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Influence of properties of SAPO's on the one-pot conversion of mono-, di- and poly-saccharides into 5-hydroxymethylfurfural†

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Synthesis of 5-hydroxymethylfurfural (5-HMF) from biomass derived mono- and poly-saccharides is gaining importance because of its usefulness in the preparation of important chemicals. In our work, we have synthesized several silicoaluminophosphate (SAPO) catalysts, and have shown that in the absence of any other pH modifying reagents, those are active in converting mono- and poly-saccharides into 5-HMF under biphasic reaction condition at 175 °C. Particularly, SAPO-44 catalyst showed the best activity in the conversion of fructose to yield 78% 5-HMF with 88% selectivity. On the contrary, all other catalysts showed lower yields (H-MOR: 63%, SAPO-5: 32%, 2DCT: 60%). Over SAPO-44, good yields for 5-HMF were observed when glucose (67%), maltose (57%), cellobiose (56%) and starch (68%) were used as substrates. Recycle study carried out with SAPO-44 catalyst in the fructose conversion reaction showed marginal decrease in the activity up to 3rd run and then afterwards constant activity was observed up to 5th run (1st: 78%, 2nd: 71%, 3rd: 66%, 4th: 65%, 5th: 65%). Catalyst characterizations revealed that SAPO catalysts have higher hydrophilic nature than H-MOR (Si/Al = 10) and hence it is postulated that this property may help in achieving better results. Further studies on the catalyst characterizations revealed that SAPO-44 undergoes modifications in its structure. However, ICP-OES data suggests that Al and/or P are not leached out in the solution indicating that change in local environment around elements is possible. The influence of acid amount, type of acid site *etc.* on the catalytic activity is discussed and found out that strong acid sites are required to boost the 5-HMF yields.

1. Introduction

Solid acid catalysts are attracting a lot of attention in carbohydrate chemistry for the conversion of polysaccharides and sugars into value-added chemicals. It is reported that solid acid catalysts can hydrolyze polysaccharides like starch,[1] cellulose[2] and hemicellulose[3] to yield monomer sugars. The dehydration reaction of fructose yields 5-hydromethylfurfural (5-HMF) over solid acid catalysts. 5-HMF, the "sleeping giant"[4] of renewable intermediate chemicals is used to produce a versatile range of important chemicals such as 2,5-furandicarboxyl acid, one of the top 12 value added chemicals,[5] 2,5-dimethylfuran, 2,5-dihydroxymethylfuran, 2,5-bis(hydroxymethyl)tetrahydrofuran and liquid alkanes by undergoing oxidation,[6–8] hydrogenation[9,10] and Aldol condensation reactions.[11,12] 5-HMF is typically synthesized from a variety of substrates such as fructose,[13–15] glucose,[14,16,17] starch,[18,19] cellulose[19,20] and inulin[4,19,21] using homogeneous catalysts such as mineral acids,[22–25] organic acids,[25,26] soluble metal halides,[27,28] heteropoly acids[29] and ionic liquids.[28,30,31] But due to the problems associated with homogeneous catalysts solid acids such as, zeolites,[13,32] ion-exchanged resins,[12,29,33,34] metal oxide,[17,35] and Sn-Mont catalyst[36] are used to convert fructose into 5-HMF. Use of polar aprotic solvents such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and acetonitrile have proven to be better solvents compared to a water-only system in HMF formation. Enhancement of 5-HMF yield to 54% is possible in DMSO compared to a water-only system (34% yield) using TiO_2 nanoparticles.[37] Ion-exchange resin also showed good catalytic activity in fructose dehydrocyclization reaction (Amberlyst-15: 100% 5-HMF, Nafion-H: 75% 5-HMF) in DMSO.[29] But the use of a high boiling solvent makes the separation process for 5-HMF from the solvent unfavourable and energy consumable. With this in mind miscible solvent systems were studied. An acetone + DMSO system yielded better 5-HMF (90%) compared to a water + acetone system (73%) at 150 °C over an ion-exchange resin.[33,34] Various metal oxides (Ta oxide, Nb oxide) were also studied in a water + 2-butanol system.[35] A recent report shows that use of a Sn-Mont catalyst can produce 79% 5-HMF yield from fructose at 160 °C using a tetrahydrofuran (THF) + DMSO solvent system.[36] Further improvement in 5-HMF yield is possible by incorporation of

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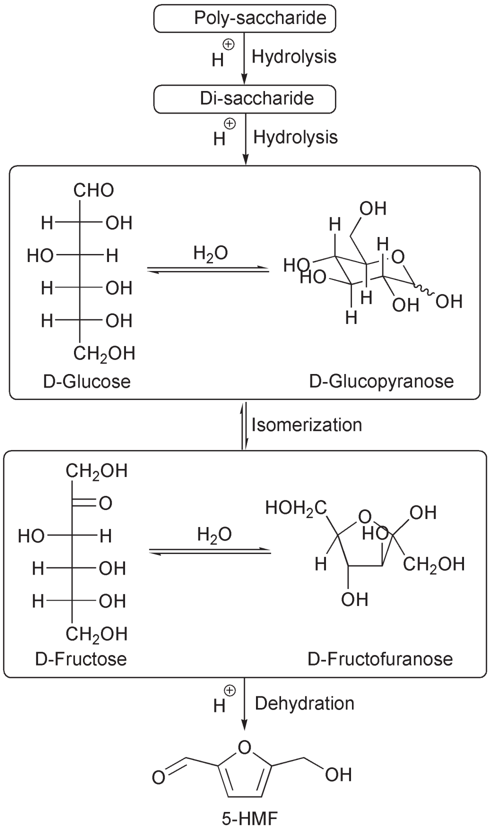
biphasic solvent where organic solvent extracts 5-HMF from the aqueous solution thus limiting possible side reactions. Heteropoly acids are examined in a water + methyl *iso*-butyl ketone (MIBK) solvent system at 115–120 °C and 74–78% HMF yield was observed.[38,39] Reactions carried out with zeolites in water + MIBK solvent system shows that H-MOR is the best catalyst (74% HMF yield) amongst all other zeolite catalysts employed (HZSM-5, 45% 5-HMF yield; Hβ, 32% 5-HMF yield).[13,32] For solid acid catalysts only a handful of reports are available for the one-pot conversion of glucose into 5-HMF even though glucose is cheaper than fructose. It is known that 5-HMF formation from glucose has to proceed through fructose formation and for this isomerisation reaction typically base catalysts are employed. Hence it becomes important to find a catalyst which is capable of carrying out isomerisation and dehydration reactions to yield 5-HMF from glucose. Additionally, the one-pot conversion of di- and poly-saccharides to 5-HMF is scarcely reported. A catalyst recycling study is reported at 130 °C for 1.5 h using a Glu-TsOH catalyst to convert fructose into *ca.* 90% yield of 5-HMF.[40] Use of a Sn-Mont catalyst allowed the reaction through six cycles with 53% 5-HMF yield and 98% glucose conversion.[36] Other reports on recycling with fructose are available with catalysts under microwave heating.[33,41] It is important to note here that in addition to there being very few reports most of the reports unfortunately fail to give details on characterization and recyclability of the catalysts. We believe that in sugar chemistry wherein water is an integral part of the reactions (hydrolysis, dehydration) and high pressures and temperatures are applied it would be challenging to use structured catalysts (well defined porous structure) since those have a tendency to collapse.[3,42] It is also essential to achieve the required properties of the amount of acid, hydrophilicity–hydrophobicity, access to active sites *etc.* in the catalyst to obtain high yields. Here we show that SAPO type catalysts can be efficiently used in the conversion of mono-, di- and poly-saccharides to yield 5-HMF with high selectivity (Scheme 1). Further, we present a detailed study on catalyst characterization and try to establish a catalyst property–activity correlation.

