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Acetylene hydrochlorination over 13X zeolite catalyst at high temperature

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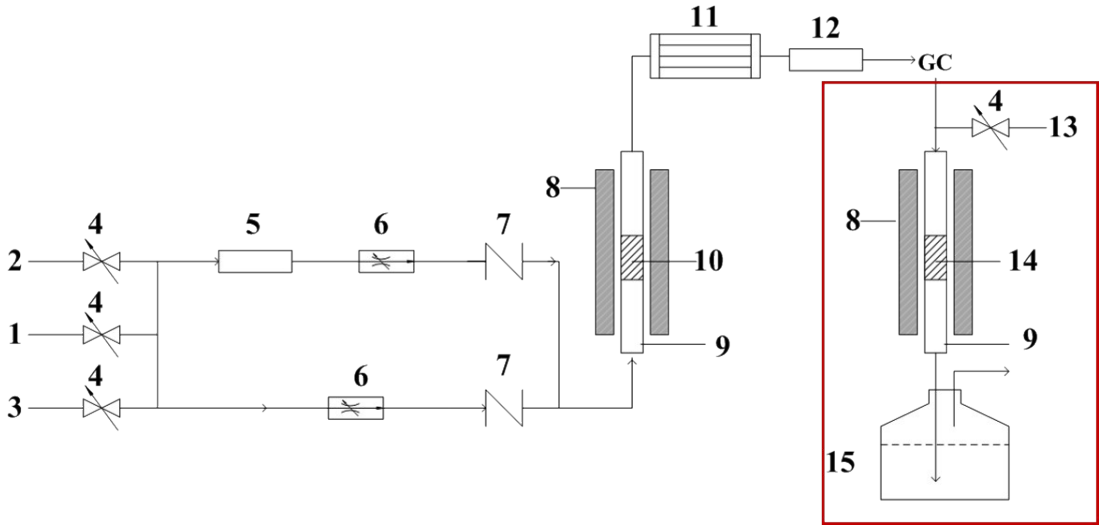
Electronic Supplementary Information

Catalyst preparation

Catalysts used in the experiments all were commercial available. Zeolite 13X (SiO_2/Al_2O_3 = 2.34) was bought from Jiangsu ALSIO Technology Co., Ltd.. Other zeolites such as USY (SiO_2/Al_2O_3 = 8.92), Beta (SiO_2/Al_2O_3 = 24.57), MOR (SiO_2/Al_2O_3 = 14.40) and ZSM-5 (SiO_2/Al_2O_3 = 35.53) were provided by Nankai University; and they were ion exchanged with NaCl aqueous solution at room temperature for 24 h. Coconut shell activated carbon (AC) was gotten from Shaowu Chem., Zhejiang.

Catalytic performance evaluation

Sketch of the catalyst experimental setup was listed below.



1. Nitrogen, 2. Acetylene, 3. Hydrogen chloride, 4. Relief valve, 5. Dry pipe (silicagel), 6. Mass flowmeter, 7. One-way check valve, 8. Furnace, 9. Reactor, 10. Catalyst bed, 11. Cold trap (0-5°C), 12. Dry pipe ($CaCl_2$), 13. Air, 14. Combustion catalyst, 15. NaOH aqueous solution. (The flow rate of air was 400-500 ml/min, the combustion temperature was 450 °C)

Analysis conditions were as follows: Agilent 7890A GC; capillary column Agilent 19095P-Q04: 50 m × 530 μm × 40 μm; inlet temperature, 200 °C; split ratio, 30:1; column temperature, 210 °C; detector type, flame ionization detector (FID); detector and vaporizer temperature, 300 °C.

Characterization

The on-line mass spectra was performed on an Omnistar GSD320 (Pfeiffer Vacuum, Germany) mass spectrometer. The X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO X-ray diffractometer using the Cu-Kα radiation (λ = 1.54059 Å), operating at 40 kV and 40 mA. The thermogravimetry analysis was carried out on a TA Q-600 analyzer from room temperature to 800 °C at a heating rate of 10 °C/min in an air flow of 100 ml/min. The total carbon content in the catalysts after reaction was determined using an instrument for total organic carbon analysis (Shimadzu TOC-L CPH) with a solid sample module (SSM-5000A). The temperature of the total carbon combustion tube of the SSM-5000A was 900 ºC. Approximately 100 mg of solid sample was loaded in a ceramic sample boat and analyzed by further combustion. The chemical composition of the solid samples was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. Textural properties of catalysts were determined by N_2 adsorption-desorption isotherms at 77 K on a Micromeritics ASAP 2020 system. The total surface area was calculated based on the BET equation, and the micropore surface area was evaluated using the t-plot method. ^{13}C solid NMR spectra were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm or 7 mm MAS probe. The resonance frequency was 150.9 MHz for ^{13}C.

