Electronic Supplementary Material (ESI) for RSC Advances.

Elucidating the deactivation mechanism of Beta zeolite catalyzed linear alkylbenzene production with oxygenated organic compounds contaminated feedstocks

Shiyong Xing [a], Xiaofei Liu [b], Yan Cui [c], Yuehua Zhao [b], Ziheng Chen [b], Sigui Xiang [a], Minghan Han [b]**

[a] Beijing Special Engineering Design and Research Institute, Beijing 100028, P. R. China.

[b] Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology

Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China.

[c] Petrochemical Research Institute, PetroChina Company Limited, Beijing 100195, China.

*Email: hanmh@mail.tsinghua.edu.cn, 13717798109@139.com

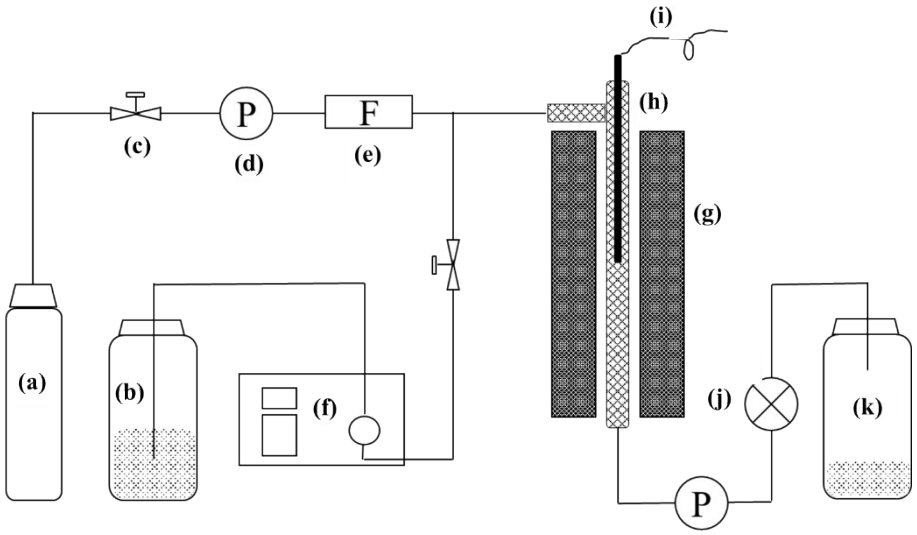

Fig. S1. The schematic flow diagram of the catalyst evaluation equipment. **(a)** N_2 cylinder, **(b)** feedstocks, **(c)** globe valve, **(d)** pressure gauge, **(e)** flowmeter, **(f)** pump, **(g)** furnace, **(h)** reactor, **(i)** thermocouple, **(j)** back pressure valve, **(k)** products.

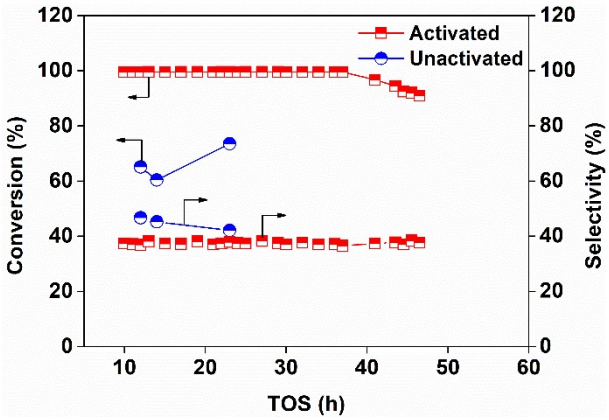

Fig. S2. Effect of activation process on the catalytic performance for the alkylation of benzene with 1-dodecene. Activation conditions: 300 °C, 100 ml·min^{-1} N_2, 3 h. Reaction conditions: 100 °C, 4.2 MPa, 15/1, 4 h^{-1}.

Generally, the catalysts loaded in the reactor should be pretreated or activated at higher temperature before pumping feedstocks. The aim of process is mainly to eliminate the impurities within the channels, especially for H_2O. As can be seen from Fig. S2, if the catalyst was used without

this activation process, significant decrease of activity would occur.