In the literature it is reported that SAPO materials are hydrothermally stable up to *ca.* 600 °C under 20% steam.[43] It is also reported that H-MOR catalyst has a hydrothermal stability up to *ca.* 240 °C.[44] It is understood that hydrothermal stability depends on various factors such as Si/Al ratio, synthesis procedures, pore structures *etc.*, hence direct comparison between hydrothermal stability of SAPO and H-MOR can not be done. Yet it was thought that SAPO catalysts may have more stability under the reaction cconditions, hence we synthesized SAPO-44 and SAPO-5 catalysts and evaluated those in these reactions.

2. Experimental section

2.1 Synthesis and characterization of SAPO's

Crystalline silicoaluminophosphate materials were synthesized according to a published report.[45,46] As a source of Al_2O_3, SiO_2 and P_2O_5, pseudoboehmite (Marathwada Chemical Industries Pvt. Ltd, grade: MCI-1524, 65–78% Al_2O_3), fumed silica (Aldrich) and orthophosphoric acid (Fisher Scientific) were used.



Scheme 1 Production of 5-HMF from poly-, di- and mono-saccharide using solid acid catalyst.

SAPO-44 material was synthesized using a molar gel composition of $1.0CHA:1.0Al_2O_3:1.0SiO_2:1.0P_2O_5:60.0H_2O$ where, CHA stands for cyclohexylamine.[45] In a typical synthesis, 4.60 g pseudoboehmite was added slowly (within 2 h) to diluted phosphoric acid (7.69 g H_3PO_4 + 12.50 g distilled water) under vigorous stirring and *gel A* was formed. In another container, 3.33 g CHA was added dropwise to 2.05 g of fumed silica suspended uniformly in 23.50 g water and the mixture was denoted as *gel B*. Now *gel B* was mixed under stirring with *gel A* and the mixture was further homogenised (6 h stirring). The resulting solution was transferred to three Teflon lined steel autoclaves and subjected to aging (crystallization) for different time periods (0 h, 48 h and 176 h) at 200 °C under atmospheric pressure at static conditions. After cooling the autoclave, the solid materials were filtered, washed with distilled water and dried. The material was calcined at 500 °C at a heating rate of 1 °C min^{-1} in a tubular furnace for 6 h in the presence of air (10 mL min^{-1}). Material with crystallization times of 0 h, 48 h and 176 h were termed as ZDCT, 2DCT and SAPO-44 respectively.

SAPO-5 material was prepared using molar gel composition of $1.0TEA:1.0Al_2O_3:0.4SiO_2:1.0P_2O_5:50.0H_2O$ where, triethylamine is abbreviated as TEA.[46] In a typical procedure, *gel A* was prepared by mixing 1.00 g pseudoboehmite to diluted phosphoric acid (1.58 g orthophosphoric acid + 5.95 g distilled water) in 2 h. To 0.69 g TEA, 0.16 g fumed silica was added to get *gel B*. Both the gels were mixed together and made homogeneous by stirring for 3 h at RT. The prepared gel was aged in an autoclave with teflon liner for 4 h at 200 °C. After cooling down the autoclave, the solid was filtered, washed and dried. Final SAPO-5 material was obtained by calcining as-synthesized solid at 500 °C for 6 h under air at 10 mL min^{-1} flow rate.

SiO_2, γ-Al_2O_3, SiO_2-Al_2O_3 were obtained from Aldrich and H-MOR (Mordenite, Si/Al = 10) was obtained from Zeolyst International.

The catalysts were characterized with XRD, NH_3-TPD, ICP, SEM, and solid state NMR techniques.

X-ray powder diffractions (XRD) were recorded in a Rigaku Miniflex diffractometer using Ni-filtered monochromatic Cu-Kα radiation (λ = 1.5406 Å).

Temperature programmed desorption (TPD) of NH_3 was carried out in a Micromeritics AutoChem-2920 instrument. Typically, the catalyst was activated at 600 °C (4 °C min^{-1}) in a helium flow (30 mL min^{-1}) for 1 h. The temperature was decreased to 50 °C and NH_3 was adsorbed by exposing the samples to 10% NH_3 in helium for 1 h. It was then flushed with helium for another 1 h at 100 °C to remove all the physisorbed NH_3. Desorption of NH_3 was carried out in a helium flow (30 mL min^{-1}) by increasing the temperature from 100 to 600 °C at a rate of 10 °C min^{-1}.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis was done on a Spectro Acros instrument equipped with winlab software. The sample was prepared using standard method.[47]

SEM micrographs of the samples were obtained on a Leo Leica Cambridge UK Model Stereoscan 440 scanning electron microscope. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging and also to protect from thermal damage due to an electron beam.

Solid state ^{29}Si,^{31}P and ^{27}Al NMR spectra were recorded on a Bruker Avence-300 MHz spectrometer, operated at a field of 7.06 tesla. A fine powdered sample was placed in a 4 mm zirconia rotor and spun at 10 kHz for all the nuclei.

