Supporting information

Alkylation of isobutane and isobutene catalyzed by trifluoromethanesulfonic acid-taurine deep eutectic solvents in polyethylene glycol

Feng-Li Yu, *[a] Yu-Long Gu, [a] Xun Gao, [a] Qi-Chun Liu, [a] Cong-Xia Xie, *[a] and Shi-Tao Yu [b]

[a.] *State Key Laboratory Base of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China. E-mail: yufliqust@163.com (F.-L. Yu); xiecongxia@126.com (C.-X. Xie).*

[b.] *College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.*

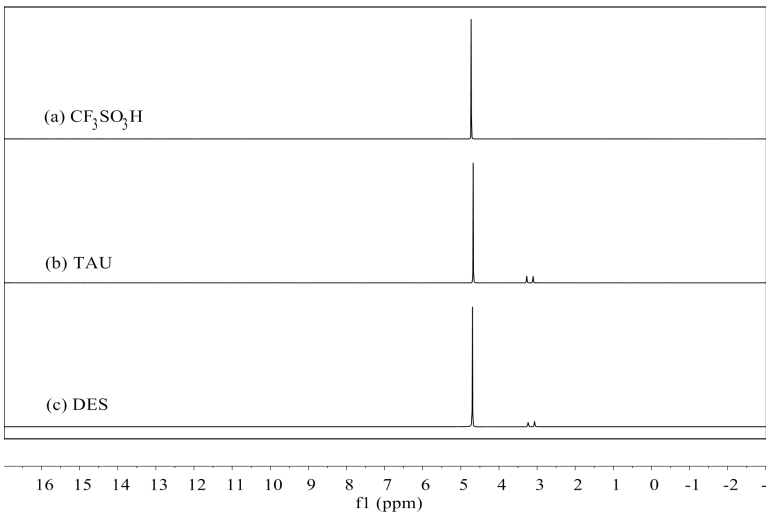

Fig. S1 ^{1}H NMR spectra of TfOH (CF_3SO_3H), TAU and DES ([TfOH]$_3$[TAU])

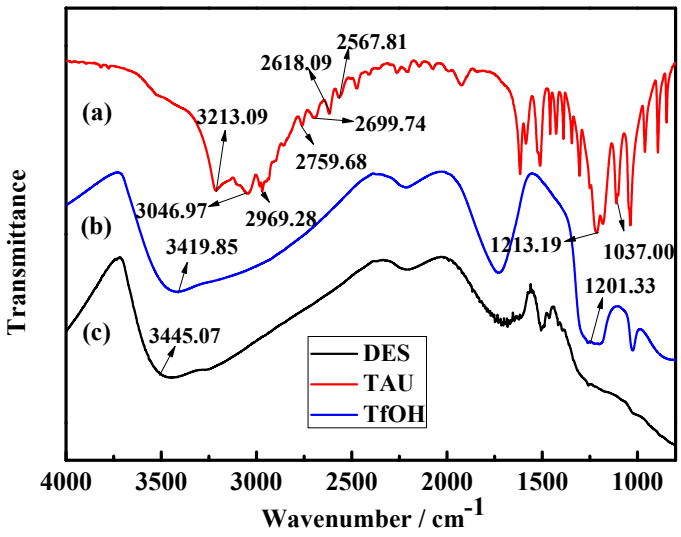

Fig. S2 FT-IR spectra of TfOH, TAU and DES ([TfOH]$_3$[TAU])

