Supporting Information

Temperature-Programmed Reduction Method for Stabilization of Inorganic Framework of SAPO-37 Materials: Promising Catalysts for MTBE Production

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Experimental

Materials & Synthesis Protocol:

The following chemicals were used: pseudo boehmite ($A1_2O_3$, 75%, BeeChems, grade PSB-M), ortho phosphoric acid (H_3PO_4, 85%, Merck), fumed silica (Aerosil 200, Aldrich), tetra propyl ammonium hydroxide (TPAOH, 40% aqueous solution), tetra methyl ammonium hydroxide (TMAOH, 25% aqueous solution, TriTech Catalyst and Intermediate), ammonium heptamolybdate tetra hydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, SRL), D-glucose (Fischer Scientific), methanol and *tert*-butyl alcohol (extra pure AR, SRL).

The SAPO-37 samples were synthesized using a hydrothermal method following a previously reported procedure.[7],[12] The molar gel composition was $(TPA)_2O$: $0.025(TMA)_2O$: Al_2O_3: P_2O_5: $0.43SiO_2$: $50.0H_2O$. Solution I was prepared by slowly adding pseudo boehmite to dilute orthophosphoric acid while stirring. Solution II was prepared by adding fumed silica to a mixture of TPAOH and TMAOH. The final gel was obtained by adding Solution II to Solution I while vigorously stirring. The resulting slurry was packed in a stainless-steel autoclave with Teflon liners and heated at 200 °C under autogenous pressure for 20 h. The product was then separated via centrifugation, washed with deionized water, and dried at 60 °C. The obtained sample was labeled as SAP-37. The as-prepared materials were dried in an air oven at 200 °C and subsequently reduced under temperature programmed mode in a hydrogen atmosphere at 550 °C. The TPR-treated sample is denoted as SAP-37R.

To stabilize SAPO-37 with improved activity, this study focused on the incorporation of Mo species during the TPR process, generating an SAPO-37 framework containing Mo carbide-type species. For the same, molybdenum blue type species was used, which was prepared according to a reported procedure using ammonium heptamolybdate tetrahydrate as the molybdenum source and D-glucose as the reducing agent (R). In this regard, it is worth mention here that the pH of the reaction mixture defines the size of molybdenum blue. The self-organization of molybdenum blue into gigantic wheel-shaped clusters containing $\{Mo_{154}\}$[11] with a diameter of 3.4 nm usually takes place at low pH ($pH < 2$) and at a low ratio of [reducing agent] to [molybdate]. Isopolymolybdate $\{Mo_{36}\}$ is formed at a pH of 1.7.[11] Here, we synthesized molybdenum blue at a pH of 2 and at a higher ratio of [reducing agent] to [molybdate], which facilitates the formation of molybdenum blue building blocks with a size of around 6 Å. These blocks can easily enter the SAPO-37 cavities.

For the incorporation of molybdenum species and subsequent stabilization of the framework via TPR, molybdenum blue with an R/Mo ratio of 4 was introduced (0.6 g of molybdenum blue per gram) into the pore volume of as-prepared SAPO-37 and subsequently dried at 80 °C for 12 h. This procedure was repeated thrice. For comparison, Mo blue with different R/Mo ratios, including 2, 5, and 6, on SAPO-37 were prepared. All the prepared samples were stabilized using the TPR method at 550 °C for 2 h. SAPO-

37 stabilized by the TPR method in the presence of molybdenum blue with different R/Mo ratios (2, 4, 5, and 6), is denoted as SAP-37MoC-2R, SAP-37MoC-4R, SAP-37MoC-5R, and SAP-37MoC-6R.

Characterization Methods:

Fourier transform infrared spectroscopy (FTIR) was conducted on the prepared catalysts using a Jasco FT-IR spectrometer in the mid-IR region 4000–400 cm^{-1} via the ATR method. Powder X-ray diffraction (XRD) analysis was performed using a PAN analytical X'pert3 powder X-ray diffractometer with Cu Kα radiation of 1.5405 Å, scanning in the range of $2\theta = 5°–80°$.

Surface elemental analysis was conducted using X-ray photoelectron spectroscopy (XPS). This analysis was performed using a photoelectron spectrometer (Pervac, Poland) equipped with a VG Scienta R3000HP analyzer and an MX650 monochromator. XPS spectra were deconvoluted to obtain various oxidation states using the Shirley method for baseline correction. The peak fit conditions used were: full-width half maxima (FWHM): 1.3±0.1 eV, $3d_{5/2}$–$3d_{3/2}$ distance 3.2 eV and the ratio of $3d_{5/2}/3d_{3/2}$=3/2.

The organic contents of the as-synthesized SAPO-37 and molybdenum-stabilized SAPO-37 were examined via thermogravimetric analysis (TGA) using a PerkinElmer STA 6000 simultaneous thermal analyzer. TGA was conducted in a nitrogen atmosphere within the temperature range of 35 to 900 °C with a heating rate of 10 °C/min. The morphologies of the synthesized materials were analyzed using scanning electron microscopy (SEM, TESCAN VEGA3) at 300 kV. TEM images were recorded using a transmission electron microscope (M/s JOEL JEM 2100). Solid state NMR spectra were obtained on Bruker Avance III HD at 9.4 T using zirconia rotors with spinning speed of 7 kHz.