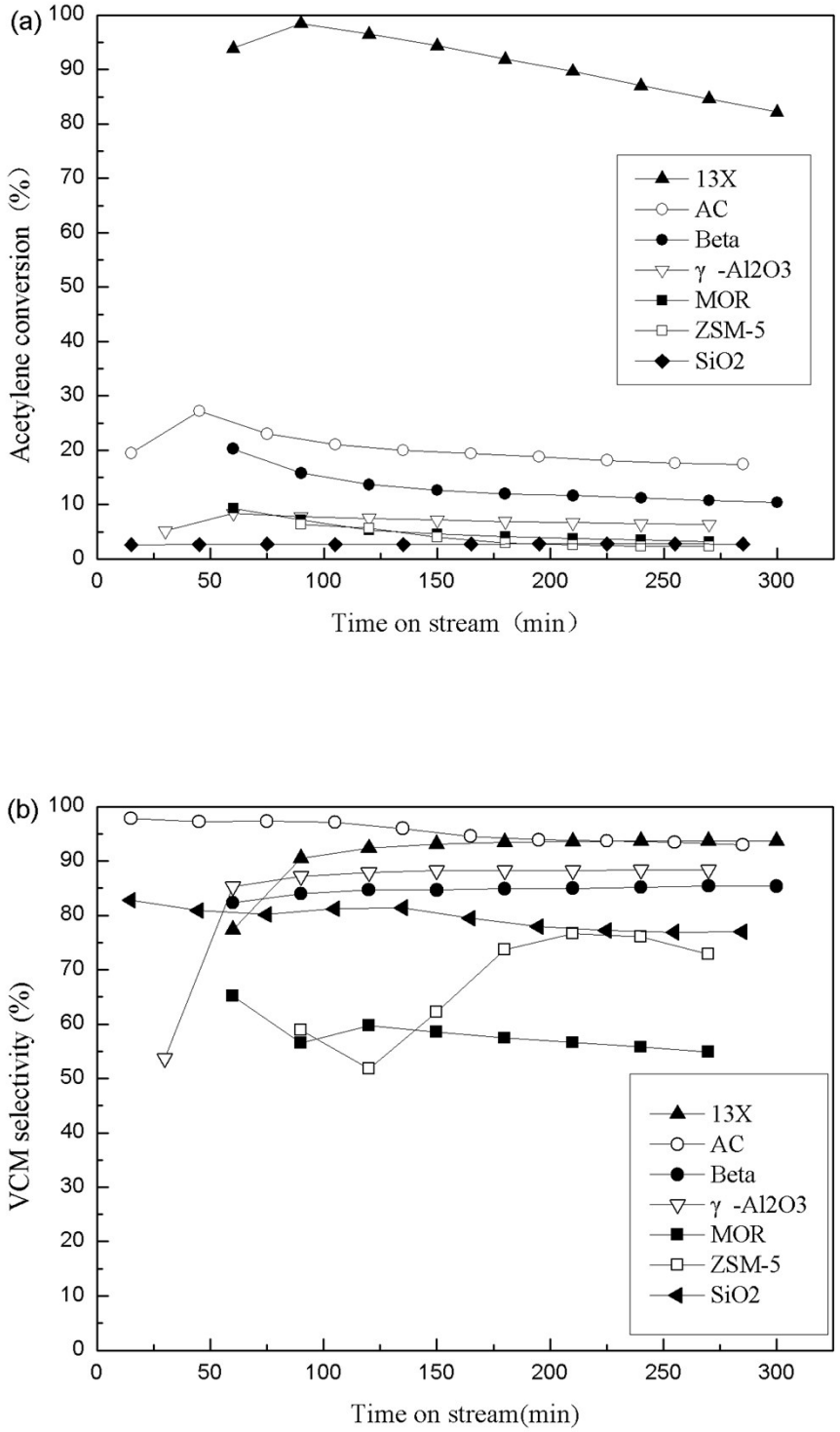


Fig. S1 Catalytic performances of different catalysts in acetylene hydrochlorination. Reaction conditions: reactor set point temperature = 320 °C.