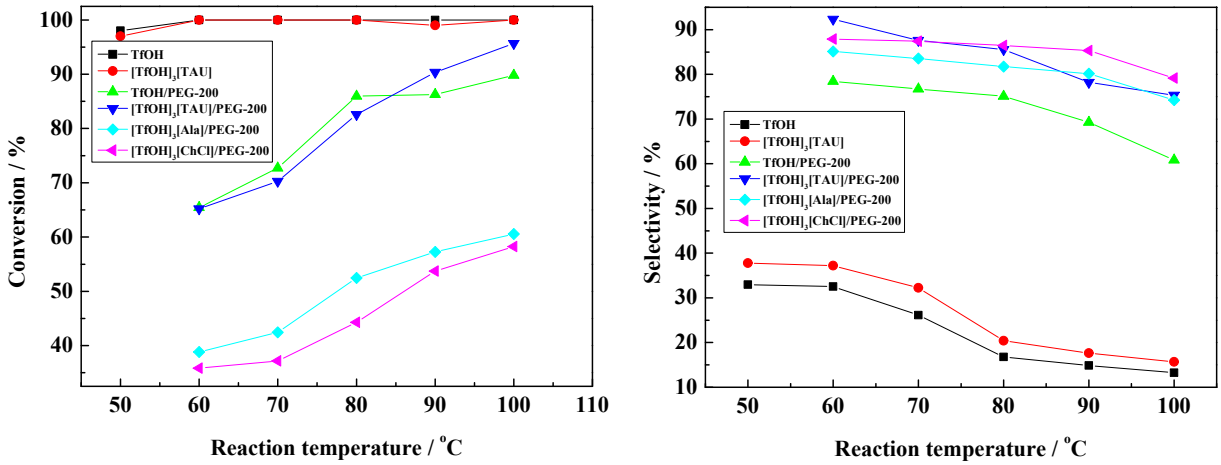

Fig. S3 Effect of reaction temperature on the alkylation over different catalysts