The acidic properties of the prepared catalysts were examined via NH_3-TPD using a BELCAT-M instrument (Japan). The sample was preheated at 400 °C for 30 min in a quartz reactor. Ammonia adsorption was conducted at 50 °C for 30 min, followed by desorption at 50 °C to remove physisorbed ammonia. The measurements were performed from 50 °C to 600 °C at a heating rate of 10 °C/min. The quantification of Brønsted and Lewis acid sites was studied by pyridine FTIR analysis performed on a NICOLET iS50 spectrometer in the range of 4000-400 cm^{-1} using an MCTB detector. The textural properties, such as BET surface area and pore volume, were determined through nitrogen

sorption analysis using an automatic micropore physisorption analyzer (Quanta Chrome Nova 10-7) at -196 °C. Prior to sorption measurements, samples were degassed at 110 °C under a pressure of 10^{-3} Torr. The chemical composition of samples was followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using the MP-AES instrument.

Catalytic Studies:

The prepared catalyst was investigated for the synthesis of MTBE from methyl alcohol and tertiary-butyl alcohol (TBA) in a 100 mL stainless autoclave. In a typical reaction, 0.05 g of catalyst was mixed with 30 mmol of methyl alcohol and 10 mmol of TBA. The reaction conditions were optimized with different temperatures (120–160 °C) and durations of 2 to 8 h. After the reaction, the products and catalysts were separated via centrifugation. The products were confirmed using authentic samples and analyzed using gas chromatography (Mayura Analytical model 1100) with a flame ionization detector equipped with an HP-5 capillary column (30 m (length) x 0.25 mm (inner diameter), 0.25 µm (film thickness)). The temperature program mode used was heating from 60 to 70 °C (1 °C/min) and then from 70 to 240 °C (10 °C/min).

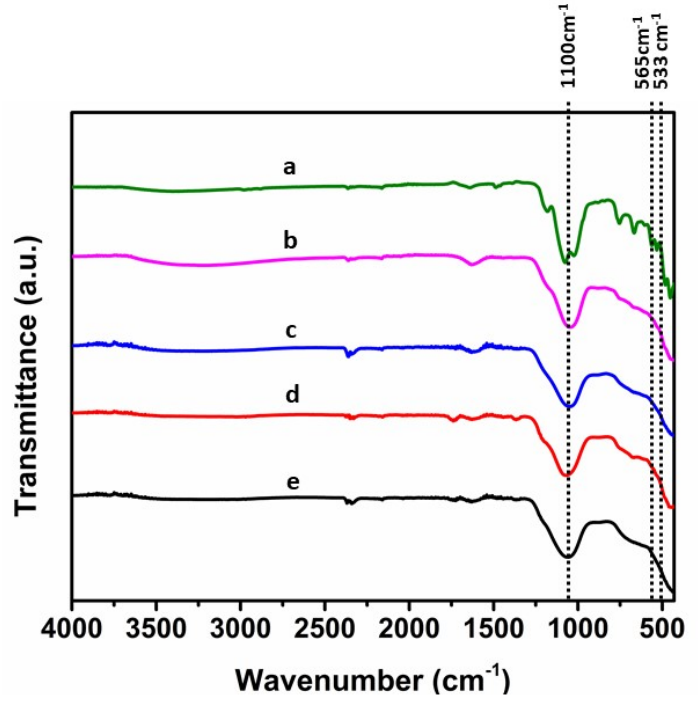


Fig. S1. FTIR spectra of a) SAP-37as, b) SAP-37MoC-6R, c) SAP-37MoC-5R, d) SAP-37MoC-4R, and e) SAP-37MoC-2R.

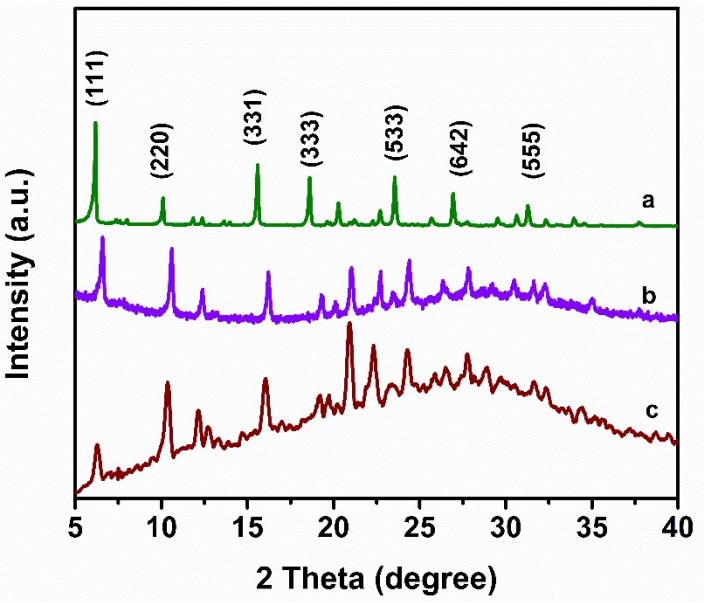


Fig. S2. Powder XRD of a) SAP-37as, b) SAP-37R, and c) used SAP-37R.