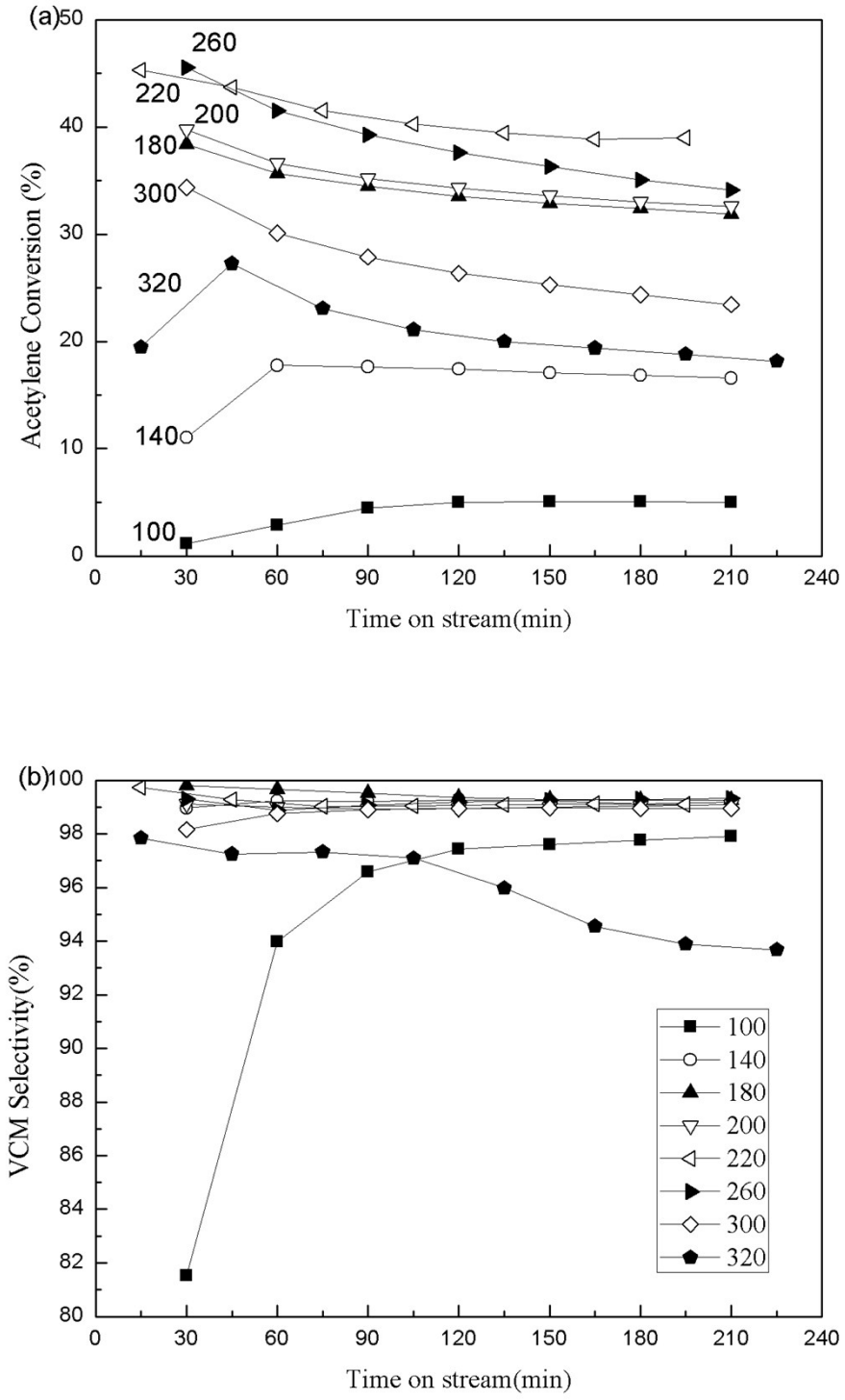


Fig. S2 Influence of temperature on catalytic activity in AC catalyzed acetylene hydrochlorination.

