Electronic Supplementary Information

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

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Details on possibility of condensation reactions between fructose and 5-HMF

Our 5-HMF stability experiments done at 175°C for 1 h over SAPO-44 and H-MOR catalyst implies that 5-HMF does not undergo any degradation reactions on both the catalysts.

To understand whether fructose and 5-HMF form any condensation by-product we carried out the following experiments.

Reaction with SAPO-44 as catalyst

At the beginning of the reaction, we charged in the reactor, 0.25 g fructose (in a typical reaction we charge 0.50 g fructose) so that means we took 50% of fructose. Next we added 0.17 g 5-HMF (considering 50% of fructose will give 0.17 g 5-HMF yield considering 88% selectivity). Subsequently in the reactor we charged solvent (water+MIBK). The reaction was conducted for 1 h at 175°C.

Initially charged fructose = 0.25 g

We observed 89% conversion of fructose. This means 0.22 g fructose is converted.

Initially we charged 0.17 g 5-HMF

After reaction we obtained 0.31 g 5-HMF

This means 0.14 g 5-HMF (0.31-0.17 g) was formed in the reaction (considering 5-HMF does not undergo any conversion under reaction conditions; as is proved in our HMF stability experiments)

Considering 100% selectivity to 5-HMF formation from 0.22 g fructose (converted) we should observe 0.15 g 5-HMF (0.22 x 126 / 180)

However, we obtained 0.14 g 5-HMF which means we observed 93% selectivity.

Reaction with H-MOR as catalyst

At the beginning of the reaction, we charged in the reactor, 0.25 g fructose (in a typical reaction we charge 0.50 g fructose) so that means we took 50% of fructose. Next we added 0.15 g 5-HMF (considering 50% of fructose will give 0.15 g 5-HMF yield considering 85% selectivity). Subsequently in the reactor we charged solvent (water+MIBK). The reaction was conducted for 1 h at 175°C.

Initially charged fructose = 0.25 g

We observed 95% conversion of fructose. This means 0.24 g fructose is converted.

Initially we charged 0.15 g 5-HMF

After reaction we obtained 0.25 g 5-HMF

This means 0.10 g 5-HMF (0.25-0.15 g) was formed in the reaction (considering 5-HMF does not undergo any conversion under reaction conditions-as is proved in our 5-HMF stability experiments)

Considering 100% selectivity to 5-HMF formation from 0.24 g fructose (converted) we should observe 0.17 g 5-HMF (0.24 x 126 / 180)

However, we obtained 0.10 g 5-HMF which means we observed 59% selectivity.

Summarizing above results, over SAPO-44 catalyst, higher selectivity for 5-HMF formation was observed (93%) compared to H-MOR (59%).

Recovery of 5-HMF and characterization using 1H NMR

After removal of catalyst from reaction mixture, MIBK layer was separated from aqueous layer. MIBK solvent was evaporated with rotary evaporator. The solid recovered after complete MIBK separation was collected and stored in cold condition. For 1H NMR study, minute amount of solid collected from MIBK layer was dissolved in deuterium oxide solvent and the result showed the peaks correspond to pure 5-HMF. Chemical shift values are given in ppm; δ_H (200MHz, D_2O, Me_4Si) (a: 2H, s, CH_2), (b: 1H, s, OH), (c: 1H, d, CH), (d: 1H, d, CH), (e: 1H, s, COH).