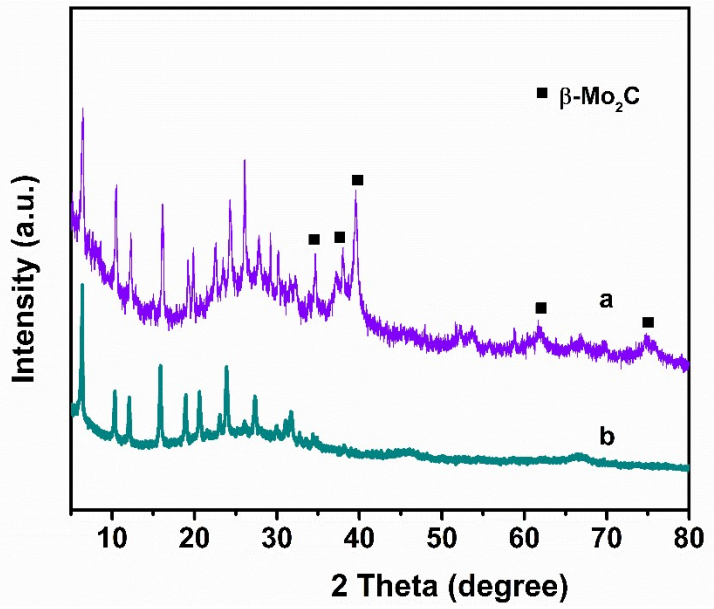
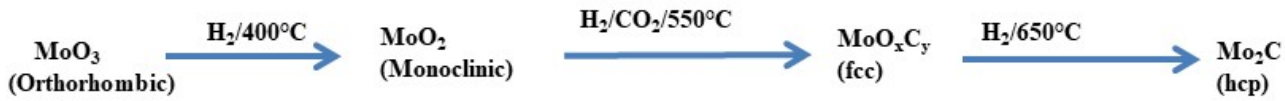


Fig. S3. Powder XRD of a) SAP-37MoC-4R', and b) SAP-37MoC-4R.

Table S1. Binding energy for various molybdenum and carbon species.

Mo species	Binding energy (eV)	
	$3d_{5/2}$	$3d_{3/2}$
Mo^{6+}	232.7	235.8
Mo^{5+}	231.7	235
Mo^{4+}	230.1	233.8
Mo^{2+}	228.8	232.1
C species	1s	
Csp^3	284.8	
C=O	288.6	
C-O	286.4	
C-O-Mo	283.9	



Scheme **S1**. Mechanism for molybdenum (oxy) carbide formation.

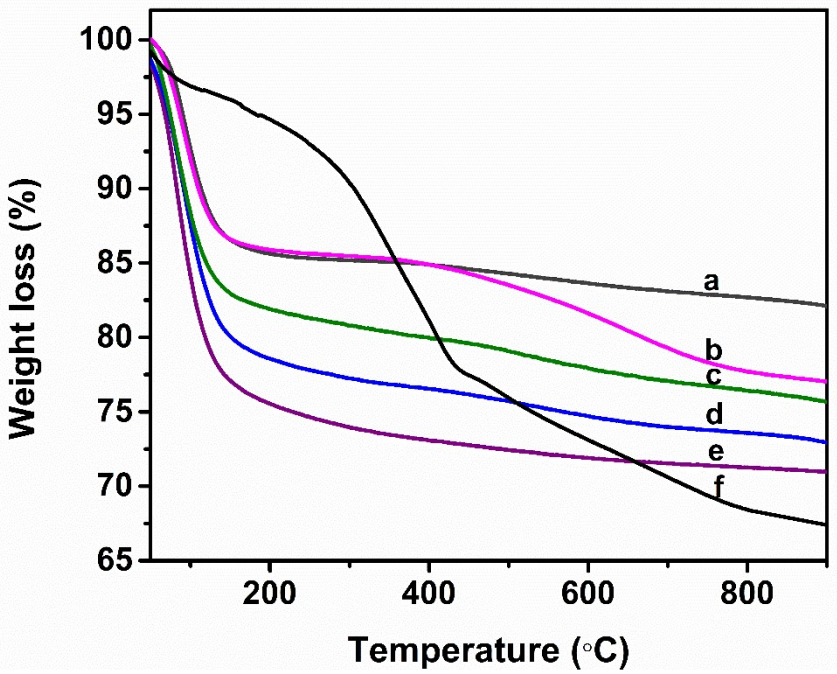


Fig. S4. TGA profile of a) SAP-37MoC-2R, b) SAP-37MoC-4R, c) SAP-37MoC-6R, d) SAP-37MoC-5R, e) SAP-37R, and f) SAP-37as.

Table S2. Thermogravimetric weight loss of TPR treated SAPO-37.

Sample	Weight loss (%)			Total (%)
	Below 200 °C	200-450 °C	Above 450 °C	
SAP-37 as	7	16	9	32
SAP-37R	24	3	1	28
SAP-37MoC-2R	14	2	2	18
SAP-37MoC-4R	14	2	7	23
SAP-37MoC-5R	20	3	3	26
SAP-37MoC-6R	18	3	4	25

Scanning Electron Micrographs

Morphological deterioration after template removal was confirmed from the SEM images. As shown in Fig. S5 (ESI), SEM images of the as-prepared SAPO-37 and TPR-treated samples (SAP-37MoC-4R) show a distorted cubic shape with good crystallinity.[18] The SEM images confirm that the TPR treatment and MoOC species in the framework helped to retain the faujasite topology of SAPO-37, which is in good agreement with the XRD pattern. Moreover, the incorporation of MoOC facilitated the homogeneous dispersion of the SAPO-37 particles. The average particle size of the parent SAPO-37 is 2–7 µm, while that of molybdenum (oxy) carbide incorporated SAPO-37 is 5-10 µm.