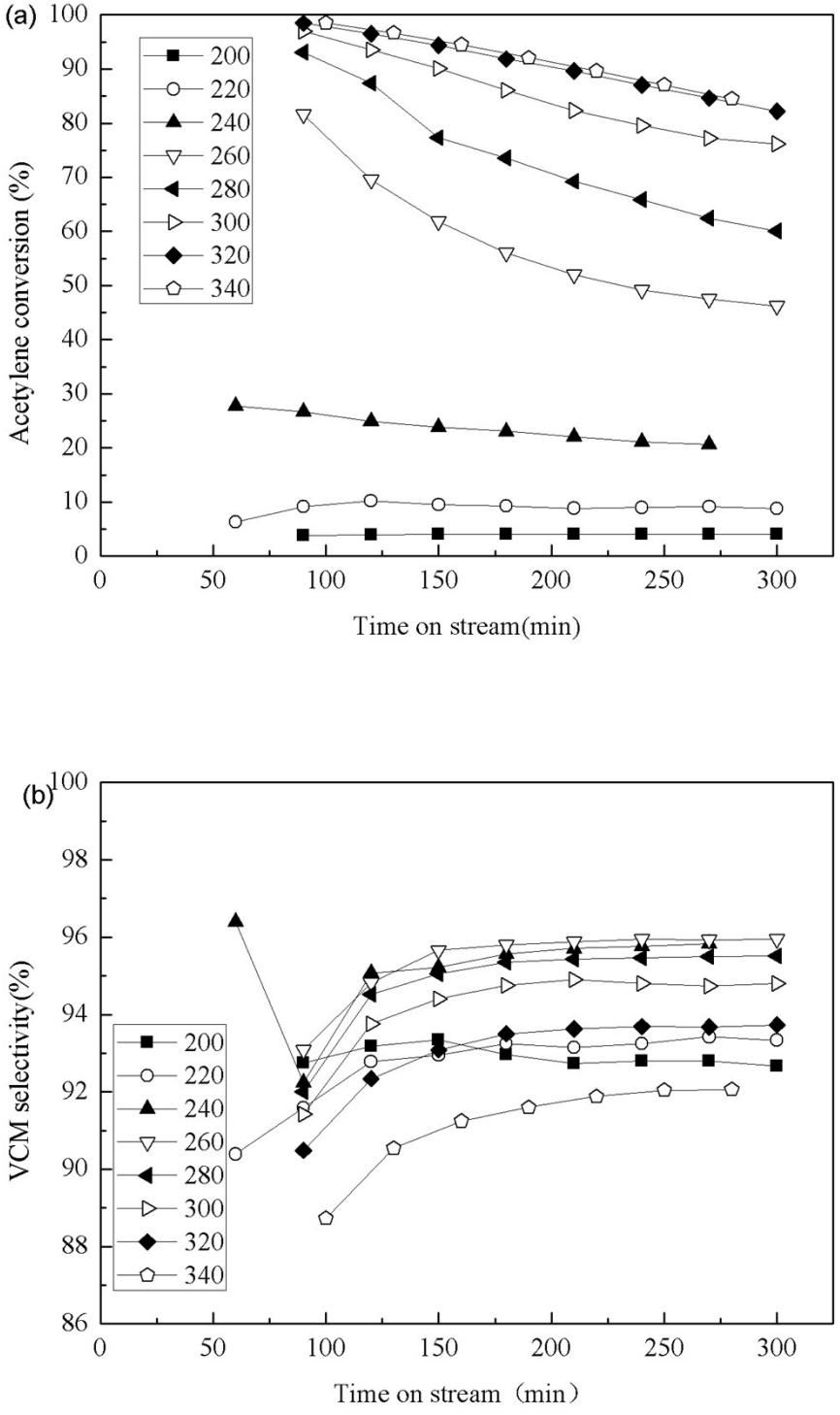


Fig. S3 Influence of temperature on catalytic activity in 13X catalyzed acetylene hydrochlorination.

