Supporting Information

Novel catalyst PTMA-PILC: structural properties and catalytic performance for the bioethanol dehydration to ethylene

Xianmei Xie*[a], Zheng Li[a], Baoru Li[a], Xu Wu[a], Xia An[a]

S1. Experimental

1.1 Catalyst characterization

The X-ray diffraction diagrams were recorded over powder sample on Riga ku D/max-2500 instrument(40 KV, 100 mA) using Cu Kα radiation(λ = 0.154056 nm) at a scanning speed of 0.13 °/s, with the scanning range of 4-35 °.

FT-IR spectra of the samples were performed on a Perkin-Elmer 1730 Infrared Fourier Transform Spectrometer between 400-4000 cm^{-1} region. One milligram of sample and 300 mg of KBr were used in the preparation of the pellets.

The surface area and pore size distribution were determined from nitrogen adsorption-desorption isotherm data by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods using a Micro-meritics ASAP 2020 instrument. The isotherms were measured at 77 K using N_2. Prior to determining the isotherms, the samples were degassed at 100 ℃ in vacuum (≈30 Pa) for 70 min.

The temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out between 10 and 750 °C using Autochem II 2920 (Micromeritics Instruments). Prior to adsorption, the sample (0.04 g) was calcined under the N_2 flow of 50 mL/min at 300 °C for 1 h and then cooled to 50 °C. After that, it was treated by 10% NH_3/He for 30 min. The nature and strength of acid sites were evaluated by IR spectroscopy of pyridine. For this analysis the sample was preheated at 300 °C for 2 h under vacuum pressure. Pyridine adsorption was run at room temperature during 30 min. Desorption was realised in vacuum at 150 °C and infrared spectra were recorded after thermal treatment.

Thermogravimetric analysis (TG) was performed on a NETZSCH-STA 409C thermobalance. Around 5 mg of sample at particle sizes of 100– 200 mesh was used for each experimental and the heating temperature in the TG was in the range of 25–800 °C, and the heating rate was controlled at 10 °C/ min. Nitrogen was used as the carrier gas in the TG which flow rate was fixed at 100 mL/min.

The microstructures of catalysts was investigated using transmission electron microscope (TEM, JEM-1011) .

1.2 Catalytic performances test

The fixed-bed micro-reactor used for the catalytic performance tests is shown as Fig. 1 and the reaction of ethanol dehydration to ethylene was used to evaluate the catalytic behaviours of the solids. 1.0 g catalysts were dispersed in 3.0 g silica sand and loaded in the middle of a stainless steel reactor. The reactor was purged by nitrogen flow for 60 min, and the liquid reactant containing water and ethanol with the volume ratio of 7:3 was injected by a pulse micro-liquid pump into a vaporizer and subsequently passed into the reactor with the LHSV of 0.65 h^{-1} with the operation temperature range from 200 to 600 ℃. The temperatures of the vaporizer and the reactor were controlled by the thermocouples. Outlet products were condensed and separated by a gas-liquid separator. The gas concentrations were quantified on line by a haixin 950 gas chromatograph equipped with a FID and a TCD detector and two packed columns (GDX-401, TDX-01). The liquid products were analyzed off-line on another gas chromatograph equipped with a Porapack Q column. Ethanol conversion was denoted as $C_{ethanol}$ and S_i represents the product distribution of i, they were calculated according to Eq. (S1) and (S2) :

$$C_{ethanol} = \frac{n(ethanol_{in}) - n(ethanol_{out})}{n(ethanol_{in})} \times 100\% \qquad (S1)$$

$$Si = \frac{n(P_i)}{\sum_{i=1}^{n} n(P_i)} \times 100\% \qquad (S2)$$

S2. Reaction mechanism of ethanol dehydration

On OH^- rich metal oxide surfaces, the following pathways have been proposed[S1]:

1. Diethyl ether formation:

$$C_2H_5OH + OH^-(s) \rightarrow C_2H_5O^-(s) + H_2O$$

$$C_2H_5OH + C_2H_5O^-(s) \rightarrow (C_2H_5)_2O + OH^-(s)$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$$

2. Ethene formation:

$$C_2H_5OH + OH^-(s) \rightarrow C_2H_5O^-(s) + H_2O$$

$$C_2H_5O^-(s) \rightarrow C_2H_2 + OH^-(s)$$

$$C_2H_5OH \rightarrow C_2H_2 + H_2O$$

On OH- poor surfaces, the following mechanisms have been suggested [S1].:

1 Diethyl ether formation:

$$2C_2H_5OH + 2O^{2-}(s) \rightarrow 2C_2H_5O^-(s) + 2OH^-(s)$$

$$2C_2H_5O^-(s) \rightarrow (C_2H_5)_2O + O^{2-}(s)$$

$$2OH^-(s) \rightarrow H_2O + O^{2-}(s)$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$$

2. Ethene formation:

$$C_2H_5OH + O^{2-}(s) \rightarrow C_2H_5O^-(s) + OH^-(s)$$

$$C_2H_5O^-(s) \rightarrow C_2H_4 + OH^-(s)$$

$$2OH^-(s) \rightarrow H_2O + O^{2-}(s)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

Table S1. The compositions of Na-MMT

Sample (wt%)	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SO_3	TiO_2	SiO_2	Loss on ignition
Na-MMT	19.55	2.58	1.71	0.68	3.63	4.06	0.08	0.07	0.06	61.18	6.4

Table S2. Textural characteristics of different catalysts

Catalyst	BET surface area (m^2/g)	Pore Size/nm	SiO_2 (wt%)[a]	Al_2O_3 (wt%)[a]	P_2O_5 (wt%)[a]	MoO_3(wt%)[a]
Na-MMT	21	3.7	61.18	19.55	0.08	--
AT-MMT	335	9.1	77.49	9.85	--	--
PILC	301	3.7	70.49	14.99	--	--
PTMA-	253	3.4	65.27	15.92	0.227	2.383

[a]The content of SiO_2, Al_2O_3, P_2O_5 and MoO_3 over the montmorillonites was determined by XRF.

Table S3. The acid distributions on different catalysts.

Catalysts	Temperature	Weak acid amount (mmol/g)
Na-MMT	90	0.086
AT-MMT	90	0.112
PICL	90	0.175
PTMA-PILC	93	0.178

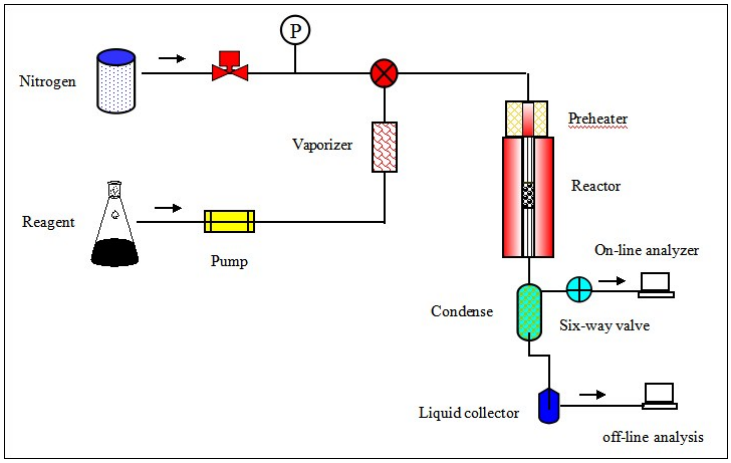


Fig. S1. Reaction equipment for the Ethanol dehydration to ethylene

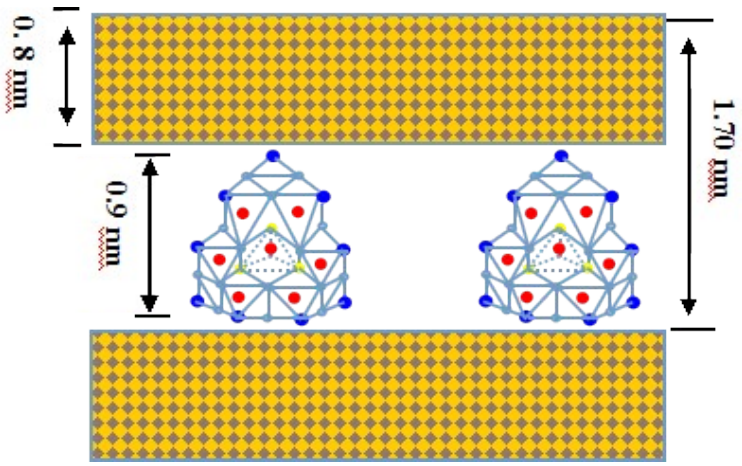
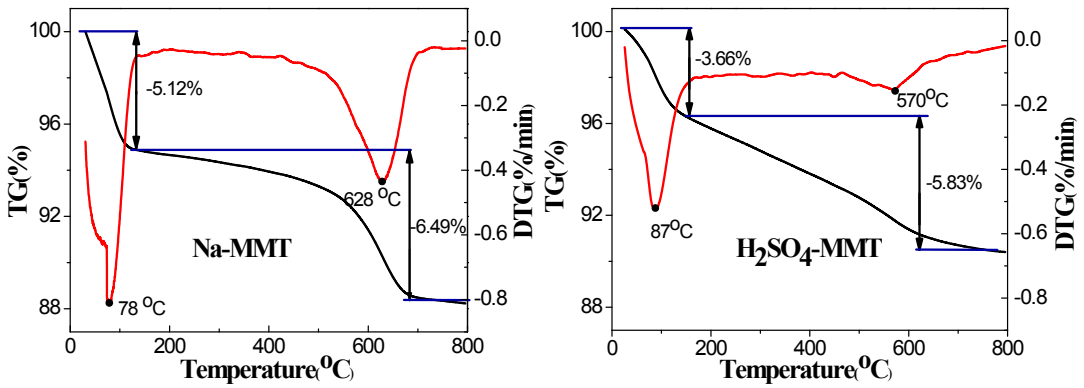