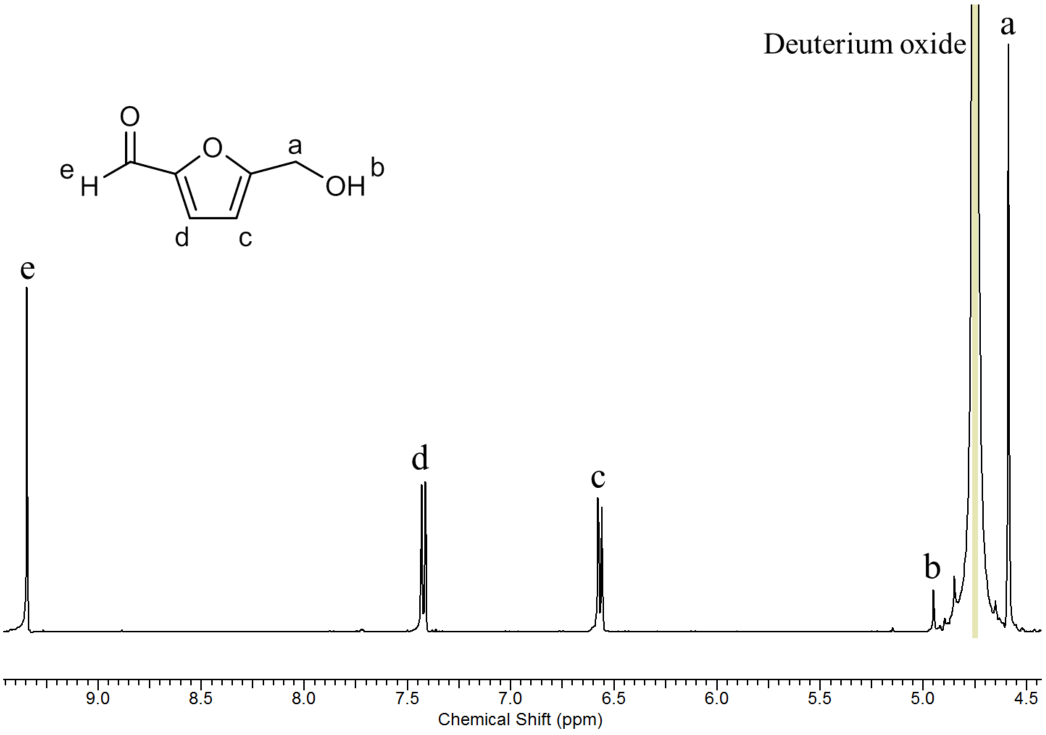

Fig. S1 ^{1}H-NMR spectra of recovered 5-HMF

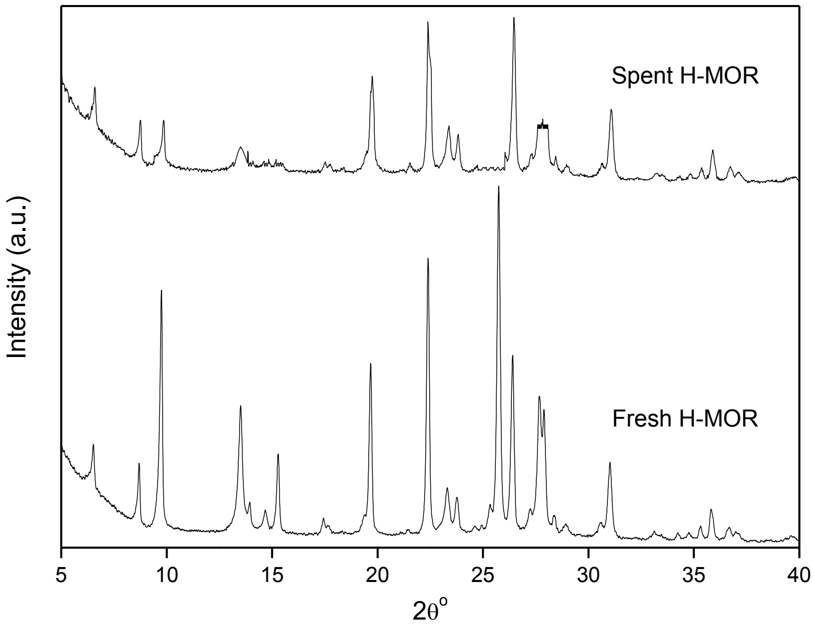

Fig. S2 XRD patterns for fresh and spent H-MOR