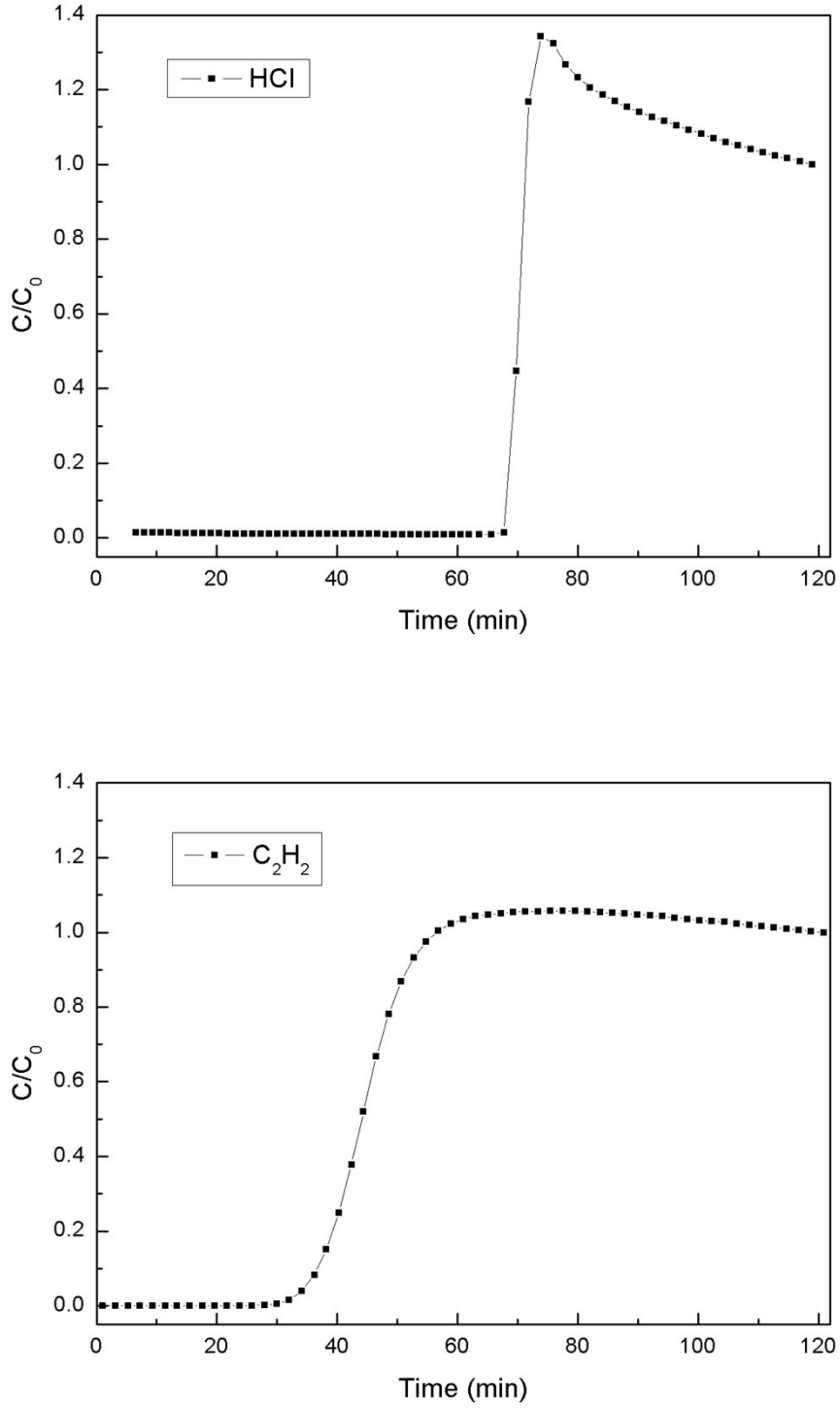


Fig. S4 The breakthrough curves of HCl (12ml/min) and C_2H_2 (10ml/min) in the reactor packed with 10 ml of 13X under reaction conditions (reactor set point temperature = 320 °C, the breakthrough curve was determined individually).