2.2 Catalytic reactions and analysis

D(-)-Fructose (s. d. fine, 99.5%), D(-)-glucose (s. d. fine, >99.0%), maltose monohydrate (s. d. fine), cellobiose (s. d. fine), potato starch (LOBA Chemie), 5-HMF (Aldrich, 99.0%), MIBK (LOBA Chemie, 99.0%), and ethanol (Chanshu Yangyuan Chemicals, 99.9%) were purchased and used as received.

All the reactions were carried out in a 100 mL Parr autoclave. In a typical reaction 0.5 g of carbohydrate (fructose, glucose, maltose, cellobiose or starch, 10% wt/wt with respect to water charge), 0.143 g catalyst (catalyst/substrate loading = 29%) were mixed with water + organic solvent = 5 mL + 25 mL or 30 mL water/organic solvent in autoclave and heated at the desired temperature under stirring. When the temperature of the reactor reached just 5 °C below the desired temperature that time was taken as zero time. After completion of the reaction the reactor was cooled to room temperature. The catalyst was separated from the reaction mixture by centrifugation and the aqueous and organic layers were separated from each other.

For the recycling study, the catalyst separated from the reaction mixture was washed with water, dried in an oven and calcined in air at 500 °C for 6 h. This catalyst was then used for the next reaction.

The aqueous layer was analysed by HPLC, equipped with a Pb^{2+} column (300 mm × 7.8 mm, 80 °C), refractive index detector (cell temperature of 40 °C) and Millipore water was used as the mobile phase with 0.6 mL min^{-1} flow rate. Organic layer analysis was done on a Varian gas chromatograph, equipped with BPX-5 column (50 m × 0.22 μm *ID*) and flame ionisation detector (FID).

Details on the calculations are mentioned below,

% Conversion = [{Initial mole of carbohydrate − unconverted mole of carbohydrate (HPLC)}/Initial mole of carbohydrate] × 100

% Yield = {Mole of product formed (HPLC + GC)/Theoretical mole of product} × 100

All the conversions and yields mentioned in this manuscript are calculated based on GC and HPLC results. In case of starch conversions were calculated as follows,

% Conversion = [{Initial weight of starch − recovered weight of starch (after reaction)}/Initial weight of starch] × 100

We considered 100% recovery of catalyst after reaction.

3. Results and discussion

3.1 Conversion of fructose to 5-HMF

Fig. 1 presents the results for fructose conversion into 5-HMF using SAPO-44, SAPO-5, SiO_2, γ-Al_2O_3, and H-MOR (Si/Al = 10)

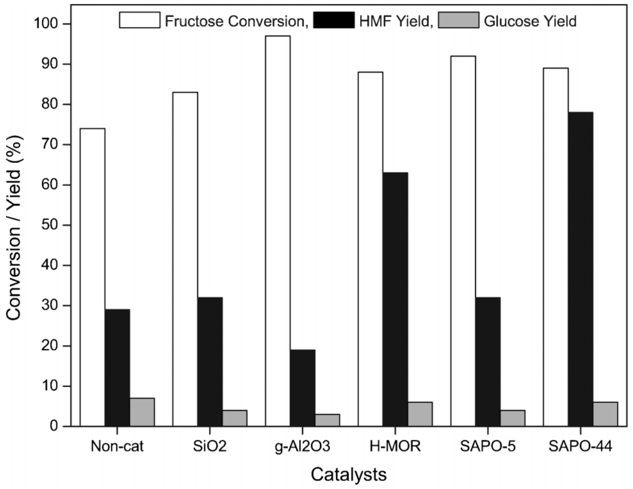


Fig. 1 Conversion of fructose using various solid acid catalysts. *Reaction conditions*: fructose (10 wt%), catalyst (0.143 g), water + MIBK (1 : 5 v/v), 175 °C, 1 h.

catalysts at 175 °C for 1 h. Zeolite H-MOR was taken as the benchmark catalyst as it was shown to be the best catalyst among the zeolites used (H-ZSM-5, H-β).[13,32] SAPO-44 catalyst showed 78% 5-HMF yield with 88% selectivity (89% conversion). Besides 5-HMF, 6% glucose was also observed. Thus, over SAPO-44 catalyst a 94% carbon balance was observed hinting that loss of carbon due to degradation reactions is much less. The elemental analysis of catalyst revealed that *ca.* 4% carbon is present on the spent catalyst. The formation of 5-HMF was confirmed by ^{1}H NMR (Fig. S1, ESI†). Under similar reaction conditions, H-MOR and SAPO-5 catalysts showed 63% and 32% 5-HMF yields, respectively. Furthermore, with H-MOR 72% selectivity for 5-HMF (88% conversion) and 6% glucose formation (79% carbon balance) was observed. The reaction without catalyst showed 29% 5-HMF yield with 74% fructose conversion. Since SAPO and H-MOR catalysts contain Si, Al and P we carried out reactions with SiO_2 and Al_2O_3. However, we observed poor yields of 5-HMF with these catalysts. This implies that the combination of Si, Al and P gives rise to Brønsted acid sites in the catalysts and is important for the reaction. Formation of humins in these reactions is known from the literature,[48] however, it is difficult to analyse those with GC and HPLC so we could not quantify this. But it is interesting to note that with SAPO-44 as catalyst a very high yield for 5-HMF is observed. Though SAPO-5 has a larger pore size (0.80 nm) than SAPO-44 (0.43 nm) its activity is lower.[38] We acknowledge here that the presence of small pore opening in SAPO-44 may hinder the access of active sites by substrate molecules. Additionally, the difference in activity between SAPO-5 and SAPO-44 might be due to the variation in the properties of the catalysts such as amount and type of acid sites, hydrophilicity-hydrophobicity (see discussions on catalyst characterization). To make sure that all the results are reproducible we have done all the reactions in triplicate and we observed ±2% variation in the results (conversion, selectivity, yield and carbon balance).

