over HPA- NH_4 /AS15 catalyst (7.12%). This result once again shows the advantage of Cs^+ compared with NH_4^+ for the HPA/AS15 preparation.

3.2.3 Effect of catalyst weight

The required catalyst amount for fructose fragrance synthesis depends on type and acidity of the catalyst. The experimental results of different HPA-Cs/AS15 catalyst weights (2, 3 and 4 wt% to reactants total mass) shown in Fig. 11 and Table S6 indicate that in the case of using cyclohexane solvent, the sample with 3 wt% (HCA-3 wt%) is suitable for fructose fragrance synthesis (EAA conv. is 81.93%). HCA-2 wt% does not have enough active sites for the reaction (EAA conv. is 73.11%). However, HCA-4 wt% has lower catalytic activity (EAA conv. is 78.86%) than HCA-3 wt%. The lower catalytic activity of HCA-4 wt%

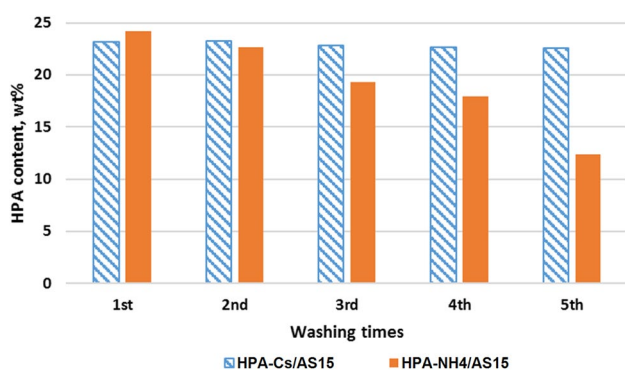


Fig. 9 Heteropoly acid (HPA) leaching stability on the AS15 support ion-exchanged with different counter cations

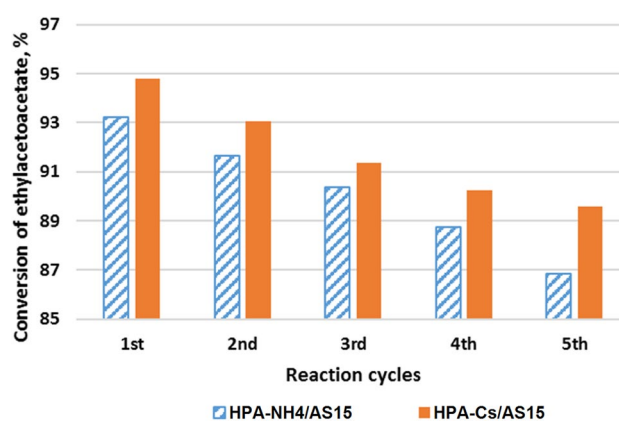


Fig. 10 Catalytic stability of HPA/AS15 samples with different counter cation ion-exchanged AS15 support in fructose fragrance synthesis

sample may be explained by the aggregation increasing the catalyst weight from 3 to 4 wt%, resulting in the reduction of active site numbers and catalytic activity of HPA-Cs/AS15.

3.2.4 Effect of the catalyst on reaction conditions

The reaction conditions of fructose fragrance synthesis such as solvent type, EAA:EG reactant molar ratio and diols reactant type were evaluated by Yang et al. over heterogenised PTSA catalyst. The results showed that the most suitable solvent was cyclohexane amongst three measured solvents of isooctane, toluene and cyclohexane. The best EAA:EG