Fig. S2. Schematic diagram of Al_{13}^{7+} in the midst of structure unit layer of PILC (a)



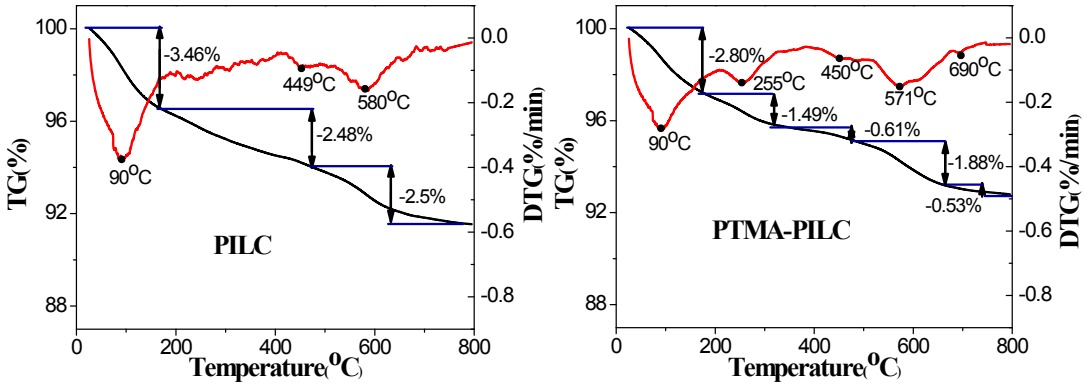


Fig. S3. TG and DTG of different catalysts

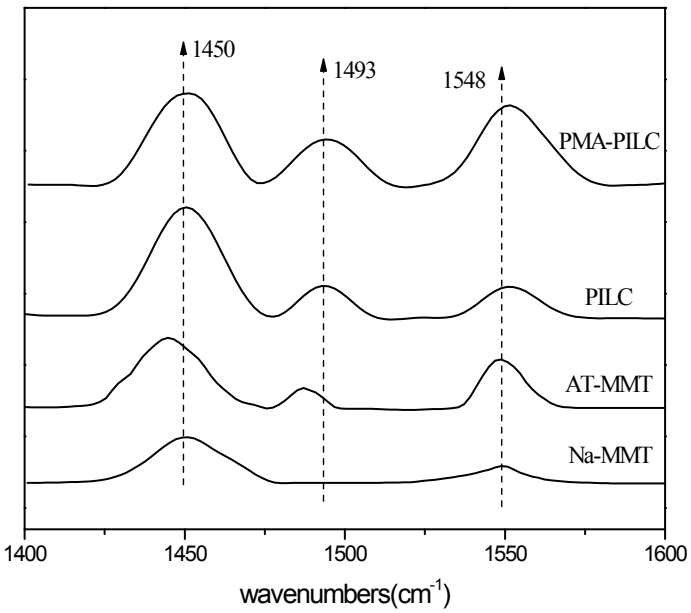


Fig. S4. IR spectras of pyridine adsorbed on different catalysts

S3 References

S1. S. Golay, L. Kiwi-Minsker, R. Doepper and A. Renken, *Chem Eng Sci.* 1999, **54**, 3593-3598.