CuH-ZSM-5 as Hydrocarbon Trap under cold start conditions

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Number of pages: 8

Number of Figures: 4

Number of Tables: 1

Sample characterization

The samples were characterized by scanning electron microscope (SEM) in a HITACHI microscope (model S-3000N). Copper loading was determined by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Perkin Elmer Optima 4300 system. NH_3–TPD profiles were obtained using a conventional flow-through reactor connected to a thermal conductivity detector (TCD). 100 mg of each zeolite were cleaned in flowing Ar at 500 ºC for 6 h, and cooled down to 125 ºC under vacuum. The samples were treated for 4 h with 1.3 kPa NH_3/Ar flow, and the weakly adsorbed NH_3 was removed afterwards by 1 h evacuation at 125 ºC. The NH_3–TPD profiles were finally obtained by heating the reactor at 5 ºC/min up to 600 ºC in 30 ml/min helium flow.

X-Ray photoelectron spectroscopy (XPS) was used to provide information on how copper is present in the sample and its oxidation state. The apparatus was an ESCA$^+$ (omicron) system equipped with a Mg Kα radiation source to excite the sample (hυ = 1253.6 eV). To obtain the XPS spectra, the pressure of the analysis chamber was maintained at 10-10 mbar. The binding energy scale was adjusted by setting the C1s transition at 284.5 eV.

The textural characterization of the zeolites was carried out by means of the adsorption of N_2 at -196 ºC (Autosorb 6, Quantachrome). Prior to the adsorption measurements, the adsorbent particles were outgassed in situ in vacuum (4 mbar) at 250 ºC for 4 h to remove any adsorbed impurities. Surface area was calculated from nitrogen adsorption isotherms using the BET equation (S_{BET}). Total micropore volume ($V_{DR}(N_2)$) was calculated applying the Dubinin–Radushkevich (DR) equation to the N_2 adsorption data at -196 ºC.

Solids prepared were characterized by X-ray diffraction (XRD), using a SEIFERT 2002 power diffractometer with a Cu-Kα radiation. The scanning rate was 2º/min in the 5-50º angle.

The morphology and crystal sizes were examined by transmission electron microscopy (TEM) in a JOEL (JEM-2010) microscope.

A FTIR spectrometer (model Infinity MI60 from Mattson) with a diffuse reflectance accessory (model COLLECTOR from Spectra Tech) was used for in situ DRIFTS experiments. An IR cell fitted with CaF_2 windows, which allowed temperature and gas flow composition control, was used. The gas composition was monitored during the experiments with a mass spectrometer Pfeiffer Vacuum (model OmniStar). Before starting the experiments in presence of propene, the samples were treated in an inert atmosphere (He) at 350 ºC for 30 min, in order to remove any adsorbed impurities. Then propene adsorption was carried out at room temperature and, finally, samples were heated up to 350 ºC at 20 ºC/min in a helium atmosphere to cause propene desorption. The gas flow used was 35 ml/min and the propene concentration was 8000 ppm.

The amount of coke formed during the CST experiments was determined by the Thermal Gravimetric Analysis (TGA; TA Instruments, model SDT 2960) for samples H-ZSM-5, CuH-ZSM-5(1), CuH-ZSM-5(2) and CuH-ZSM-5(3), after being used. In these experiments, approximately 10 mg of the zeolite were used and the temperature was increased from 25 to 950 ºC, with a heating rate of 10 ºC/min under a constant flow rate of 80 ml/min in Air.

Figure S1. XRD diffractograms of the samples H-ZSM-5 and CuH-ZSM-5.

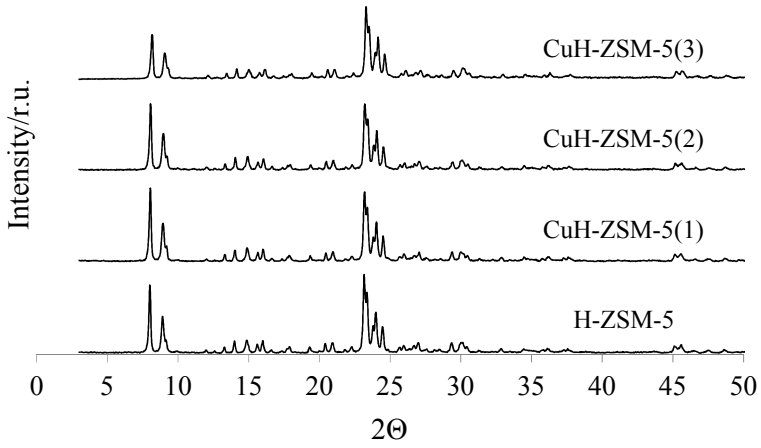

Figure S2. NH_3-TPD profiles of the samples H-ZSM-5 and CuH-ZSM-5.