3.2 Effect of reaction parameters in fructose reactions

It is suggested in the literature that the temperature may influence the degradation or side reactions of fructose and 5-HMF. Hence reactions were conducted at 165 and 185 °C to check the effect of temperature on the 5-HMF yield. The reaction carried out over SAPO-44 for 1 h at 165 °C (43% yield, 56% conversion, 77% selectivity) and 185 °C (45% yield, 92% conversion, 49% selectivity) gave poor yields of 5-HMF compared to the reaction carried out at 175 °C (78% yield). The poor yield of 5-HMF at 165 °C might be because of lower conversion (56%) and at 185 °C is due to predominant degradation reactions (49% selectivity). H-MOR and SAPO-5 catalysts gave 43% yield (69% conversion, 62% selectivity) and 28% yield at 165 °C respectively.

To know if the reaction atmosphere has any effect on the conversions and yields of 5-HMF, reactions were performed under nitrogen and air atmosphere. In both reactions similar activity with SAPO-44 catalyst was observed (78 ± 2% yield at 175 °C after 1 h).

It is desirable to use concentrated solutions of substrates and hence reactions were carried out using 10% (wt/wt, 5 g water/0.5 g substrate) and 30% (wt/wt, 5 g water/1.5 g substrate) solutions keeping the S/C ratio constant. The increase in concentration decreased the 5-HMF yield to 66% compared to 78% observed with 10% (wt/wt) solution. This decrease may be attributed to the formation of condensation products or degradation reactions as the selectivity to 5-HMF was decreased to 73% even if conversion (91%) was almost same as that with 10% (wt/wt) solution (89% conversion, 88% selectivity).

In the presence of acidic catalysts, it is observed that the reaction yields formic and levulinic acids and is thus hampering the 5-HMF yields. To overcome formation of these acids from 5-HMF in the literature use of organic solvents such as MIBK, 2-butanol, DMSO, ethyl acetate, THF *etc.* is reported. Our study showed that with only water as solvent, 39% 5-HMF yield (59% selectivity) is obtained with SAPO-44 catalyst within 1 h at 175 °C. Under similar reaction conditions, fructose conversion was carried out using only ethanol (fructose and 5-HMF can dissolve) and we observed 56% yield of 5-HMF. Later, a biphasic (water + MIBK) system was found to be suitable to achieve high yields (78%). To check the effect of the water + MIBK ratio on the 5-HMF yield and selectivity, reactions were conducted with 1 : 1 (v/v) and 1 : 5 (v/v) solvent ratios. It was observed that with 1 : 5 (v/v) ratio a higher yield of 5-HMF (78%) was seen compared to 1 : 1 (v/v) ratio (47%). Though in both the reactions 5-HMF selectivity was almost same (*ca.* 85%). Similar results of change in solvent ratio were observed in earlier work.[12,19]

3.3 Hydrophilicity-hydrophobicity

It is important to note here that the total acid amount in SAPO-44 and H-MOR is the same (1.2 mmol g^{-1}, Table 1), yet H-MOR gave a lower yield of 5-HMF (63%) than SAPO-44 (78%) and that selectivity was lower in the case of H-MOR (72%) compared to SAPO-44 (88%). This indicates that not only the acid amount but other factors are also playing an important role in achieving higher activity in SAPO-44. Over SAPO-5 catalyst 34% 5-HMF yield was observed, however with poor selectivity. To understand the catalyst behaviour, we undertook a comparative study on the hydrophilicity-hydrophobicity property of all three catalysts (H-MOR, SAPO-5, and SAPO-44) under similar conditions. In three different test tubes equal amounts of H-MOR, SAPO-5 and SAPO-44 were taken and to it water was added. Then to these test tubes carbon tetrachloride was added (d = 1.58 g mL^{-1} at 25 °C) and maintaining 1 : 1 v/v ratio of solvents. We could easily see that immediately after addition of carbon tetrachloride the SAPO-44 went to the aqueous layer (upper layer) giving a clear organic phase (Fig. 2). However, H-MOR was almost equally distributed in both the layers. The SAPO-5 catalyst was distributed more in the water layer compared to the organic layer. After 10 min of settling time some of the H-MOR was still present in the organic layer (lower layer). It is noteworthy that though the density of SAPO-44 (0.61 g mL^{-1}) is higher than that of H-MOR (0.35 g mL^{-1}) still it was present in the upper layer (water). Similarly, most of the SAPO-5 was observed in the water layer after 10 min settling time. This reveals that the hydrophilicity of the catalysts is in the following order, SAPO-44 > SAPO-5 > H-MOR.

Table 1 NH_3-TPD study of catalysts

Catalyst	Total acid amount (mmol g^{-1})	Acid amount distribution (mmol g^{-1}) 100–250 °C (weak)	250–350 °C (moderate)	350–500 °C (strong)
SAPO-44 (Fresh)	1.2	0.7	0	0.5
SAPO-44 (Spent)	0.5	0.5	0	0
ZDCT	0.3	0.3	0	0
2DCT	0.4	0.4	0	0
SAPO-5	0.8	0.8	0	0
SiO_2	0.1	0.1	0	0
γ-Al_2O_3	0.4	0.1	0.3	0
SiO_2–Al_2O_3	0.6	0.3	0.3	0
H-MOR	1.2	0.5	0	0.7

Later, we used a water-MIBK (1 : 1 v/v ratio) system to check how the catalyst distribution would be under the reaction conditions. MIBK (d = 0.8 g mL^{-1} at 25 °C) was added to H-MOR, SAPO-5 and SAPO-44 already dispersed in water. It can be seen that a maximum amount of SAPO-44 came in the water layer and very little amount of SAPO-44 remains at the interface of MIBK-water. This is because MIBK has some solubility in water (16.6 g L^{-1} at 30 °C, 12.2 g L^{-1} at 90 °C)[49]. On the other hand most of the H-MOR remains in the MIBK layer (Fig. 2). Similarly, SAPO-5 was seen distributed equally in both the layers after immediate addition of MIBK. However, after 10 min settling time SAPO-5 was observed at the interface of both the layers but more in the organic layer. This study indicates that SAPO-44 is more hydrophilic in character than SAPO-5 and H-MOR and this is due to local electronegativity differences in the framework Si, Al and P in SAPO-44 and also due to presence of 'P' in the framework. Moreover, it is reported in the literature that in different SAPO materials the hydrophilicity varies.[43]