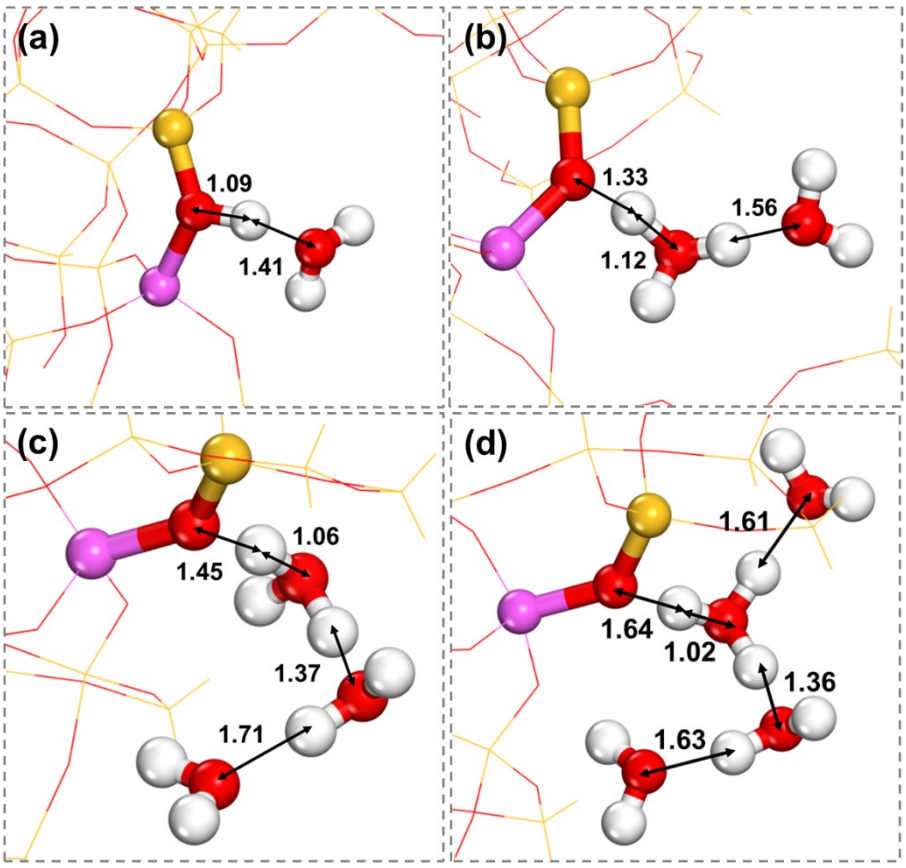

Fig. S3. Effect of H_2O on the acid sites of Beta.

Considering the small size of H_2O, it can be gathered around the acid sites of zeolite catalysts. As can be seen from Fig. S3, as the number of H_2O increases, the O-H bond length of acid site also increases gradually, indicating the higher proximity of H_2O with the acid site. And the decrease of activity and life in Fig. S2 should be mainly caused by the competitive adsorption of H_2O. Therefore, H_2O should be avoided in the zeolite catalyzed reactions.