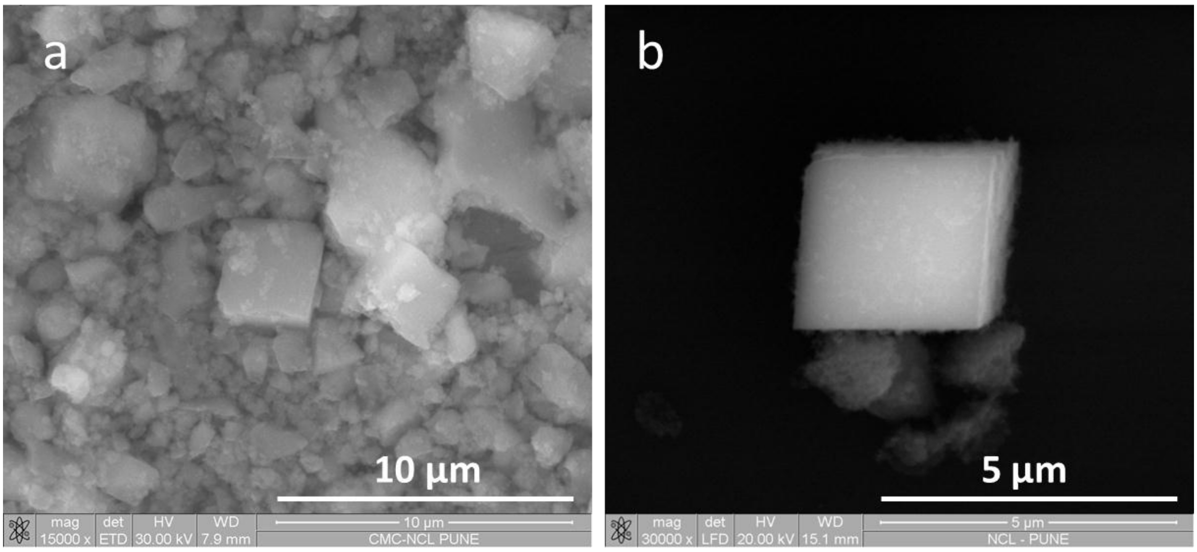

Fig. S3 SEM images of SAPO-44; (a) Fresh SAPO-44, (b) Spent SAPO-44

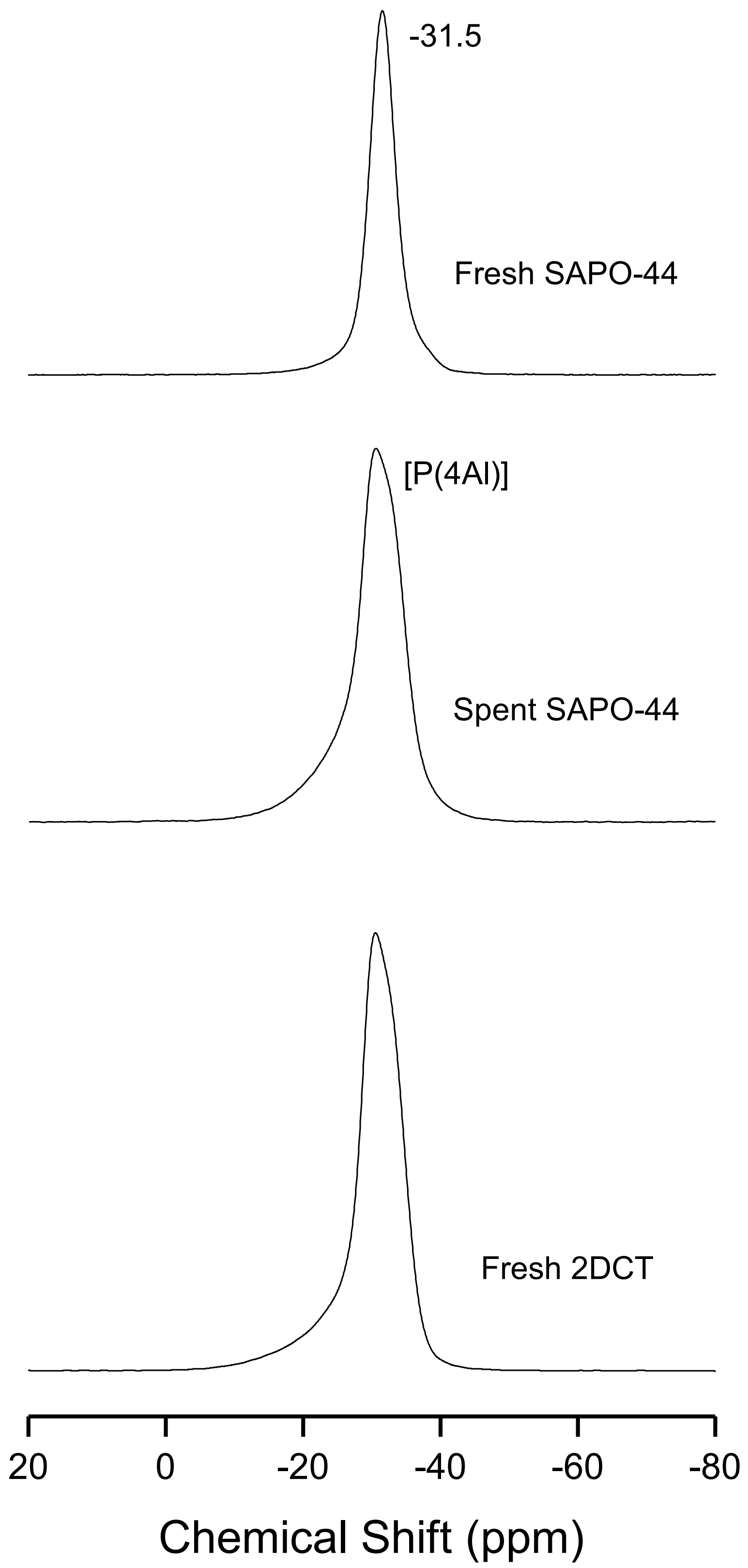