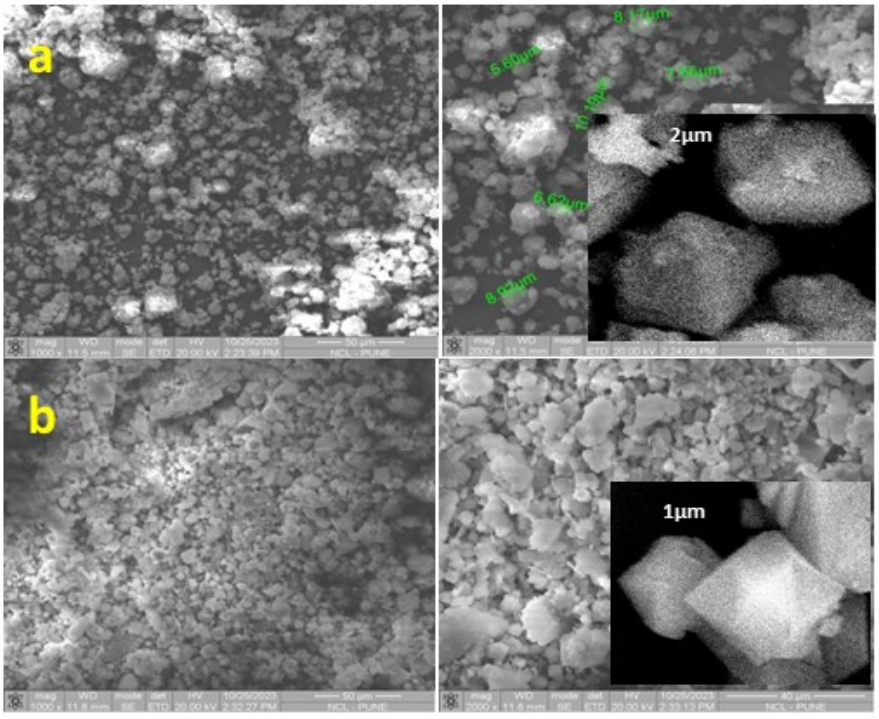
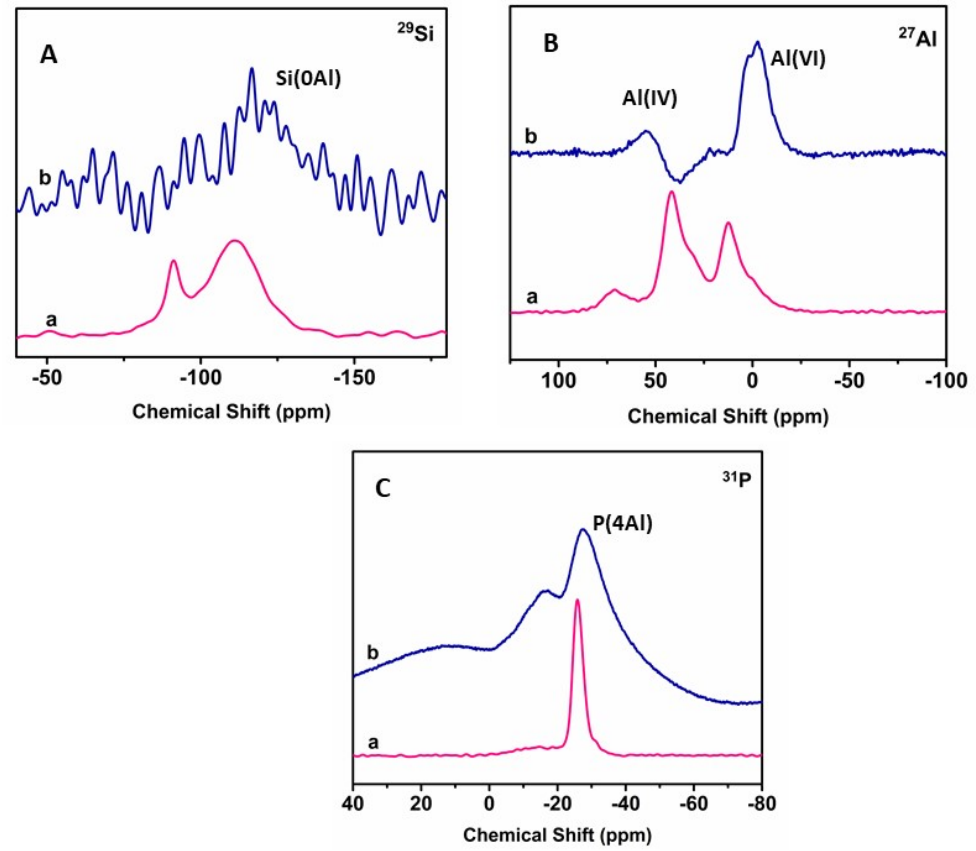


Fig. S5. Scanning Electron Micrographs of a) SAP-37MoC-4R, and b) SAP-37as.