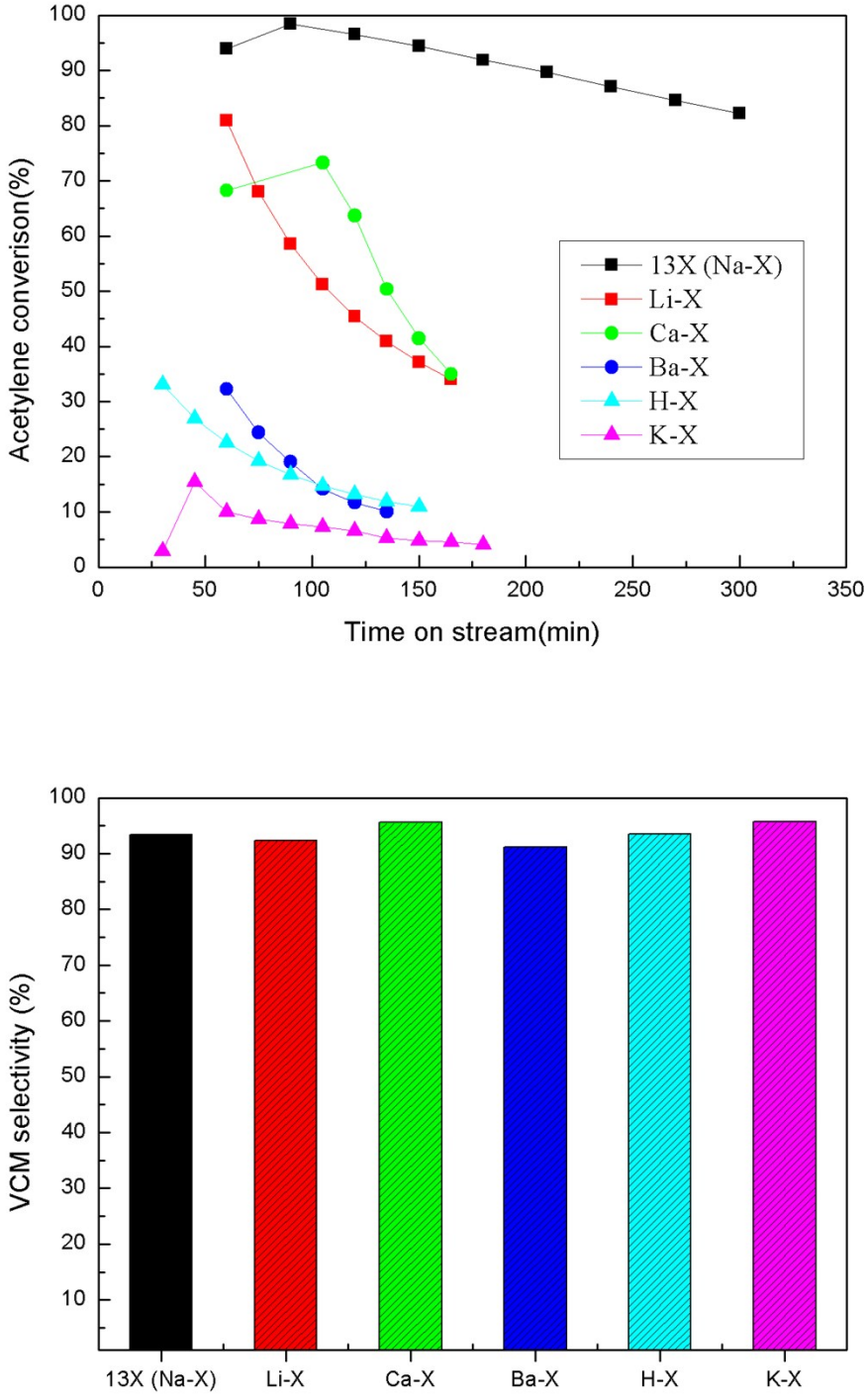


Fig. S5 Catalytic performances of X zeolites with different types of cation in acetylene hydrochlorination. Reaction conditions: reactor set point temperature = 320 °C

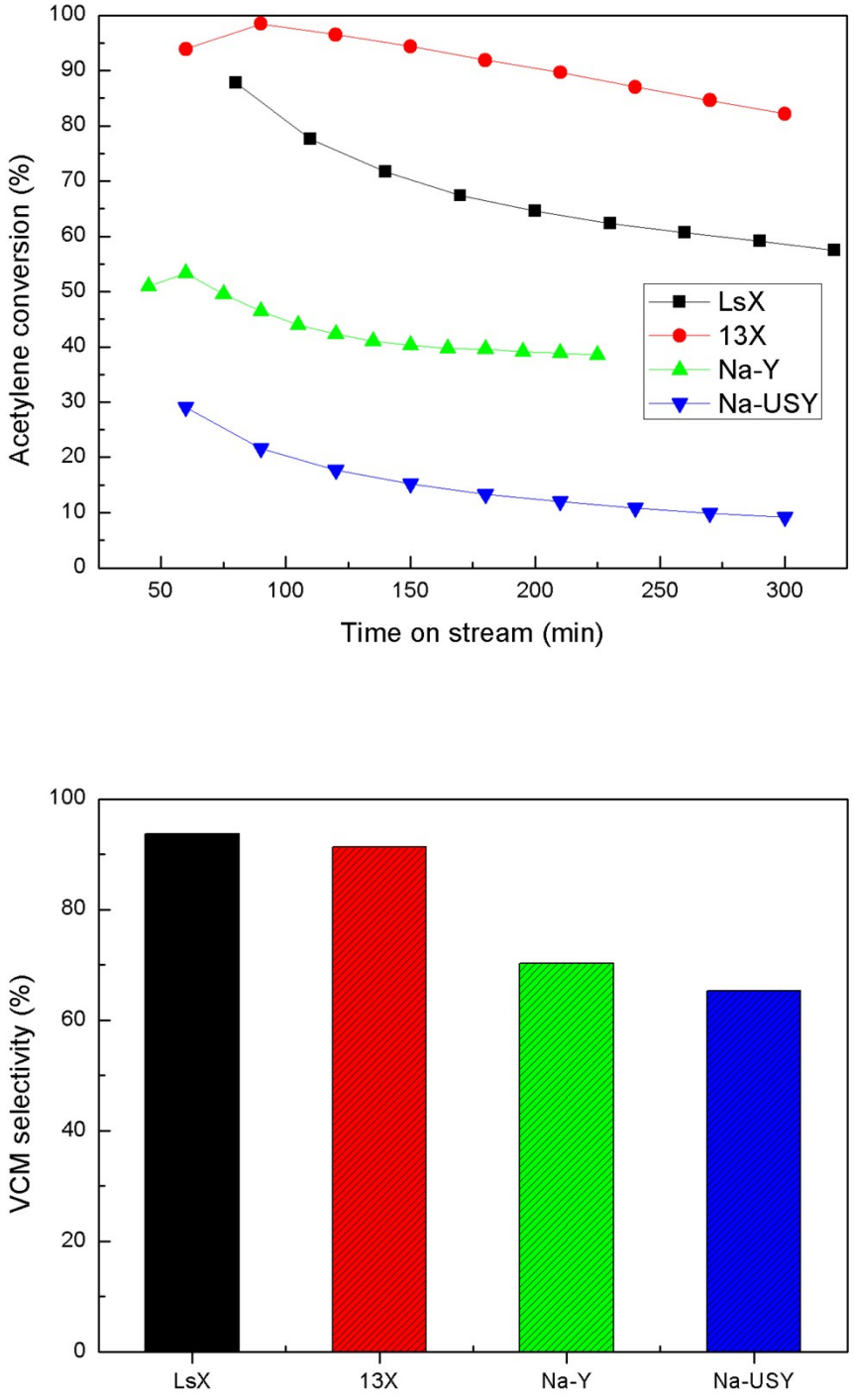


Fig. S6 Catalytic performances of faujasite zeolites with different SiO_2/Al_2O_3 ratio in acetylene hydrochlorination. Reaction conditions: reactor set point temperature = 320 °C.