Fig. S4 ^{31}P solid state NMR study of catalysts.

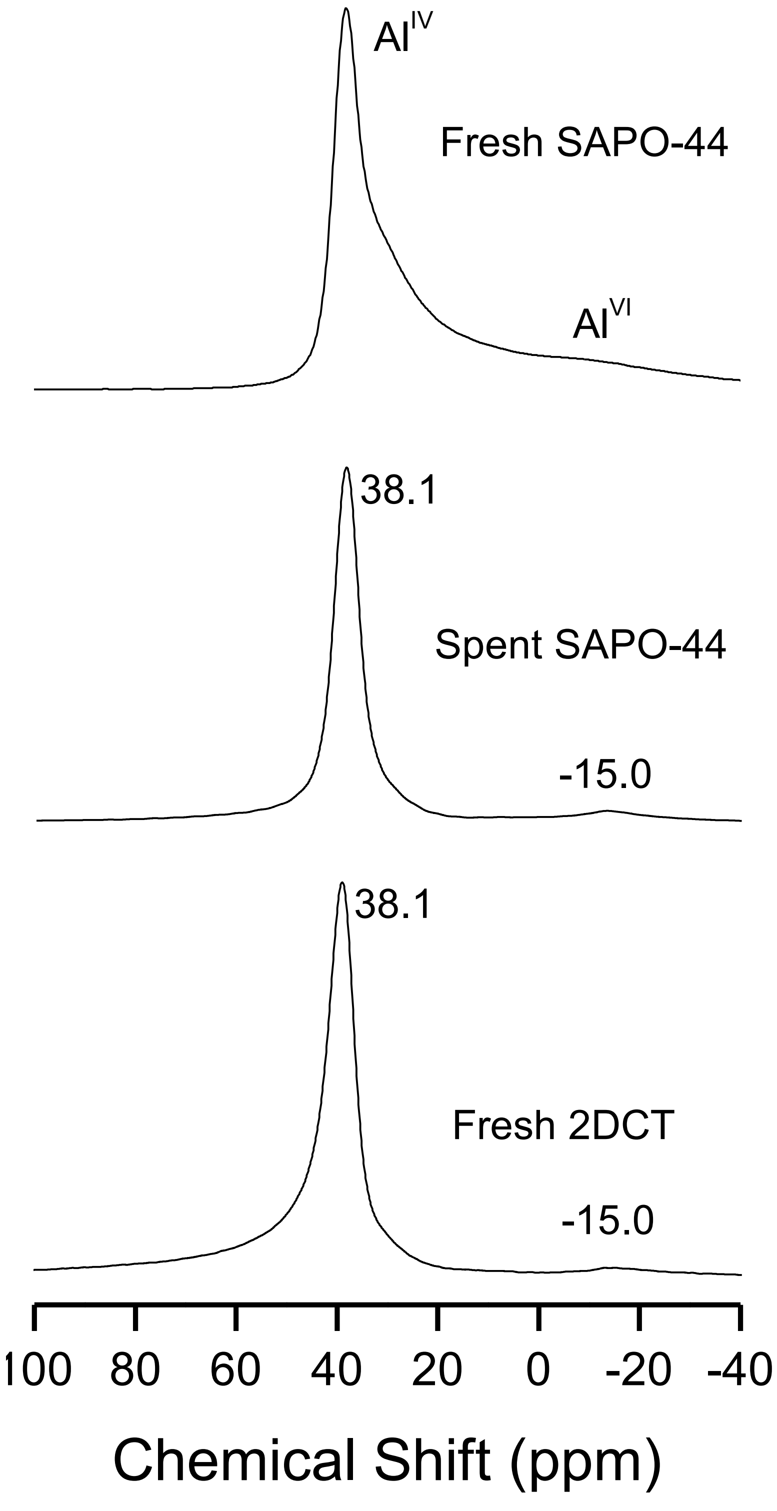

Fig. S5 ^{27}Al solid state NMR study of catalysts.