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2 Fig. S6. ^{29}Si (A), ^{27}Al (B), and ^{31}P (C) MAS NMR spectra of a) SAP-37R, and b) SAP-37MoC-
3 4R.

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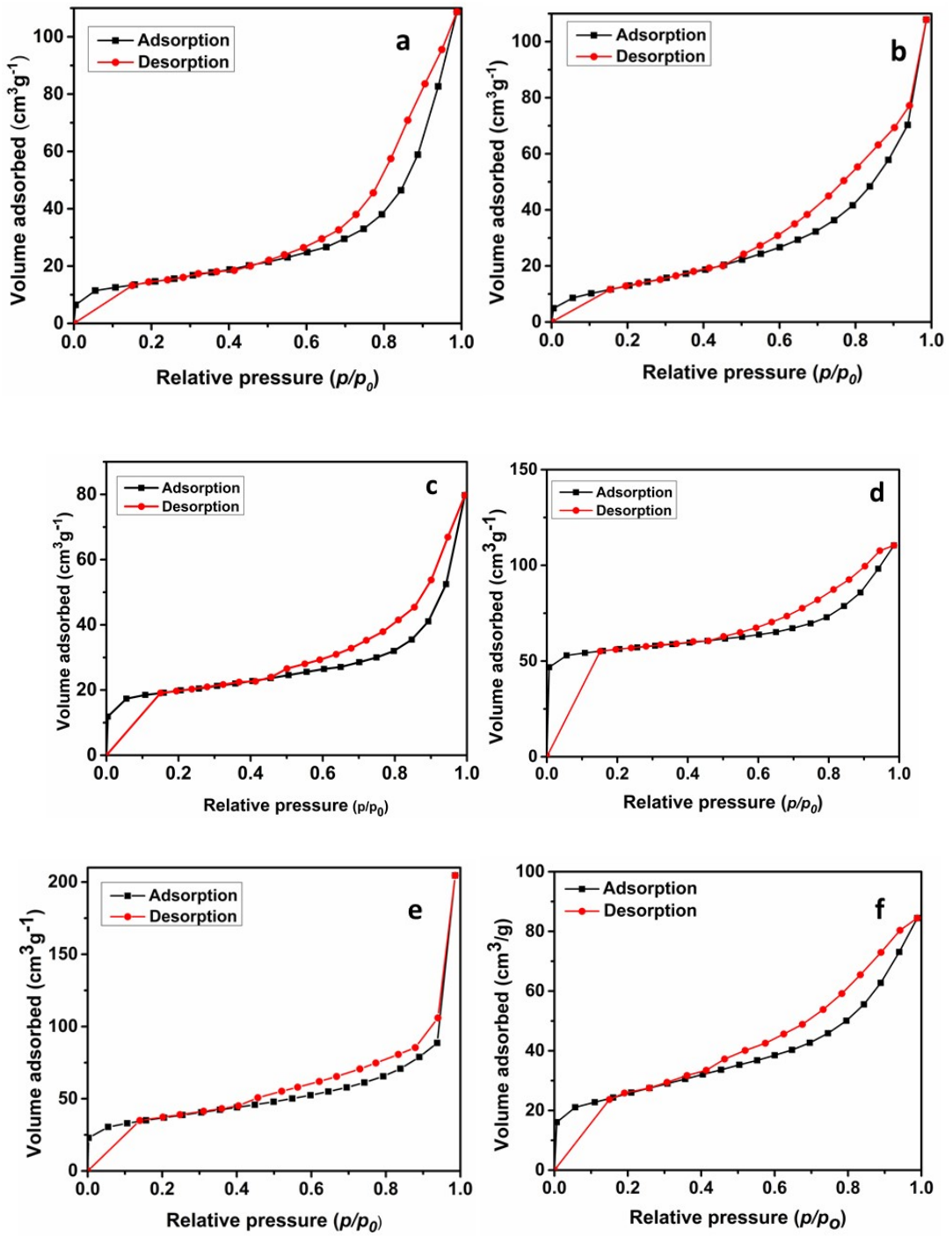

Fig. S7. N_2 sorption isotherm of TPR reduced SAPO-37 a) SAP-37R, b) SAP-37MoC-2R, c) SAP-37MoC-5R, d) SAP-37MoC-6R, e) SAP-37MoC-4R, and f) Used SAP-37MoC-4R.

Nitrogen sorption analysis (Fig. S7, ESI) shows Type-I isotherm with a sharp uptake in the p/p_0 range of 0.1, which is characteristic of the microporous SAPO-37 framework. Moreover, additional isotherms show continuous adsorption in the higher p/p_0 range owing to interparticle mesoporosity. The low surface area of 128 m^2/g can be attributed to the incorporation of molybdenum species into the faujasite structure. BET surface area and pore volume of TPR treated samples summarized in Table S4 (ESI). The introduction of molybdenum blue precursor and subsequent reduction increases the pore volume (SAP-37MoC-4R) due to the stabilization of the SAPO-37 framework and accessibility of channels and cavities. However, the increase in the R/Mo ratio facilitates carbon deposition and the reduction in the pore volume of SAP-37MoC-5R and SAP-37MoC-6R. SAP-37MoC-6R showed a high surface area due to the formation of porous carbon.