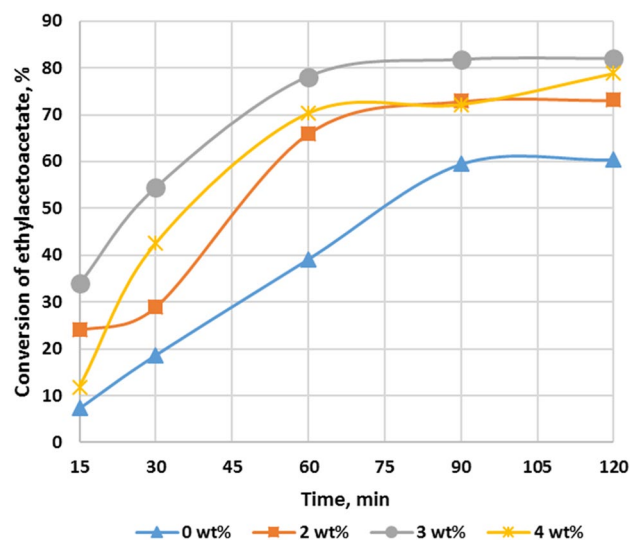


Fig. 11 Catalytic activity of HPA-Cs/AS15 by catalyst weight in fructose fragrance synthesis (other reaction conditions—solvent: cyclohexane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

reactant molar ratio and diols reactant type were 1:1.5 and EG, respectively [4].

The results shown in Figs. 12 and 13 and Tables S7, S8 illustrate the agreement results of fructose fragrant synthesis over HPA-Cs/AS15 catalyst with that over heterogenised PTSA studied by Yang et al. in terms of EAA:EG reactant molar ratio (1:1.5) and diols reactant type (EG). This agreement is because these reaction conditions are not affected by the catalyst type. However, in terms of solvent type, the obtained result of fructose fragrant synthesis over HPA-Cs/AS15 catalyst was different from that over heterogenised PTSA catalyst. The results shown in Fig. 14 and Table S9 indicate that toluene is the most suitable solvent (EAA conv. is 95.58%). Isooctane solvent is also a good solvent with inconsiderably lower efficiency (EAA conv. is 94.82%) in comparison to toluene solvent. The explanation for this result may be the boiling temperatures of the solvents. Amongst isooctane, toluene and cyclohexane solvents, cyclohexane has the lowest boiling temperature of 81.4 °C, toluene has the highest one of 110.6 °C, isooctane has the medium one of 99 °C. For the refluxing, temperature of reaction needs to achieve the boiling point of the solvent. HPA-Cs/AS15 is a mesoporous catalyst with the presence of HPA inside the pore system. A high temperature can promote the diffusion of the reactants into the pore system of HPA-Cs/AS15 catalyst to contact with immobilised HPA molecules. Because of this reason, the toluene and isooctane solvents should be the better candidates compared to cyclohexane solvent. The good result obtained with isooctane solvent shows that the temperature around 100 °C may be good for fructose fragrant synthesis over HPA-Cs/AS15 catalyst.

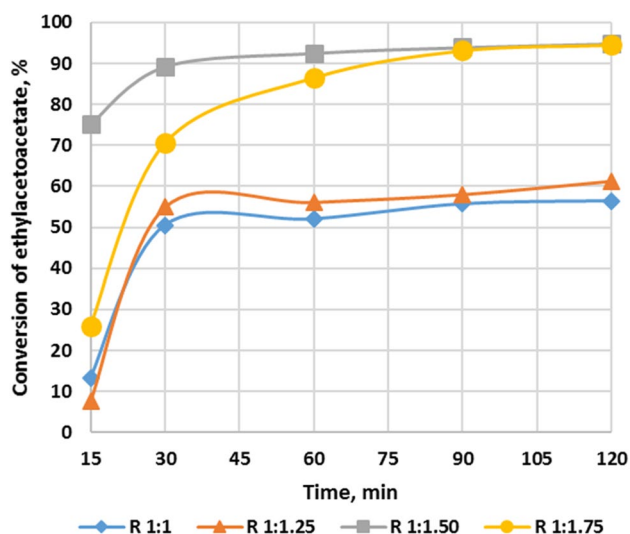


Fig. 12 Catalytic activity of HPA-Cs/AS15 by different EAA:EG reactants molar ratios in fructose fragrant synthesis (other reaction conditions—catalyst weight: 3 wt%; solvent: isooctane; diols reactant: EG)