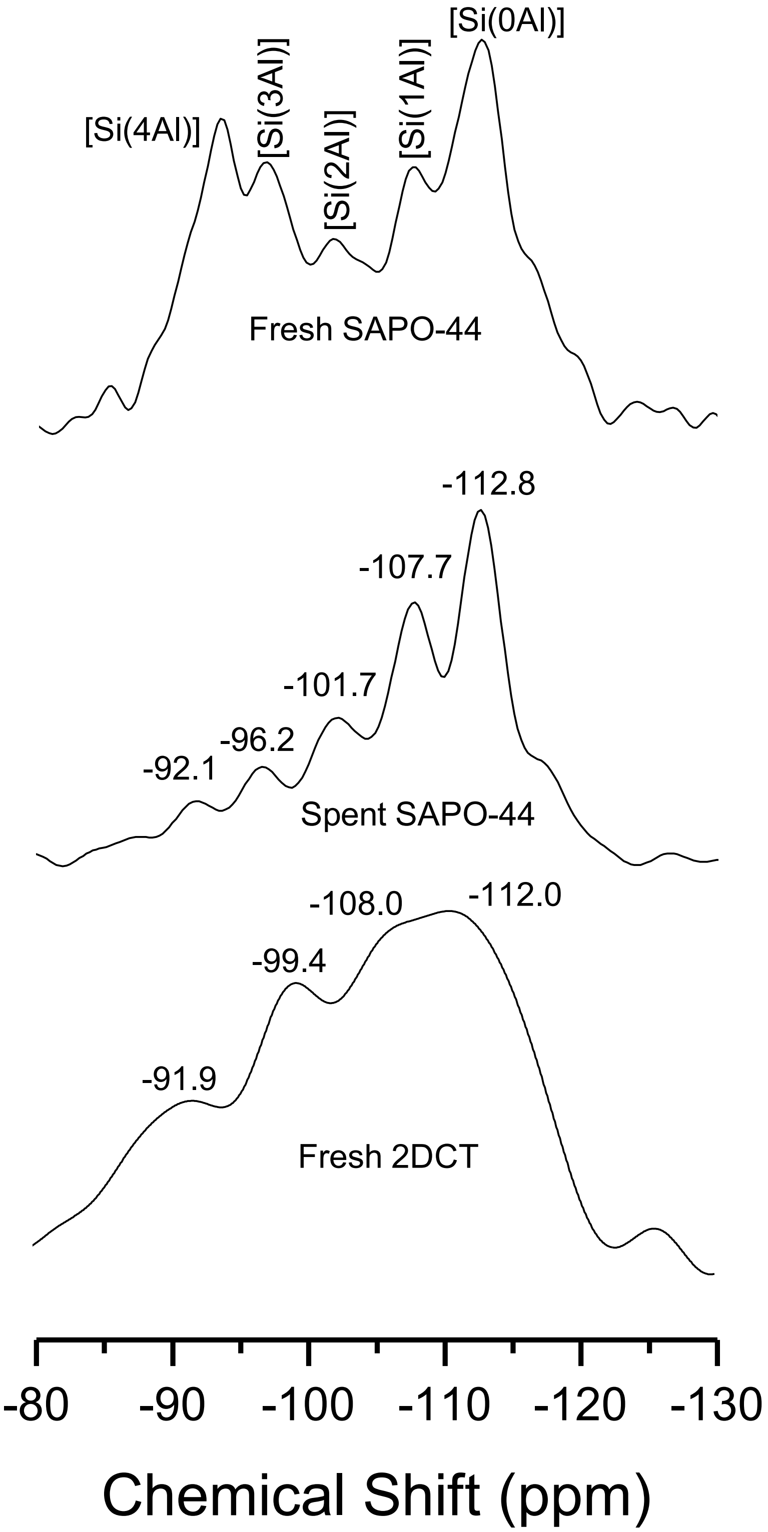

Fig. S6 ^{29}Si solid state NMR study of catalysts

Table S1 Specific surface area of catalyst

Catalyst	Surface area ($m^2\ g^{-1}$)
Fresh SAPO-44	358
Spent SAPO-44	133
Fresh 2DCT	155
Fresh SAPO-5	309