Table S3. Elemental composition of reduced SAPO-37 samples

Samples	Elemental composition (weight %)≠			
	Si	Al	P	Mo
SAP-37R	4.9	12.7	11.6	0
SAP-37MoC-2R	5.7	14.8	13.0	5.1
SAP-37MoC-4R	5.4	13.9	11.8	5.2
SAP-37MoC-6R	5.2	13.5	11.6	4.4

Table S4. BET surface area and pore volume of TPR treated samples

Samples	BET surface area (m^2/g)	Pore volume (cc/g)
SAP-37R	51	0.176
SAP-37MoC-2R	51	0.190
SAP-37MoC-4R	128	0.295
SAP-37MoC-5R	72	0.116
SAP-37MoC-6R	123	0.139

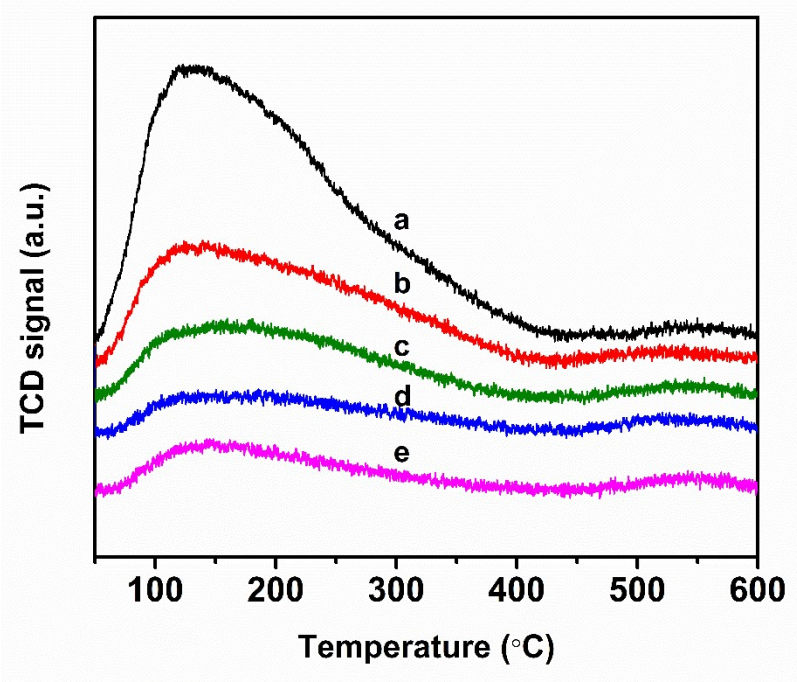

Fig. S8. NH_3 –TPD of a) SAP-37MoC-4R, b) SAP-37MoC-5R, c) SAP-37MoC-2R, d) SAP-37MoC-6R, and e) SAP-37R.

Table S5 Total amount of acid sites of TPR treated SAPO-37 samples.

Catalyst	Amount of ammonia desorbed (mmol/g)
SAP-37- R	0.125
SAP-37-MoC-2R	0.275
SAP-37-MoC-4R	0.700
SAP-37-MoC-5R	0.350
SAP-37-MoC-6R	0.125