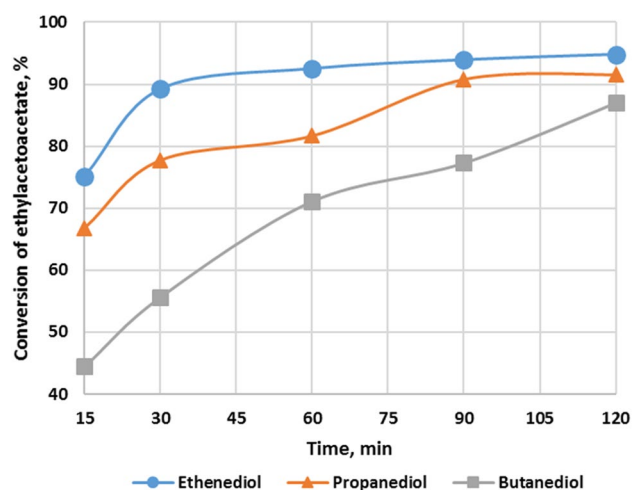


Fig. 13 Catalytic activity of HPA-Cs/AS15 by different reactant type in fructose fragrant synthesis (other reaction conditions—catalyst weight: 3 wt%; solvent: isooctane; reactants molar ratio of EAA:EG=1:1.5)

3.2.5 Comparison study

Heterogenisation efficiency of the HPA-Cs/AS15 catalyst was further measured by catalytic comparison to those of pure HPA and the homogeneous strong acid catalysts (PTSA and H_2SO_4) in the fructose fragrant synthesis. Figure 15 and the data shown in Table S10 demonstrate the positive result that HPA-Cs/AS15 catalyst shows better catalytic activity compared with commercial pure HPA catalyst. After 120 min of acetalisation, EAA conversion of fructose fragrant synthesis over commercial pure HPA is 89.52%, lower than that over HPA-Cs/AS15 sample (94.82%). The

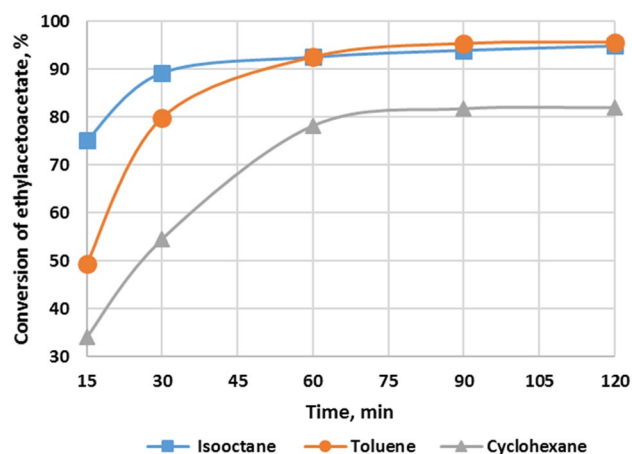


Fig. 14 Catalytic activity of HPA-Cs/AS15 by different solvent in fructose fragrant synthesis (other reaction conditions—catalyst weight: 3 wt%; reactants molar ratio of EAA:EG=1:1.5; diols reactant: EG)

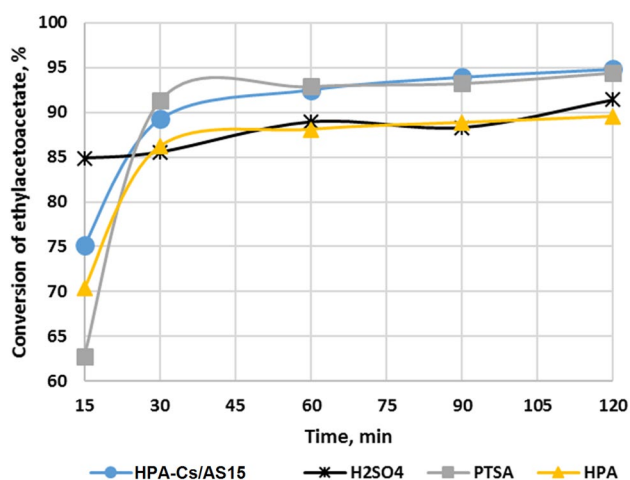


Fig. 15 Catalytic activity of HPA-Cs/AS15 compared to some homogeneous catalysts in fructose fragrant synthesis (other reaction conditions—solvent: isoctane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