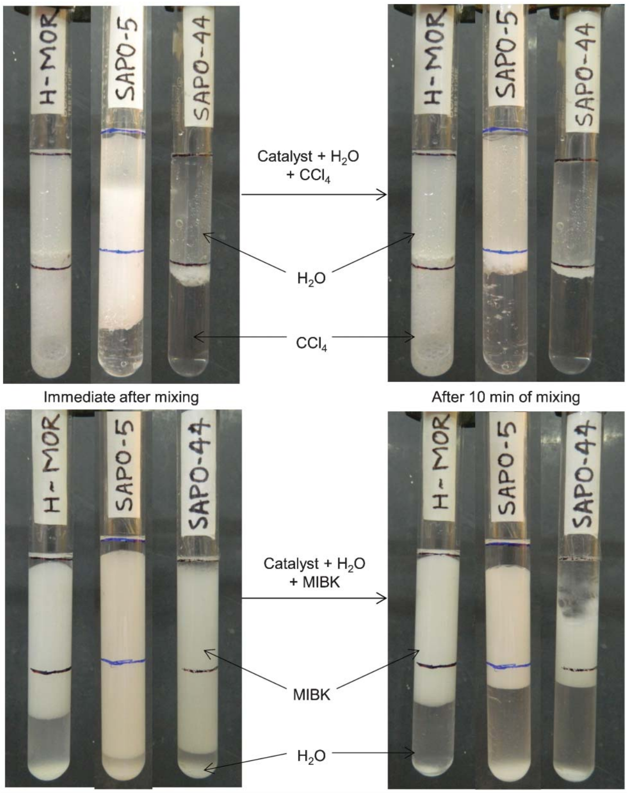


Fig. 2 Study on hydrophilicity-hydrophobicity property of catalysts. The line mark on the test tube is to show the boundary between two layers.

It is known that fructose is soluble in water and thus higher a concentration of catalyst in the water layer will be useful for the conversion of fructose into 5-HMF and suppressing the 5-HMF degradation or condensation reactions once it is extracted into the organic layer. On the other hand, if a higher concentration of catalyst is present in the organic layer then it will adversely affect the 5-HMF yields: first, a lower concentration of catalyst present in the water layer means that fructose may undergo non-catalytic reactions (refer Fig. 1) to give lower yields of 5-HMF. Secondly, whatever quantity of 5-HMF is formed in the water layer, once it is extracted into the organic layer it will undergo degradation or condensation reactions (see section 3.9).

As shown in Fig. 2, H-MOR has a tendency to remain in the organic phase and because of that 5-HMF can undergo further degradation reactions on the catalytically active sites of H-MOR catalyst.

A similar study is also done with 1 : 5 (v/v) ratio of water + MIBK as this ratio is used in the reactions. With a 1 : 5 (v/v) ratio similar results were observed as were seen with 1 : 1 (v/v) ratio.

The above study has been done to the best of our knowledge for the first time to correlate the catalyst activity and property in this reaction, which may be helpful in tailoring the catalyst. The poor yield of 5-HMF in SAPO-5 cannot be attributed to the hydrophilic character of the catalyst alone. In the following sections, further studies are discussed to understand the effects of catalyst properties on the reactions.

3.4 Effect of catalyst morphology

To understand the correlation between catalytic activities with morphology-property of catalyst (SAPO-44) a study on synthesis time *vs.* activity was undertaken. It was also contemplated that a similar hydrophilic nature can be observed for all the samples of the catalysts synthesized with different crystallization times. In view of this, during the synthesis of SAPO-44

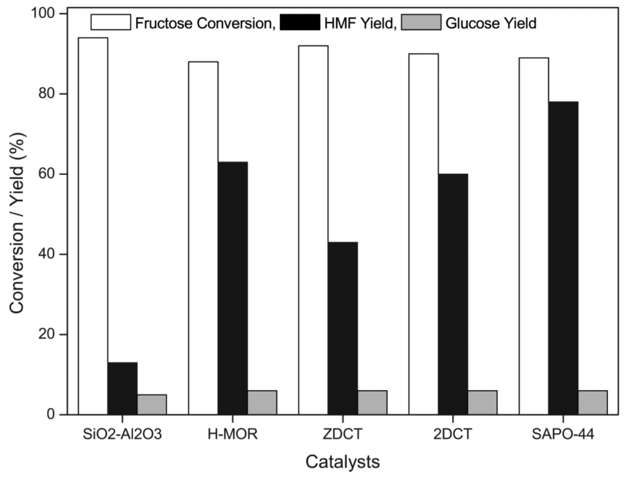


Fig. 3 Effect of catalyst morphology on fructose conversion. *Reaction conditions*: fructose (10 wt%), catalyst (0.143 g), water + MIBK (1 : 5 v/v), 175 °C, 1 h.

catalyst, samples were withdrawn after 0 day crystallization time and 2 days crystallization time. The samples were named ZDCT and 2DCT, respectively (see section 2.1 for details on synthetic procedure). Reactions were carried out with ZDCT and 2DCT catalysts along with SiO_2–Al_2O_3 catalyst at 175 °C for 1 h (Fig. 3). The ZDCT catalyst (amorphous analogue of SAPO–44) showed 43% yield of 5-HMF whereas SiO_2–Al_2O_3 (amorphous analogue of H-MOR) gave only 13% 5-HMF yield (mainly form black solids). Though SiO_2–Al_2O_3 (0.6 mmol g^{-1}) has a higher total acid amount than ZDCT (0.3 mmol g^{-1}) (Table 1, Fig. 3) the catalytic activity was lower in SiO_2–Al_2O_3. It is noteworthy that in 2DCT catalyst the total acid amount is less (0.4 mmol g^{-1}) compared to H-MOR (1.2 mmol g^{-1}), however similar activity was observed for both the catalysts (*ca.* 60%) (Fig. 3). Moreover, it is interesting to note that although the complete structure is not formed in 2DCT catalyst, it showed good activity compared to a structured catalyst like H-MOR. This may be attributed to more hydrophilic nature of SAPO materials than H-MOR.