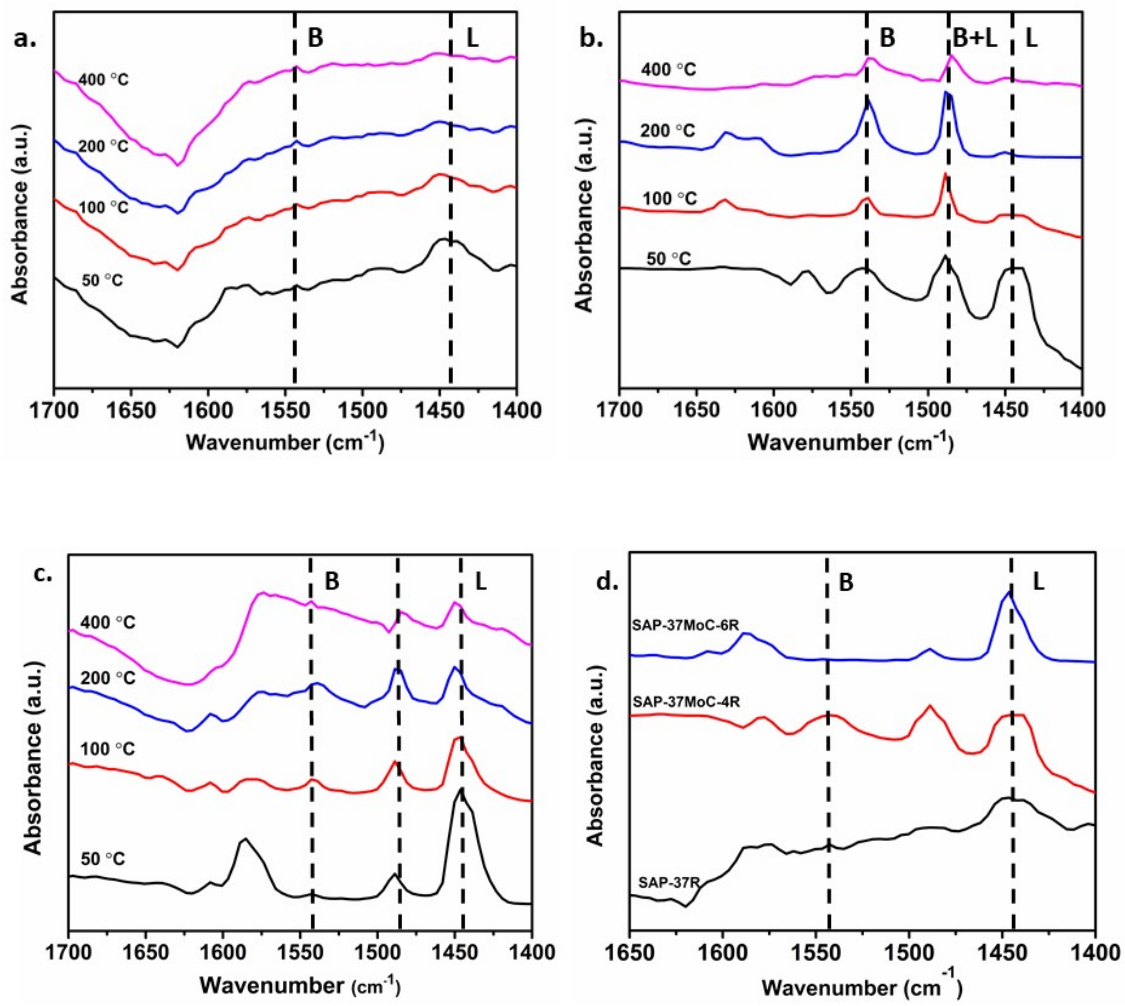

Fig. S9. The effect of molybdenum loading on pyridine-desorption FTIR spectra a) SAP-37R, b) SAP-37MoC-4R, c) SAP-37MoC-6R, and d) pyridine-desorption spectra obtained at 50 °C for various TPR treated samples.

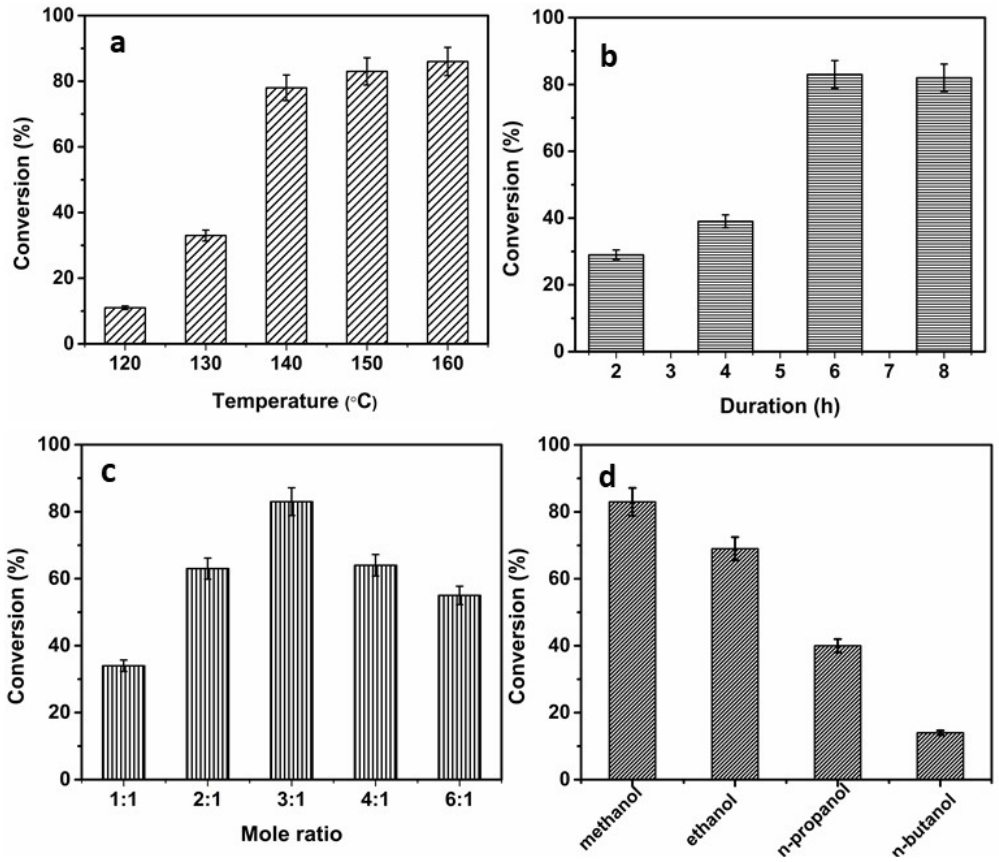

Fig. S10. Effect of a) Temperature, b) Duration, c) Mole ratio of methanol to TBA, and d) different alcohols on MTBE synthesis using SAP-37MoC-4R.