soluble property of commercial pure HPA in the EG polar reactant limits the contact of HPA with EAA reactant (which is much less polar than EG), therefore resulting in the catalyst deactivation in fructose fragrant synthesis.

In comparison to H₂SO₄ and PTSA homogeneous catalysts, the performance of HPA-Cs/AS15 sample was higher than H₂SO₄ catalyst (EAA conv. is 91.43%), but nearly equal to PTSA catalyst (EAA conv. is 94.44%) in the fructose fragrant synthesis. PTSA is a strong organic acid. Therefore, it has high dispersibility in the reaction media to have ideal contact ability with the reactants, conducting the high catalytic performance of this catalyst for fructose fragrant synthesis. The results show that HPA-Cs/AS15 is an effective inorganic catalyst for fructose fragrant synthesis with known advantages of heterogeneous catalysts.

4 Conclusions

The new HPA-Cs/AS15 was successfully prepared and applied as catalyst for the fructose fragrant synthesis. The obtained results proved that cesium ion was an effective counter cation of the ion-exchanged AS15 support (that was P123 structural chemically oxidatively removed) for preparing of HPA-Cs/AS15 material. This catalyst had high acidity (confirmed by NH₃-TPD spectrum), good immobilised HPA content (23.16 wt%), very good HPA leaching stability (the HPA lost content was only 2.55% after five washing times) and high catalytic performance (the highest EAA conversion was 95.58%, the activity reduced only by 5.52% after five reaction cycles, the better activity of HPA-Cs/AS15 compared to those of HPA-NH₄/AS15, pure HPA and H₂SO₄ homogeneous catalyst).

The use of HPA-Cs/AS15 catalyst did not affect the reaction conditions of the fructose fragrant synthesis such as EAA:EG reactants molar ratio and diols reactant type. The suitable solvent was not only depended on the reaction type, but also affected by catalyst type. Toluene and isoctane which had the higher boiling temperatures than 100 °C were the most suitable solvents in comparison to cyclohexane solvent (with the lower boiling temperature of 81.4 °C) for promoting the diffusion of the reactants into the mesopore system of HPA-Cs/AS15 catalyst to contact with the immobilised HPA molecules. The catalytic performance of HPA-Cs/AS15 catalyst in the fructose fragrant synthesis is expected to open the potential of this catalyst for other organic synthesis reactions with polar reactant compounds.

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Compliance with ethical standards

Conflict of interest There are no conflicts to declare.