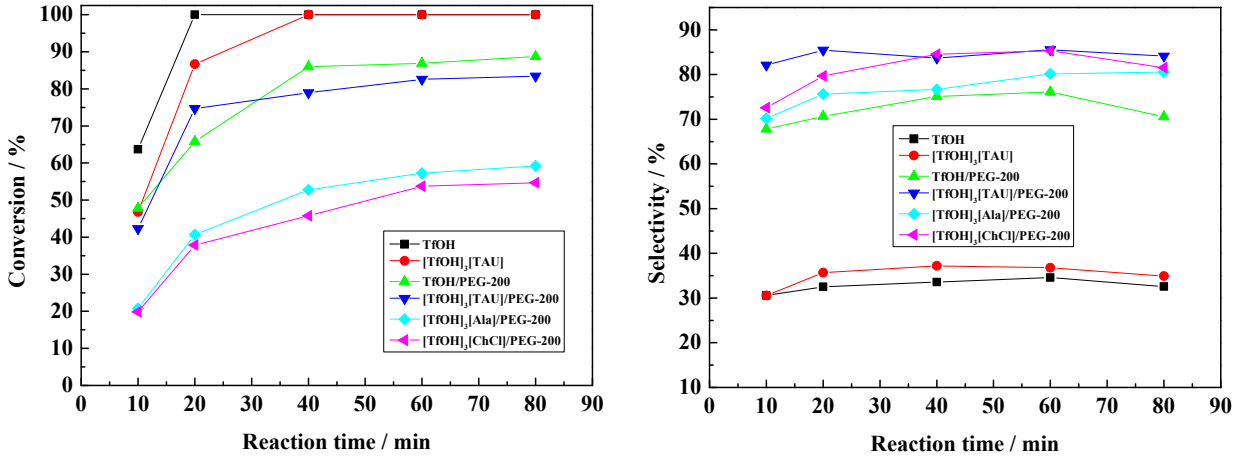

Fig. S4 Effect of reaction time on the alkylation over different catalysts

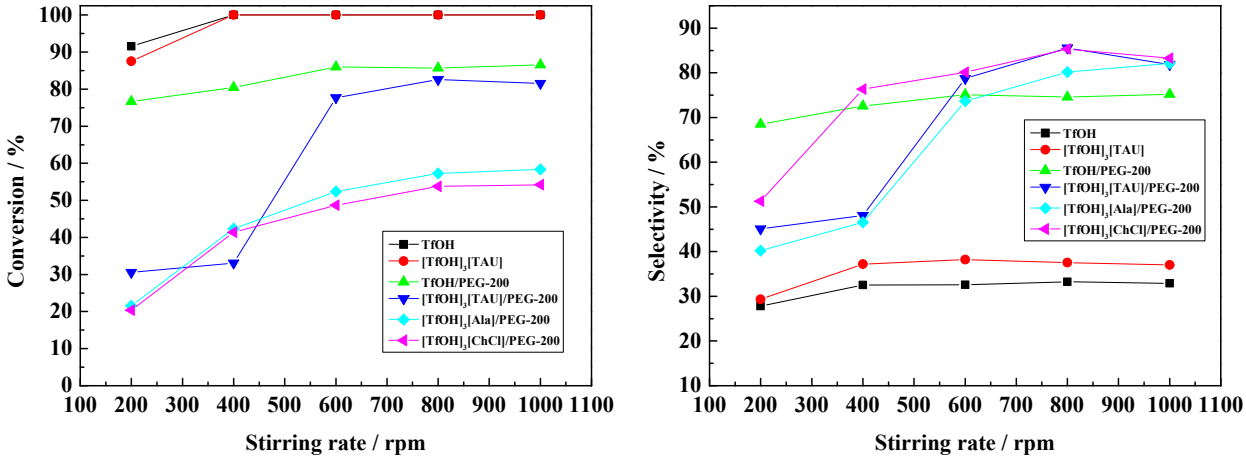

Fig. S5 Effect of stirring rate on the alkylation over different catalysts

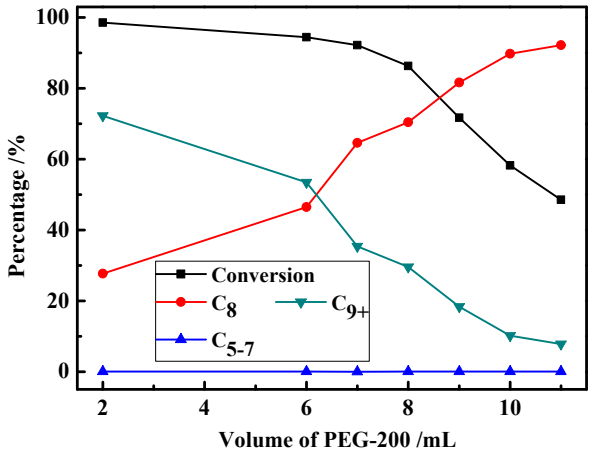

Fig. S6 Effect of volume of PEG-200 on the alkylation

（T = 60 °C, SR = 800 rpm, t = 40 min, n_{TfOH}: n_{TAU} = 2: 1）

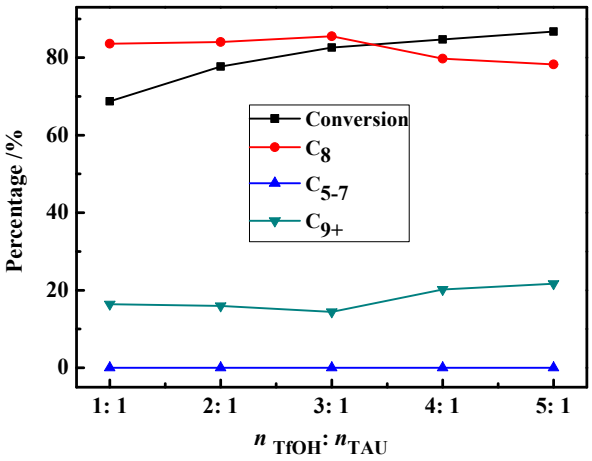

Fig. S7 Effect of n_{TfOH}: n_{TAU} on the alkylation

（$V_{\mathrm{PEG\text{-}200}}$ = 10 mL, T = 80 °C, SR = 800 rpm, t = 60 min）

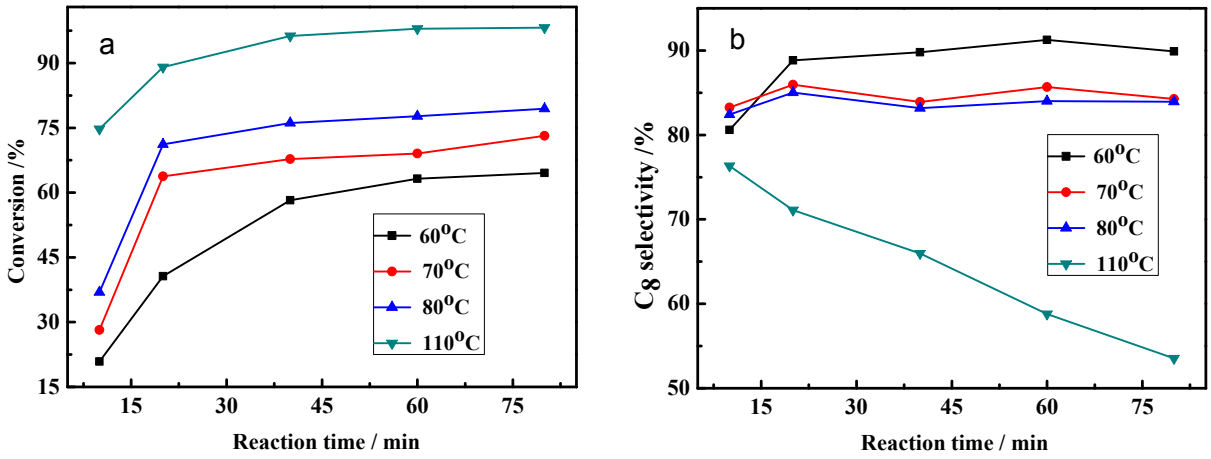