Table S1 Chemical compositions of X zeolites[a].

Sample	SiO_2/Al_2O_3 ratio[b]	Na_2O/Al_2O_3 ratio[b]
13X (Na-X)	2.82	0.92
Li-X	2.95	0.10
Ca-X	2.94	0.04
Ba-X	2.90	0.11
H-X	2.86	0.19
K-X	2.90	0.05

[a] X zeolites with different cation types were obtained by ion exchange of 13X. [b] SiO_2/Al_2O_3 ratio and Na_2O/Al_2O_3 ratio were received by XRF.

Table S2 Chemical compositions of faujasite zeolites.

Sample	SiO_2/Al_2O_3 ratio[a]	Na_2O/Al_2O_3 ratio[a]
LsX	2.07	0.80
13X	2.82	0.92
Na-Y[b]	7.44	0.47
Na-USY[b]	8.92	0.31

[a] SiO_2/Al_2O_3 ratio and Na_2O/Al_2O_3 ratio were received by XRF.

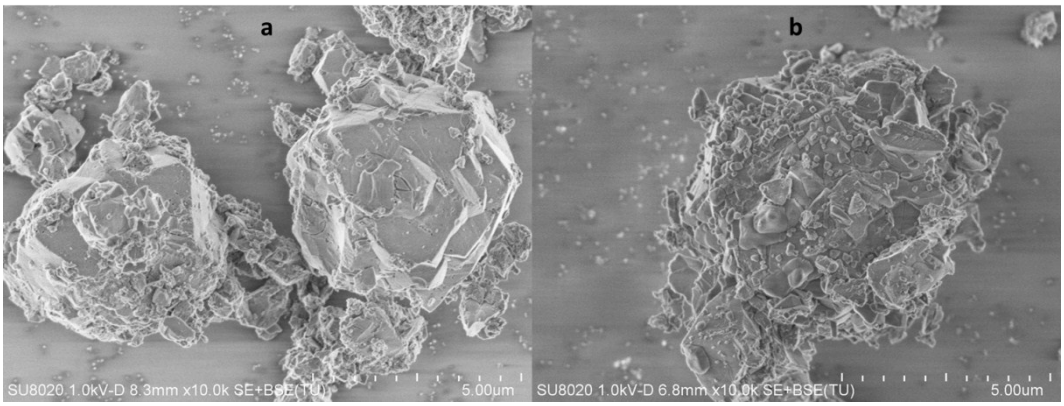


Fig. S7 The SEM images of the fresh (a) and spent (b) 13X catalysts.

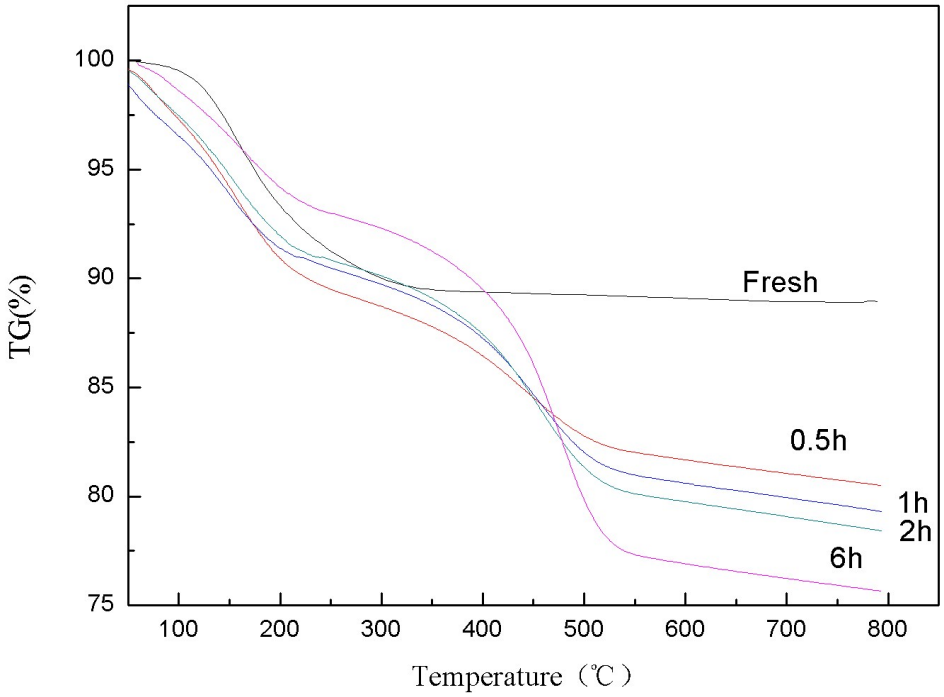
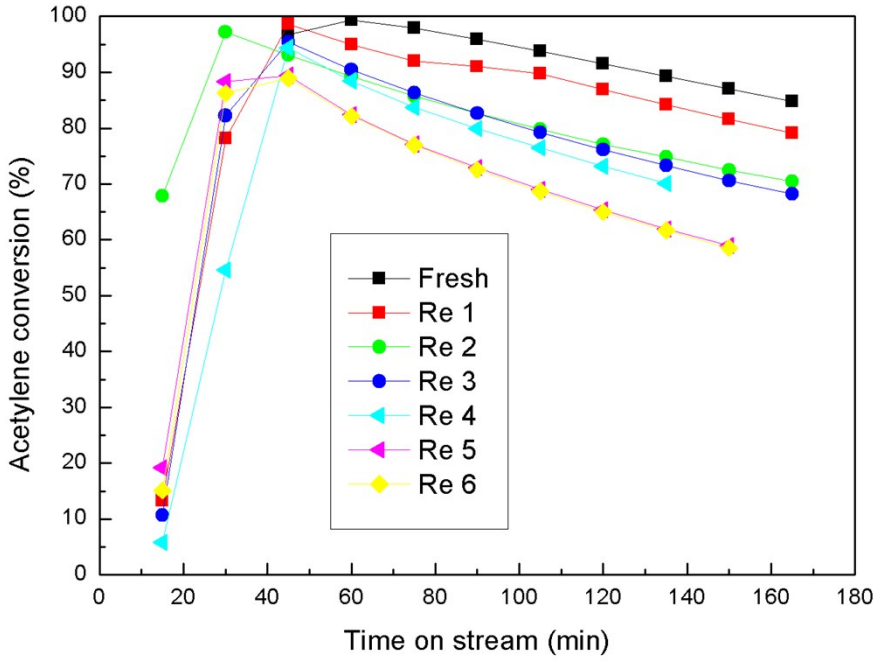