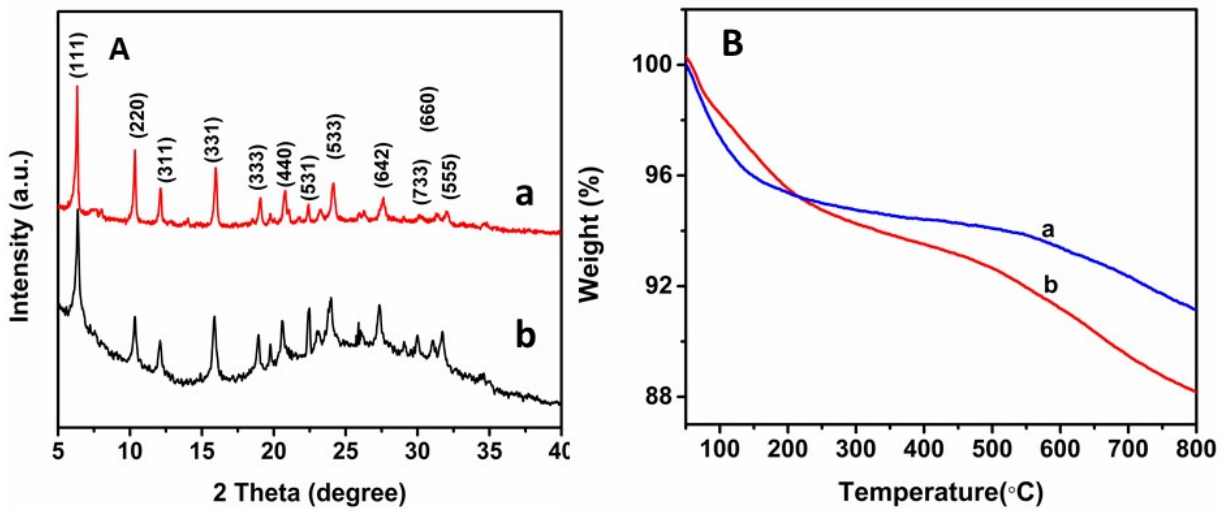

Fig. S11. Analysis of spent catalyst SAP-37MoC-4R A) powder XRD of a) SAP-37MoC-4R, and b) spent catalyst; B) TGA profile of a) regenerated catalyst, and b) spent catalyst.

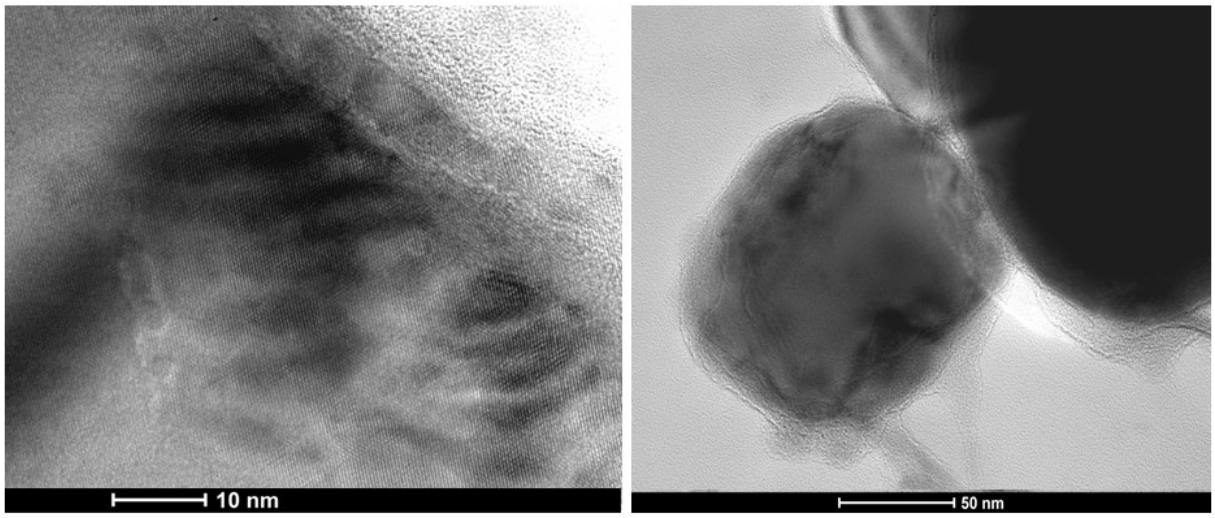

Fig. S12. TEM images of used SAP-37MoC-4R catalyst.

Table S6. MTBE synthesis using different catalysts.

Catalyst	Experimental condition	TBA conversion (%)	MTBE selectivity (%)
Mo-P/TiO_2[13]	150 °C, 20 bar, LHSV= 1.0	78	75
W-P/TiO_2[13]	150 °C, 20 bar, LHSV= 1.0	77	77
W-P/SiO_2[13]	150 °C, 20 bar, LHSV= 1.0	81	89
W-P/Al_2O_3[13]	150 °C, 20 bar, LHSV= 1.0	76	81
SAP-37MoC-4R	150 °C, 6 h, autogenous pressure	83	99
Catalyst	Experimental condition	isobutene conversion (%)	isobutene selectivity (%)
Amb-15[RS1]	90 °C, 2 Mpa, WHSV=14 h^{-1}	90	97
Zeolite beta[RS1]	90 °C, 2 Mpa, WHSV=14 h^{-1}	82	90

References

RS1. F. Collignon, R. Loenders, J. A. Martens, P. A Jacobs and G. Poncelet, *J. Catal*., 1999, **182**, 302.