Fig. S8 Effect of reaction temperature and time on the alkylation

（$V_{PEG\text{-}200}$ = 10 mL, *SR* = 800 rpm, n_{TfOH}: n_{TAU} = 2: 1）

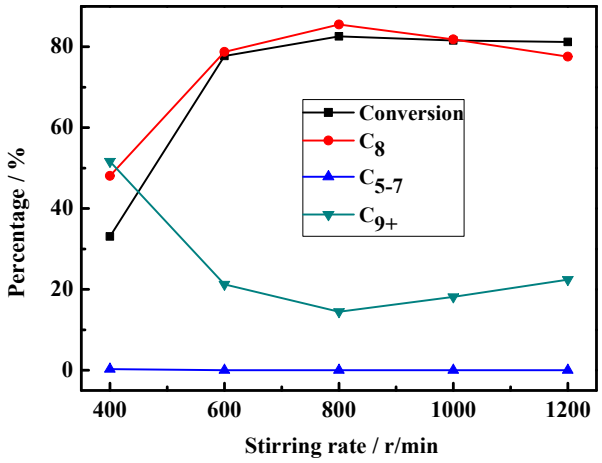

Fig. S9 Effect of stirring rate on the alkylation

（$V_{PEG\text{-}200}$ = 10 mL, *T* = 80 °C, n_{TfOH}: n_{TAU} = 3: 1, *t* = 60 min）

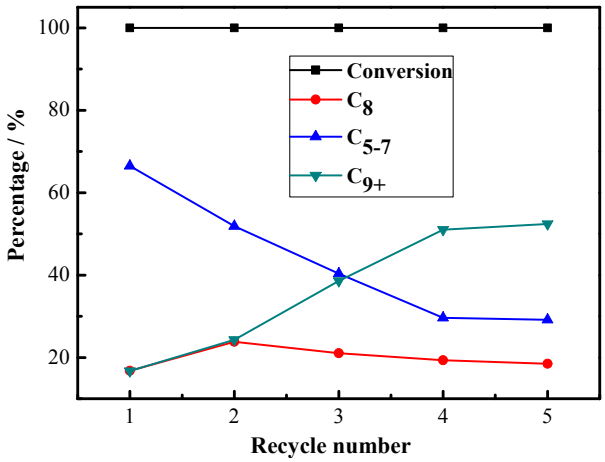

Fig. S10 Recycling efficiency of TfOH catalytic system

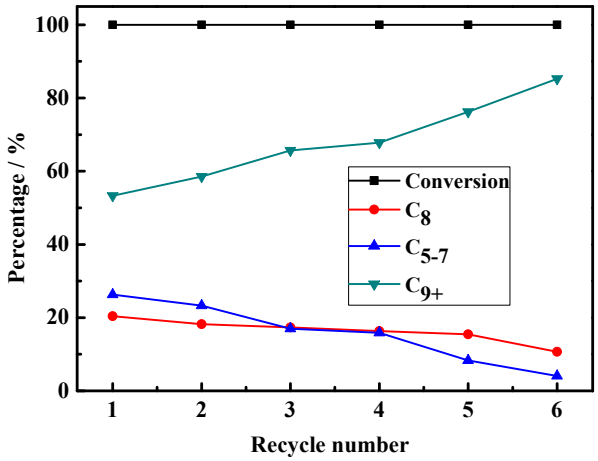

Fig. S11 Recycling efficiency of $[TfOH]_3[TAU]$ catalytic system

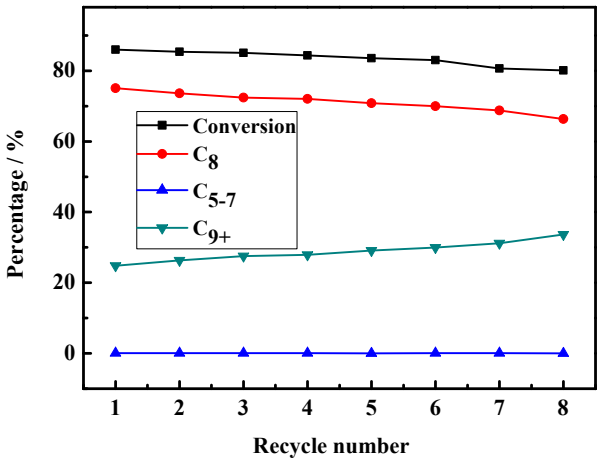

Fig. S12 Recycling efficiency of TfOH/PEG-200 catalytic system.