Fig. S8 TG curves of fresh catalyst and catalysts reacted after different times. Reaction conditions: reactor set point temperature = 320 °C.



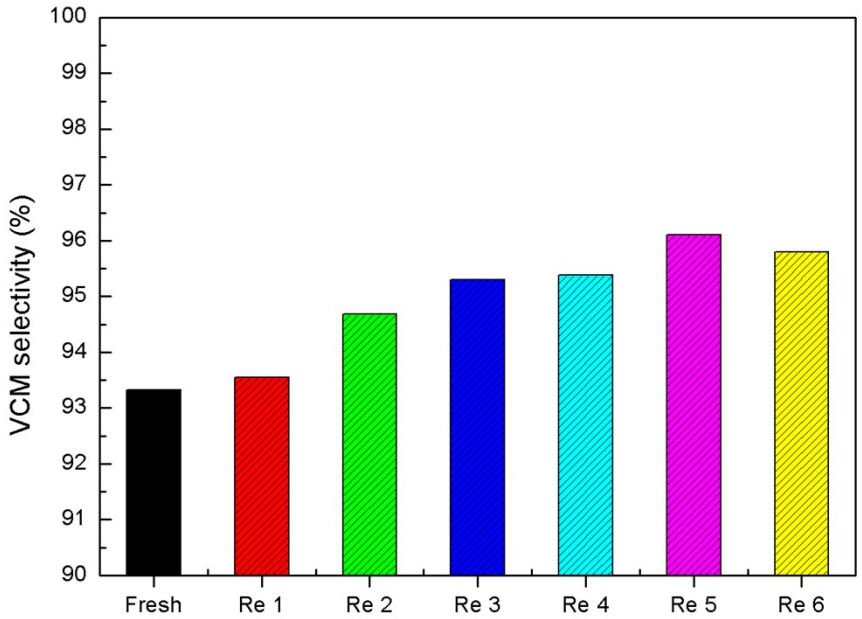


Fig. S9 Catalytic performances of fresh and regenerated spherical 13X catalysts. Reaction conditions: reactor set point temperature = 320 °C.

Regeneration of spherical 13X catalyst was also conducted by the same method

as mentioned before.

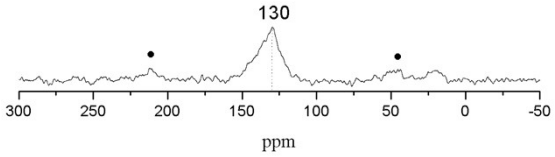


Fig. S10 ^{13}C CP MAS NMR spectra of 13X catalyst reacted 9h. ● denotes spinning sideband. Reaction conditions: reactor set point temperature = 320 °C.

The ^{13}C CP MAS NMR spectra of deactivated catalyst indicated that aromatics (130ppm) were the main cokes species.