3.5 Effect of acid amount and type of acid site

Fig. 3 shows the results for different catalysts with same catalyst loading (0.143 g, S/C weight ratio constant). The 2DCT and ZDCT catalysts had a total acid amount of 0.4 and 0.3 mmol g^{-1} and the yields were 60% and 43%, respectively. The SAPO-44 catalyst had a total acid amount of 1.2 mmol g^{-1} and showed 78% yield. To compare the catalytic results reactions were performed using similar acid amounts (S/C molar ratio constant). However, even by increasing the charge of the 2DCT and ZDCT catalysts in the reactions, the yields for the catalysts remained same. This may emphasize that to boost the 5-HMF yields further, strong acid sites are required which are not present in ZDCT and 2DCT catalysts but present in SAPO-44 (Table 1). If this is true then the reaction over H-MOR catalyst higher activity should have been obtained compared to SAPO-44 since H-MOR has more strong acid sites (0.7 mmol g^{-1}) compared to SAPO-44 (0.5 mmol g^{-1}). However, results show that H-MOR gives lower activity (63% yield, 72% selectivity) than SAPO-44 (78% yield, 88% selectivity). Hence we may conclude that higher number of strong acid sites may also help degradation reactions. In case of SAPO-5 catalyst the absence of strong acid sites may be responsible for lower activity. Considering all the above discussions it is possible to say that in the formation of 5-HMF, catalyst properties like acid amount, ratio of weak and strong acid sites, hydrophobicity-hydrophilicity play important role. Overall, SAPO-44 has optimum properties which are required to achieve higher 5-HMF selectivity.

3.6 Catalyst recycles study

The fresh SAPO-44 catalyst showed 78% 5-HMF yield but in the recycling study, a decrease in the activity was observed (50% 5-HMF yield). This might be due to the adsorption of carbonaceous deposits on the catalytically active sites as we observed a total of 94% carbon balance (see section 3.1). Elemental analysis of the catalyst also showed the presence of carbon on the spent catalyst. To remove the deposits from the catalyst, it was calcined (550 °C for 12 h) and used in further reactions. As observed in Fig. 4, with fresh catalyst 78% 5-HMF yield was observed which decreased to 71% in the 2nd run. These results prove that removal of carbonaceous deposits is necessary to achieve higher activity in subsequent runs. In the 3rd recycle run, 66% yield was obtained. However, beyond the 3rd run the activity remained almost constant up to the 5th run (4th run: 65%, 5th run: 65%). The decrease in activity in recycle runs can be attributed to the fact that SAPO-44 undergoes minor morphological changes (see section 3.10 for discussion on catalyst characterization). The NH_3-TPD study (Table 1) reveals that in 2DCT (weak, 0.4 mmol g^{-1}) and spent SAPO-44 catalyst (0.5 mmol g^{-1}) almost similar total acid amount and same type of acid site (weak) is present and hence both the catalysts offered comparable activities (65 and 60%). The H-MOR catalyst showed a decrease in activity in each consecutive run up to the 5th recycle run (1st run: 63%, 2nd run: 40%, 3rd run: 34%, 4th run: 30%, 5th run: 28%).

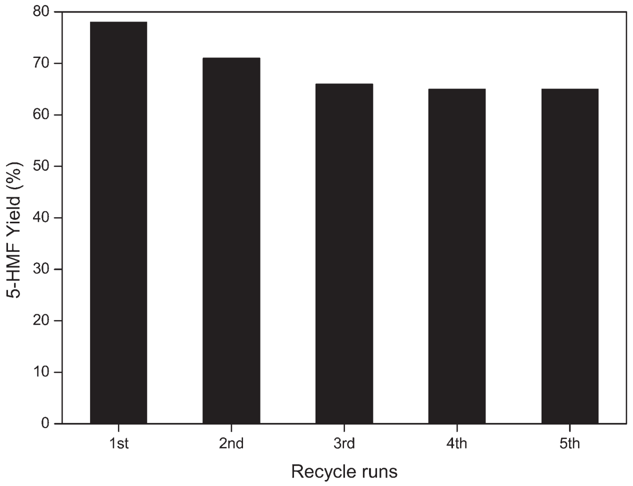


Fig. 4 Recycle study of SAPO-44 catalyst. *Reaction conditions*: fructose (10 wt%), SAPO-44, water + MIBK (1 : 5 v/v), 175 °C, 1 h.

After the 4th recycle run the catalyst showed activity similar to the non-catalytic reaction (29% yield).

3.7 Glucose as a substrate for 5-HMF synthesis

It would be desirable to use cheaply and abundantly available glucose as a substrate to synthesize 5-HMF. However, glucose forms a stable pyranose ring structure in the aqueous phase and thus is difficult to convert. The first step in 5-HMF production from glucose would be an isomerisation reaction to give fructose. This is typically achieved over base catalysts.[50–55] There are reports on the use of mineral bases, carbonate and hydroxide forms of hydrotalcite,[50] alkali metal exchanged zeolites,[51] metallosilicate,[52] zirconia[53,54] and aluminate resin[55] for the isomerization of glucose. It is demonstrated that the use of Lewis acid Sn-beta zeolite can isomerize glucose to fructose and further addition of mineral acid produces a very low yield of 5-HMF (11%).[56] It is mentioned that an intramolecular hydride shift mechanism may be responsible for the isomerisation of glucose to fructose in Sn-beta catalyst.[50] Additionally, there are few reports on using sulphated zirconia-alumina,[15] Sn-W oxide,[57] HT/Amberlyst-15,[14] phosphoric acid treated metal hydroxide,[35] Sn-Mont[36] to convert glucose into 5-HMF by either using Lewis acid properties of catalysts or combining base-acid properties in a catalyst. But these reaction systems suffer from disadvantages like lower yields, longer reaction times, no recyclability of catalyst, use of mineral acid with solid acid *etc.* To overcome these drawbacks we used SAPO-44 catalyst in the conversion of glucose.

With glucose as a substrate, SAPO-44 catalyst gave 67% 5-HMF yield (83% conversion of glucose, 81% selectivity) after 4 h at 175 °C. Besides 5-HMF we observed fructose (13%) in the reaction mixture which was not a surprise as it is an intermediate product. Further, various other catalysts were used for the glucose conversion to yield 5-HMF [SiO_2 (30%), SAPO-5 (28%), 2DCT (44%) and H-MOR (49%)]. Nonetheless these catalysts showed lower activity than SAPO-44. It is noteworthy to point out here that SAPO-44 could convert glucose efficiently into 5-HMF without addition of any other catalyst. We assume that similar type of mechanism which is responsible for Sn-beta catalyst[50] may be predominant in SAPO-44 catalyst.