References

- K. Kakaei, M.D. Esrafil, A. Ehsani, *Interface Sci. Technol.* **27**, 1 (2019)
- E. Rafiee, S. Eavani, *RSC Adv.* **6**, 46433 (2016)
- B. Hu, C. Li, S.X. Zhao, L.M. Rong, S.Q. Lv, X. Liang, C. Qi, *Molecules* **15**, 5369 (2010)
- S. Gao, X.Z. Liang, J.G. Yang, M.Y. He, *Sci. China Ser. B* **51**, 646 (2008)
- A. Vinu, J. Justus, V.V. Balasubramanian, S.B. Halligudi, K. Ariga, T. Mori, *Collect. Czech. Chem. Commun.* **73**, 1112 (2008)
- F. Zhang, C. Yuan, J. Wang, Y. Kong, H. Zhu, C. Wang, *J. Mol. Catal. A Chem.* **247**, 130 (2006)
- Y. Liu, Y.T. Wang, T. Liu, D.J. Tao, *RSC Adv.* **4**, 22520 (2014)
- V.Z. Sasca, O. Verdes, L. Avram, A. Popa, A. Erdöhelyi, A. Oszko, *Appl. Catal. A Gen.* **451**, 50 (2013)
- E.Y. Safronova, A.K. Osipov, A.E. Baranchikov, A.B. Yaroslavlsev, *Inorg. Mater.* **51**, 1157 (2015)
- E. Rafiee, F. Rahimi, *Monatsh. Chem.* **144**, 361 (2013)
- Y. Iwase, S. Sano, L. Mahardiani, R. Abe, Y. Kamiya, *J. Catal.* **318**, 34 (2014)
- T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru, M. Misono, *Chem. Mater.* **12**, 2230 (2000)
- Z. Huo, J. Zhao, Z. Bu, P. Ma, Q. Liu, J. Niu, J. Wang, *Chem. Cat. Chem.* **6**, 3096 (2014)
- X. Lia, R. Cao, Q. Lin, *Catal. Commun.* **69**, 5 (2015)
- E. Rafiee, F. Mirnezami, *J. Mol. Liq.* **199**, 156 (2014)
- Y. Leng, J. Liu, P. Jiang, J. Wang, *Chem. Eng. J.* **239**, 1 (2014)
- E. Rafiee, M. Kahrizi, *Res. Chem. Intermed.* **41**, 2833 (2015)
- Y. Chen, Y. Cao, G.P. Zheng, B.B. Dong, X.C. Zheng, *Adv. Powder Technol.* **25**, 1351 (2014)
- E. Rafiee, S.H. Shahebrahimi, M. Feyzi, M. Shaterzadeh, *Inter. Nano Lett.* **2**, 29 (2012)
- A. Popa, V. Sasca, D. Bajuk-Bogdanović, I. HolclajtnerAntunović, *J. Porous. Mater.* **23**, 211 (2016)

21. R.M. Ladera, M. Ojeda, J.L.G. Fierro, S. Rojas, *Catal. Sci. Technol.* **5**, 484 (2015)
22. S.R. Mukai, T. Masuda, I. Ogino, K. Hashimoto, *Appl. Catal. A: Gen.* **165**, 219 (1997)
23. S.R. Mukai, L. Lin, T. Masuda, K. Hashimoto, *Chem. Eng. Sci.* **56**, 799 (2001)
24. L. Zhao, Y. Chi, Q. Yuan, N. Li, W. Yan, X. Li, *J. Colloid Interface Sci.* **390**, 70 (2013)
25. X. Zheng, L. Zhang, J. Li, S. Luo, J.P. Cheng, *Chem. Commun.* **47**, 12325 (2011)
26. R. Tayebee, M.M. Amini, M. Akbari, A. Aliakbari, *Dalton Trans.* **44**, 9596 (2015)
27. E. Grinerval, F. Bayard, J.M. Basset, F. Lefebvre, *Inorg. Chem.* **53**, 2022 (2014)
28. X. Chen, H. Li, P. Yin, T. Liu, *Chem. Commun.* **51**, 6104 (2015)
29. T.H. Truong, V.C. Do, N.M. Do, T.Q. Hung, H.V. Doan, T.N. Nguyen, T.H. Doan, T.H.N. Le, T.V. Nguyen, L.G. Bach, Q.V. Tran, *Mol. Catal.* **478**, 110571 (2019). <https://doi.org/10.1016/j.mcat.2019.110571>
30. M. Chamack, A.R. Mahjoub, H. Aghayan, *Chem. Eng. J.* **255**, 686 (2014)
31. Z. Zhang, K.G. Marek, J.S. Watson, J. Tian, M.R. Ryder, K.A. Tarach, L.L. Pérez, J.M. Triguero, I.M. Cabrera, *Nat. Sus.* **2**, 39 (2019)
32. M.J. Nash, A.M. Shough, D.W. Fickel, D.J. Doren, R.F. Lobo, *J. Am. Chem. Soc.* **130**, 2460 (2008)

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