Experimental Section

Reagents and instruments

All the chemicals were of analytical grade and used as received without further purification. Typically, isobutane and isobutene were purchased from Dalian Special Gas Co., Ltd. Trifluoromethanesulfonic acid (TfOH), taurine (TAU), alanine, choline chloride, and polyethylene glycol (PEG-200) were obtained from Aladdin Reagent Inc.

The alkylation products were analyzed using a GC-9790 Plus gas chromatograph with a FID detector and a HP-PONA capillary chromatographic column (50 m × 0.2 mm × 0.5 μm; Zhejiang Fuli Analysis Ltd. Co.). The prepared deep eutectic solvent (DES) was characterized by using Netzsch-TG209 thermogravimetric analyzer (TGA), Nicolet 510P FT-IR spectrometer with the KBr method (frequency range from 4000 to 400 cm^{-1}), and Brucker AV500 nuclear magnetic resonance (NMR) instrument with tetramethylsilane as the internal standard and deuterated water as the solvent and the external reference. The alkylation reactions were performed in a 100 mL miniature high-pressure reaction kettle with double trace injection pump plungers (Xi'an Taikang Biological Technology Co., Ltd.).

Preparation of DES

A certain quality of TAU was added to a three-necked, round-bottomed flask equipped with a reflux condensing tube in 40 ^{o}C constant temperature water-bath. Under the stirring, 4 mL of TfOH was slowly dropwise added to the flask. After the dropping, the mixture was stirred for 30 min at 50 ^{o}C to afford the DES of [TfOH][TAU]. After that, 10 mL of PEG-200 was added to the DES. After an violent mixing for 30 min at 70 ^{o}C , [TfOH][TAU]/PEG-200 catalytic system was afforded.

Preparation of alkylate gasoline

The alkylation reaction occurred in the device, as shown in Fig. S10. First, 10 mL of the prepared [TfOH][TAU]/PEG-200 solution was added to the mechanical mixing high-pressure reaction kettle. After sealing the kettle, the atmosphere was replaced by nitrogen for 4 times, and 30 mL of feed gas (isobutane:isobutene=10:1)

was subsequently filled. After reaching the preset temperature, the mixture was mechanically stirred for a certain time. After the reaction, the kettle was cooled down. Subsequently, the gas in the kettle was collected and the isobutene conversion was determined by gas chromatography (GC). After pressure relief, the upper liquid was removed and washed with saturated sodium bicarbonate solution for 3 times. After drying and centrifugation, the upper clear liquid was analyzed by GC to determine the amount of alkylate product. The lower catalyst phase did not require processing and could be directly reused.

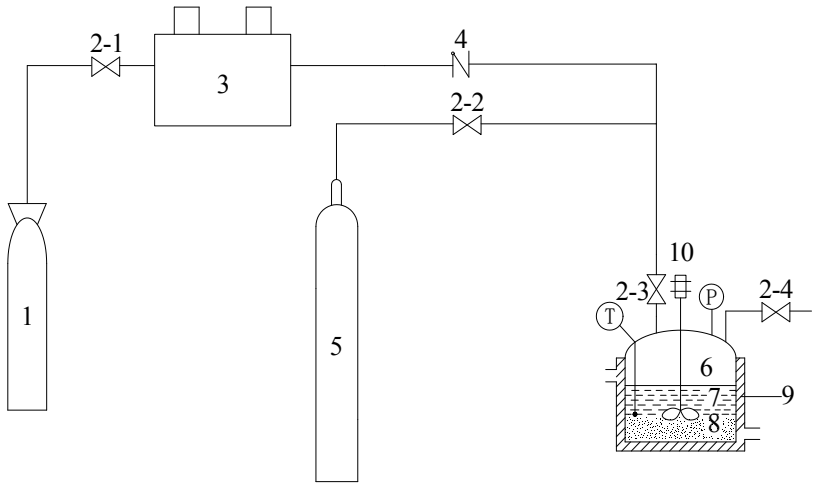

Fig. S13 Installation diagram for the alkylation reaction: (1) feed storage tank, (2) needle valve, (3) double piston metering pumps, (4) one-way valve, (5) constant pressure nitrogen, (6) autoclave, (7) reactant, (8) catalyst, (9) constant temperature circulating water, and (10) stirrer.