3.8 Di- and poly-saccharides as substrates for 5-HMF synthesis

For the conversion of β-glucose dimer (cellobiose) to 5-HMF researchers have used homogeneous catalysts such as mineral acids,[19,20] mineral acid with Sn-beta zeolite and metal chloride in ionic liquids.[28,36,58,59] Cellobiose conversion over HT/Amberlyst-15 catalyst at 120 °C yields 35% 5-HMF.[14] The Sn-W oxide catalyst is also known to convert dimers yielding 39% 5-HMF after 18 h.[57] Recently, it was shown that Sn-Mont catalyst converts cellobiose to 42% 5-HMF.[36] Yet another report showed that from maltose (dimer of α-glucose) 14% 5-HMF yield can be obtained under microwave heating using TiO_2 NPs.[37]

We used SAPO-44 for the one-pot conversion of dimers of glucose such as maltose and cellobiose to yield 5-HMF and the results are summarized in Table 2. In all the reactions we observed complete conversion of substrates. As seen, at 175 °C SAPO-44 converts maltose to 5-HMF with 57% yield within 4 h reaction time. Along with 5-HMF, 14% yield for glucose and fructose was obtained. On the contrary, H-MOR gave 41% and 2DCT gave 44% 5-HMF yield under similar reaction conditions. While cellobiose is used as a substrate 56% yield of 5-HMF, along with 12% yield of glucose and fructose at 175 °C within 6 h of reaction time was observed over SAPO-44. The 2DCT catalyst showed 44% 5-HMF yield and H-MOR gave 43% 5-HMF yield under similar reaction conditions.

Few reports are available in the literature on the one-pot conversion of glucose polymer such as starch to 5-HMF with homogeneous mineral acids[19] or metal chloride in ionic liquid.[18,58] Production of 5-HMF from starch using heterogeneous Sn-beta zeolite mixed with HCl is reported.[60] Another report showed use of Sn-W oxide to produce 41% 5-HMF from starch within 36 h.[57]

We used SAPO-44 catalyst for starch conversion which at 175 °C and within 6 h showed 68% yield of 5-HMF (Table 2). Along with 5-HMF, formation of glucose (15% yield) and fructose (7% yield) was also observed. However, when the reaction was conducted for 8 h 5-HMF yield decreased to 61%, which may be due to the occurrence of side reactions which leads to brown solid (humins).[40] Under similar reaction conditions H-MOR (41%) and 2DCT (40%) were also active to give 5-HMF. To the best of our knowledge this is the first time that using

Table 2 Dehydration of glucose dimer and polymer to 5-HMF[a]

Substrate	Reaction Time (h)	Catalyst	Glucose yield (%)	Fructose yield (%)	5-HMF yield (%)
Maltose	4	No catalyst	17	8	22
Maltose	4	H-MOR	1	2	41
Maltose	4	2DCT	2	3	44
Maltose	4	SAPO-44	5	9	57
Cellobiose	6	No catalyst	21	9	15
Cellobiose	6	H-MOR	2	3	43
Cellobiose	6	2DCT	2	3	44
Cellobiose	6	SAPO-44	7	5	56
Starch	6	No catalyst	17	7	29
Starch	6	H-MOR	10	8	41
Starch	6	2DCT	8	7	40
Starch	6	SAPO-44	15	7	68

[a] *Reaction conditions*: substrate (10 wt%), 175 °C, water + MIBK (1 : 5 v/v).

only solid acid catalyst a 68% yield of 5-HMF is achieved directly from starch.

3.9 Possible degradation reaction pathways

It was rather disappointing that in the literature none of the reports claimed 100% selectivity and 100% yield for 5-HMF formation. This indicates that besides fructose to 5-HMF reactions, the catalysts are active for the other side reactions such as: 1) Conversion of 5-HMF into degradation products or 2) Conversion of fructose to unwanted products or 3) Condensation reactions between fructose and 5-HMF. To understand which of these reactions are playing major role in decreasing the selectivity for 5-HMF, we carried out a 5-HMF stability study at 175 °C for 1 h with H-MOR, SAPO-44, 2DCT and SAPO-5 catalysts. The results showed that 5-HMF does not undergo any reaction on any of these catalysts and hence the possibility of further degradation of 5-HMF is ruled out. The study on the second possibility of conversions of fructose cannot be performed since in any case fructose will give rise to 5-HMF and other products. The third possibility is the formation of condensation products arising from fructose and 5-HMF. To study this we carried out reactions with simultaneous addition of fructose and 5-HMF as substrate. It was observed that 5-HMF and fructose do undergo condensation reactions and that H-MOR catalyst is more active for these reactions compared to SAPO-44 (for details on experiments and discussions please refer to the ESI†). This is not surprising since the majority of H-MOR is present in the organic phase (hydrophilicity-hydrophobicity study) and the presence of strong acid sites in the catalyst (Table 1).

3.10 Catalyst characterization study

The XRD patterns for fresh and spent SAPO catalysts are presented in Fig. 5. The peak characteristics of AFI morphology are observed for SAPO-5 catalyst.[61] In case of SAPO-44, peak pattern matches well with the CHA morphology.[62] After a gel was obtained (formed by mixing Si, Al and P precursors) immediately a sample was taken (filtered, washed, dried) and the XRD was performed to reveal formation of a tridymite amorphous phase (ZDCT, 0 h).[63] The diffraction peaks due to AFI morphology start appearing as crystallization time is increased (SAPO-5, 4 h) and further increase in time yields SAPO-44 with CHA morphology (176 h).[63] Therefore, it is expected that 2DCT sample withdrawn after 48 h crystallization time may have an intermediate phase between AFI and CHA or contribution from both the phases. The XRD pattern of 2DCT sample shows few of the peaks similar to AFI morphology, however, their intensities are less. At the same time in the XRD pattern of 2DCT sample it was observed that a few extra peaks start appearing which may give rise to CHA morphology. In case of spent SAPO-44 material, the XRD pattern matches well with the fresh SAPO-44 material, however, peak intensities are decreased implying that crystallinity of the SAPO-44 is lower. A similar phenomenon was also observed in case of 2DCT catalyst samples. It is important to note here that though peak intensities in spent catalysts (SAPO-44 and 2DCT) are reducing none of the peak(s) completely vanished. Fig. S2 (ESI†) shows the XRD patterns for the fresh and spent H-MOR samples. In the XRD of spent H-MOR sample compared to fresh H-MOR sample lower peak intensity for all the peaks was observed. Moreover, it can be seen that the highest intense peak due to (202) at $2\theta = 25.8°$ present in the fresh H-MOR sample is absent in the spent H-MOR sample. This clearly indicates that during the reaction H-MOR catalyst undergoes serious morphological changes compared to SAPO-44.