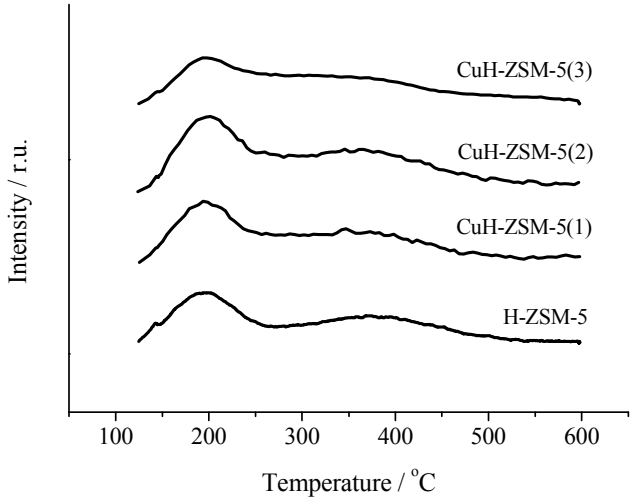

Figure S3. CST performed with the parent H-ZSM-5 zeolite. Conditions: 100 ppmv propene, 90 ppmv toluene, 1% v/v O_2, 10% v/v H_2O and Ar balance. GHSV = 10000 h^{-1}. Red lines represent propene concentration profiles and black lines represent toluene. Straight lines represent the first cycle and dotted lines represent the third cycle.

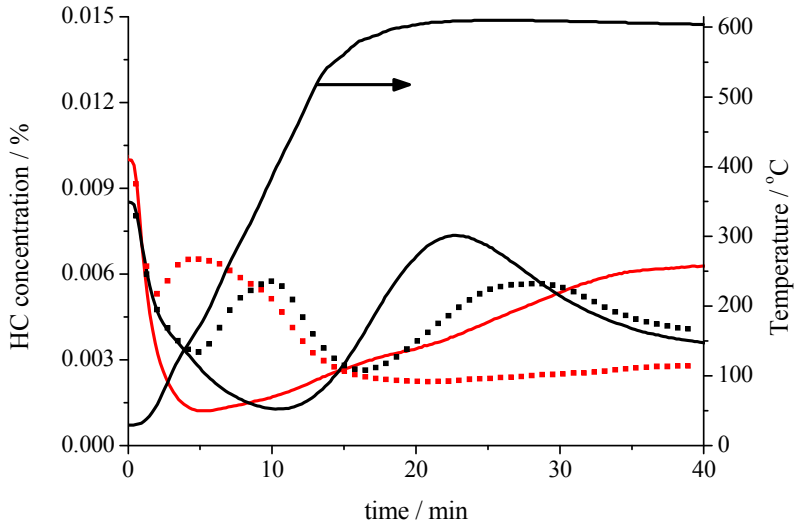

Figure S4. Simulated cold start test for the different zeolites, CO_2 evolution during the third CST. Conditions: 100 ppmv propene, 90 ppmv toluene, 1% v/v O_2, 10% v/v H_2O and Ar balance. GHSV= 10000 h^{-1}. Black line represents H-ZSM-5 CO_2 concentration profile, red represents CuH-ZSM-5(1), black dotted line presents CuH-ZSM-5(2) and red dotted line represents CuH-ZSM-5(3).

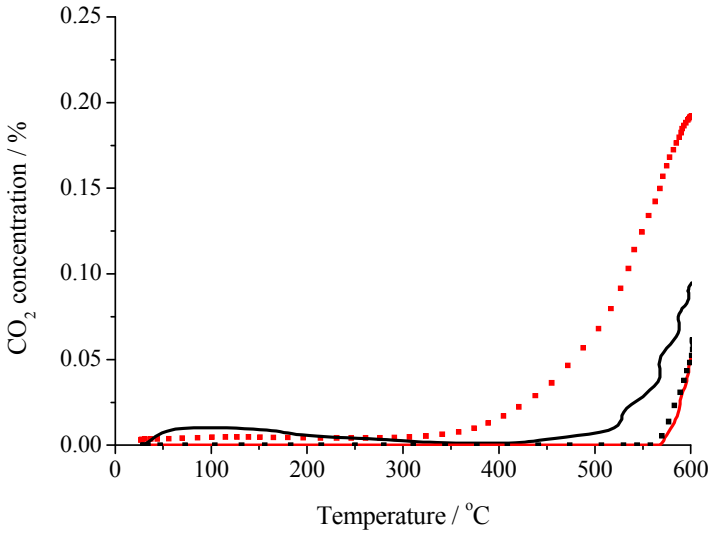

Table S1. Ion-exchange conditions.

Sample	Cu^{2+} concentration (M)	Temperature (ºC)	Time (h)
CuH-ZSM-5(1)	3.45×10^{-3}	77	18
CuH-ZSM-5(2)	3.45×10^{-3}	77	22
CuH-ZSM-5(3)	0.1	40	13