

Simultaneous and Cooperative Gas Storage and Gas Production using Bifunctional Zeolites

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Supplementary Material

Experimental Section

Synthesis of zeolite-X. In polyethylene bottles, sodium aluminate (46.423g, 0.5663mol, Riedel de Haën, Al as Al₂O₃ 50-56%, Na as Na₂O 40-45% and Fe as Fe₂O₃ 0.05%), was added to distilled water (72.095g, 4.005mol). Then, sodium hydroxide (5.38g, 0.1345mol, Fisher Scientific, 99.56%, 40g/mol) was introduced to adjust the sodium concentration in the batch. The mix was stirred until dissolution at 100°C. The resultant gel (23.853g) was added to distilled water (145.718g, 8.095mol) and sodium hydroxide (14.099g, 0.3525mol), and mixed until dissolution. Finally, this gel was combined quickly with a sodium silicate solution (52.331g, 0.2160mol, Riedel de Haën, NaOH 10%, SiO₂ 27%, 242.23g/mol, d=1.39) and stirred for 30 minutes. Crystallization took place at 90°C during 8 hours without stirring in autoclaves. The product was filtered and washed until the pH was below 10. The product (13.2898g) was obtained with a yield of 75.3%. Zeolite ZSM-5 (Si/Al = 60) was purchased from Zeolyst.

Copper exchange. Copper nitrate (6.0453g, 0.025mol, Alfa Aesar 98%, 241.6g/mol) was dissolved in distilled water (100mL) in a conical flask equipped with a stirring bar. Then, 1g of zeolite was added and both were stirred during 24h at room temperature. The product was recovered by filtration and washed three times with distilled water to remove the metal precursor from the outer surface of the zeolite.

Activation of the copper-containing zeolites. Zeolites (~20mg) were placed in glass ampoules inside a Schlenk tube at room temperature till the vacuum reached 0.01mbar. The Schlenk tube was heated at 300°C during 3hours, under vacuum, in a Büchi glass oven. It was then cooled down at room temperature and placed under NO for 1hour. Eventually, the system was purged with vacuum and placed under argon to remove any NO which was not adsorbed within the zeolite: this process was repeated three times before sealing the glass ampoules.

Characterization of Cu-exchanged zeolites. A Stoe diffractometer system (Bragg-Brentano assembly) combined with the Stoe WinX^{POW} software were used. The sample was inserted in between two plastic films which were inserted in the sample-holder. XRD showed that the synthesized compound was the one expected and that ion exchange had little effect on the crystallinity of the sample.

ICP (Argilent 7500a ICP-MS) was used to estimate the copper exchange within the zeolites as well as to check the Si/Al ratio. The sample was mixed with Teflon (1:4), and pressed using a 13mm die so as to make pellets for laser ablation. The copper exchange for zeolite-X equalled 49% and for ZSM-5 was 92%.

Quantification of NO release using chemiluminescence experiments. The buffer (2.6mL, pH7.4, MOPSO) was placed in a sealed vial equipped with a stirring bar and nitrogen was bubbled through the solution 10 minutes before starting the experiment. The zeolites were then introduced quickly into the vial and the measurements started immediately. Note that zeolites preadsorbed with NO were previously kept in a sealed glass ampoule. Usually, any NO release was monitored for at least 60minutes and then nitrites were added. NO release measurements were performed using a Sievers NOA 280i chemiluminescence Nitric Oxide Analyser. The sensitivity of the method is less than 1ppb with repeatability of 5% for gas measurement. The instrument was calibrated by passing air through a zero filter (Sievers, <1 ppb NO) and 89.48 ppm

NO gas (Air Products, balance nitrogen). The flow rate was set to 175 mL/min with a cell pressure of 8.5 Torr and an oxygen pressure of 6.1 psig. Experiments were recorded at 22°C.