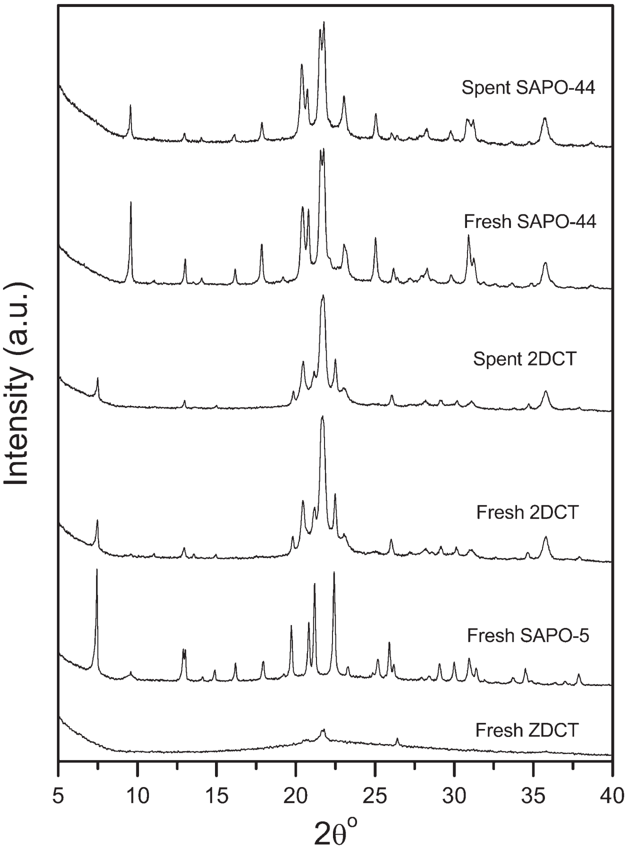


Fig. 5 Powder XRD pattern of catalysts.

The ICP-OES study shows that the amount of Al (fresh, 22.5 ppm; spent, 21.7 ppm) and P (fresh, 24.6 ppm; spent, 25.3 ppm) remains similar in the fresh and spent catalysts. Moreover, the absence of Al and/or P in the reaction solution confirms that elements are not leached out during the reaction. These analyses indicate that since Al and/or P are not leached out the local environment around Si, Al and P has altered.

Fig. S3 (ESI†) presents the SEM images for fresh and spent SAPO-44 catalyst. SEM images of both fresh and spent SAPO-44 indicate the presence of cubic morphology with similar edge length.

Solid state ^{27}Al, ^{31}P and ^{29}Si MAS NMR spectra were recorded to understand the local environment in SAPO-44. In ^{31}P MAS NMR spectra we observed a peak at −31.5 ppm in both fresh and spent SAPO-44 catalysts (Fig. S4, ESI†). This peak is characteristic of tetrahedrally co-ordinated phosphorous [P(4Al)] in the SAPO-44 framework. Careful observation suggests that in spent catalyst the peak has broadened which may imply that few other P species are forming. The ^{31}P NMR spectra of 2DCT catalyst also showed a broad peak at −31.5 ppm (Fig. S4, ESI†). The ^{27}Al MAS NMR spectrum shows a major peak at 38.1 ppm which can be assigned to the presence of tetrahedrally co-ordinated aluminium in the framework of fresh and spent SAPO-44 (Fig. S5, ESI†).[45] Additionally, in both fresh and spent catalyst a minor peak was observed at *ca.* −15.0 ppm for octahedral Al species. In fresh SAPO-44 catalyst, peak broadening was observed which may indicate that few other Al (5-cordinated, distorted 4-cordinated) species may present.

The ^{29}Si MAS NMR spectra for fresh and spent SAPO-44 catalyst show multiple signals suggesting that Si is present in multiple environments. In a fresh SAPO-44 sample the peak observed at −92.1 ppm is typically ascribed to [Si(4Al)] species (Fig. S6, ESI†). This indicates that Si is incorporated in the framework. Beside this peak, other moderately intense peaks were also observed [Si(3Al)] (−96.2 ppm), [Si(2Al)] (−101.7 ppm) and [Si(1Al)] (−107.7 ppm). The presence of these peaks indicates surface hydroxyl groups might be present in SAPO-44 to give rise to Brønsted acid sites. Another peak at −112.8 ppm is indicative of the presence of Si[(0Al)] species.[45] The ^{29}Si MAS NMR spectra for spent catalyst (Fig. S6, ESI†) indicate that SAPO-44 undergoes morphological changes during the catalytic runs. NMR spectra for 2DCT catalyst showed a major peak for [Si(0Al)] species (Fig. S6, ESI†).

The specific surface area data of catalysts is summarized in Table S1 (ESI†). It was observed that after the catalytic run, the surface area of SAPO-44 decreased from 358 $m^2 g^{-1}$ (fresh) to 133 $m^2 g^{-1}$ (spent). The decrease in surface area might be due to the fact that SAPO-44 undergoes some morphological changes during the reaction. In the case of SAPO-5 sample, a surface area of 309 $m^2 g^{-1}$ was observed. Taking into account all the catalyst characterization results, it is suggested that during the reaction SAPO-44 undergoes slight morphological changes.

Conclusion

We demonstrate in this work that SAPO-44 catalyst shows good yields and selectivity for 5-HMF formation from fructose. The high activity achieved may be attributed to the properties associated with the catalyst such as hydrophilicity, acid amount, strong to weak acid site ratio, *etc*. The SAPO-44 catalyst is also active in one-pot conversions of mono- (glucose), di- (maltose, cellobiose) and poly-saccharide (starch) directly into 5-HMF, indicating that a separate reactor is not required to form fructose from these substrates. In a recycling study, a marginal decrease in the catalytic activity was observed until the 3rd run however it remained constant up to the 5th run. A thorough catalyst characterization study allows us to state that the catalyst undergoes slight morphological changes during the reaction. In future, work should be devoted on the synthesis of hydrophilic catalysts which will help achieve complete separation of catalyst from 5-HMF to suppress the degradation reactions and achieve higher 5-HMF selectivity.

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