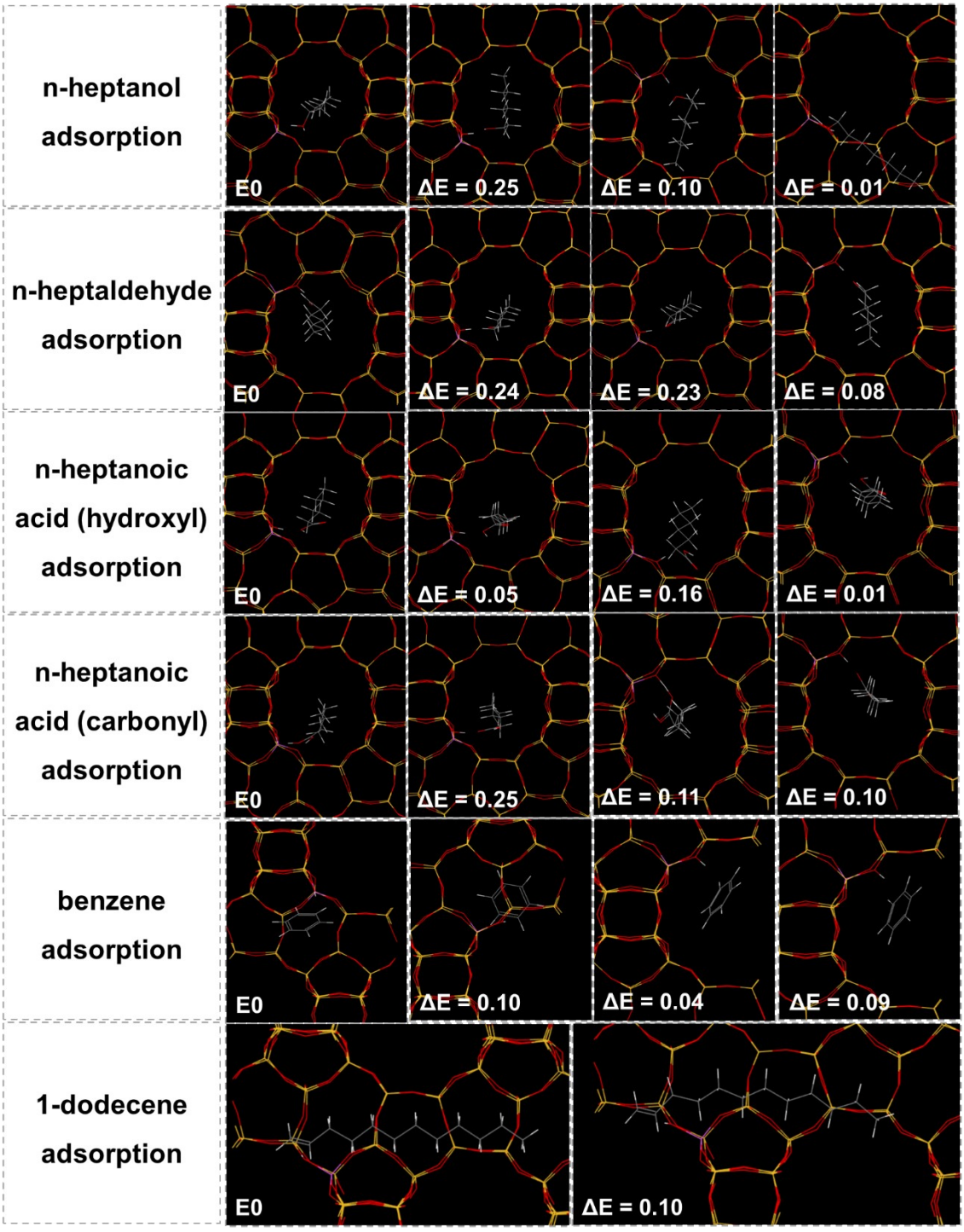

Fig. S4. All the considered orientations for each molecule adsorbed on the acid site of Beta.

Different orientations for each molecule adsorbed on Beta has been considered. For more accuracy, at least four orientations around the acid site were constructed and the most stable orientations were determined by DFT calculations as shown in Fig. S4. As can be seen, the structure

orientation has a significant effect on the thermostability. Therefore, it's essential to do multi-geometries searching in the zeolite catalyzed systems before analyzing the detailed process.

Purification method for the oxygenated organic compounds contaminated feedstocks

Through extensive experiments, an effective method to purify the feedstocks was proposed by our group. As a typical run, 13X zeolite, HY and acid clay were firstly activated at 450 ℃ for 5 h to purify the channels. And then, 500 ml feedstocks contaminated with 100 ppm oxygenated organic compounds (n-heptanol) were mixed with 333 g activated 13X, and the mixture is then filtered after 12 h. From this step, a part of oxygenated organic compounds can be removed. After that, 1.74 g Na was mixed with 300 ml feedstocks after treated with 13X zeolite. The mixture should be stirred at 90 ℃ for 2 h, so that the oxygenated organic compounds can react with Na thoroughly. And then, the mixture was filtered to separate the residual Na. Then, the filter liquor was mixed with 8 g HY and 4 g acid clay, and stirring at room temperature for 4 h to remove the organic sodium salts. And then, the mixture was filtered to obtain the pure feedstocks.

Herein, MWW was selected to test the effectiveness of this method, mainly due to its more sensitivity to the oxygenated organic compounds. As can be seen from Fig. S5, obvious decrease of lifetime occurred after 100 ppm n-heptanol added into the feedstocks. However, after treatment according to the method proposed above, the catalytic performance was as good as the pure feedstocks. For the deactivated catalyst, the activity of it can also be completely recovered by extraction with benzene at 250 ℃, further evidencing the effectiveness of this method.

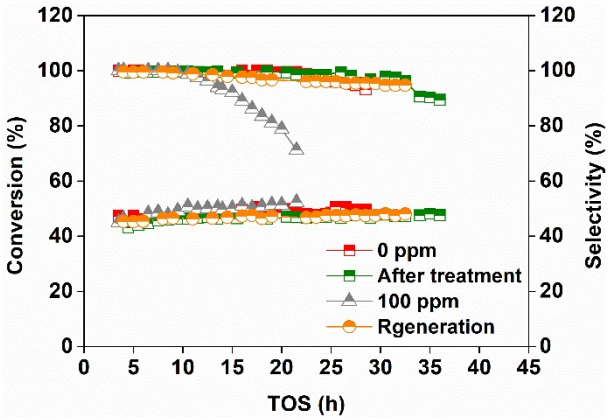

Fig. S5. Effect of oxygenated organic compounds on MWW catalyzed alkylation of benzene with 1-dodecene.