Supplementary Material

SSZ-13 Synthesis

First 32 g of de-ionized (DI) H_2O were mixed with 20 mL of 1M NaOH (Sigma-Aldrich) and 25 g of sodium silicate (Sigma-Aldrich) and stirred for 15 min. After adding 2.5 g of NH_4-Y zeolite (Zeolyst CBV 300) the mixture was stirred for another 30 min. The structure directing agent used was N, N, N-trimethyl-1-adamantylammonium hydroxide in a 25 wt.% aqueous solution (Sachem, Inc.). 10.5 g of the structure directing agent were added and the solution was allowed to mix for 30 more min. Using four PTFE lined acid digestion vessels (Parr Model 4744, 45 mL each), the solution was heated in an oven for 6 days at 140˚C with agitation at 50 rpm. The zeolite and template solution was removed from the oven and allowed to cool. The zeolite was vacuum filtered out of solution, washed with 1L of DI H_2O and dried overnight in air. The dried powder was calcined in air at 550˚C for 8 hrs with a ramp rate of 0.5˚C min^{-1}, leaving the zeolite in the Na-form. The Na-SSZ-13 was mixed into 0.1M NH_4NO_3 solution for 8 hrs at 80˚C to produce the H-form of the zeolite after calcining again at 550˚C for 8 hrs with a ramp rate of 0.5˚C min^{-1}.

The resulting SSZ-13 zeolite structure was identified using x-ray diffraction (XRD) showing good agreement with the literature (Figure S7). [1-4] XRD was collected on a Bruker D8 XRD with a 2Theta scan range from 15 to 50 at 0.5 deg min^{-1} and yielded a highly structured solid. Comparing this XRD pattern with those in the literature and provided by the International Zeolite Association (i.e. S. I. Zones) indicated that we synthesizes highly crystalline SSZ-13. In all cases the major peaks identified in our sample at 2Theta values of 16.1, 17.8, 20.6, 23.1, 25, 26, 30.8 and 31.2 were also present in the references. The minor peaks at 19.2, 22.2, 22.7, 27.9, 28.3, 34.7, 36.243.1, 43.7, 48 and 49.2 2Theta were more difficult to identify in some references, but those that could be identified overlapped with those measured in our SSZ-13 zeolite.

The BET surface area of the as prepared H-SSZ-13, degassed at 400˚C overnight, was measured using a Micromeritics 2020 ASAP. Over a P/P_0 range of 1×10^{-5} to 0.99 the zeolite had a surface area of 601 $m^2\ g^{-1}$ using N_2 at 77 K; the t-plot pore volume was 0.26 $cm^3\ g^{-1}$. BET surface areas for H- SSZ-13 of 638 and 704 $m^2\ g^{-1}$ were reported by Zecchina et al. and Sommer et al., respectively. [4, 5] Sommer et al. also reported a t-plot pore volume of 0.25 $cm^3\ g^{-1}$. The zeolite had a Si:Al ratio of 18, measured by AAS.

Experimental setup of in situ *XAS reactor and benchtop reactor*

The *in situ* reactor has been described previously[6] and is a standard design used for *in situ* experiments at MRCAT at APS. 10-12 mg of each catalyst were hand-pressed into a sample holder designed to hold up to six samples. The amount of catalyst, and therefore thickness of the pellets was chosen to give a total absorbance at the Cu k-edge of 2 (μx) and an edge step around 1 (Δμx). The sample holder was placed in an 18 in. long tube of 0.75 in diameter. Each end was fitted with custom vacuum (Swagelok Ultra-Torr) fittings which contained polyimide windows.

The fitting on one end was equipped with a thermocouple that could measure the temperature of the sample holder. Both fittings had a gas inlet and outlet valves to isolate to samples in a desired gas atmosphere or to allow continuous flow over the sample holder containing the pressed catalyst pellets. This reactor will not force gas flow through the packed sample pellet but instead bathes the sample holder in the reaction mixture and thus, the reactants must diffuse into the channel of an individual reactant to contact the catalyst. Flow rates used were 600 sccm with all the same concentrations used in the *operando* reactor. A furnace was used to heat the entire length of the tube to 200 ˚C and heat tape and insulation were used to maintain an elevated temperature at the inlet and outlet, without going above the melting temperature of the polyimide windows, to prevent H_2O condensation and NH_4NO_3 formation.

The benchtop reactor in which NO oxidation experiments were completed were collected on a 1 in diameter vertical downflow reactor. About 100-300 mg of catalyst sample were loaded into the sample tube between two sheets of quartz wool and were held in place by a porous frit. The 2.5 foot long reactor was encased in a clamshell over that heated the catalyst from 290-325 ˚C for kinetic tests. The catalyst was sieved to 125-250 μm sized powder. A thermocouple centered within the tube measure temperature just above the catalyst bed, while a second measures outlet temperatures just below the frit. The temperature difference between the two thermocouples was kept below 4 ˚C. A total flow rate of 3.5 L min^{-1} and concentrations of 450 ppm NO, 150 ppm NO_2 and 10% O_2 were used. Effluent gases and bypass were analyzed by a Nicolet Antaris IGS gas analyzer.

Generation of isolated Cu(I) in zeolite reference

An under exchanged 1.1 wt.% Cu/ZSM-5 (~40% ion exchange, Cu/Al = 0.2) was used to generate a Cu(I) reference. The catalyst was treated *in situ* in 1000 ppm NH_3 for 45 min. followed by Standard SCR conditions at 200˚C for 30 min. The resulting XAS showed a very sharp pre-edge feature associated with Cu(I) which was taller than the white line for Cu(II). There is little to no evidence of the presence of either Cu(II) or Cu(0) species on this catalyst, which are therefore assumed to be negligible. No other catalyst in our inventory has shown this level of reduction in similar experiments. Considering the low level of ion exchange of the catalyst, it is likely that the majority of the Cu was in isolated positions and had not formed either small CuO clusters or Cu-dimers, which has also been well documented in the literature. [7-9] Therefore, for the purpose of XANES data fitting, it is presumed that this catalyst is very nearly, if not entirely, isolated Cu(I) within the zeolite framework.

References

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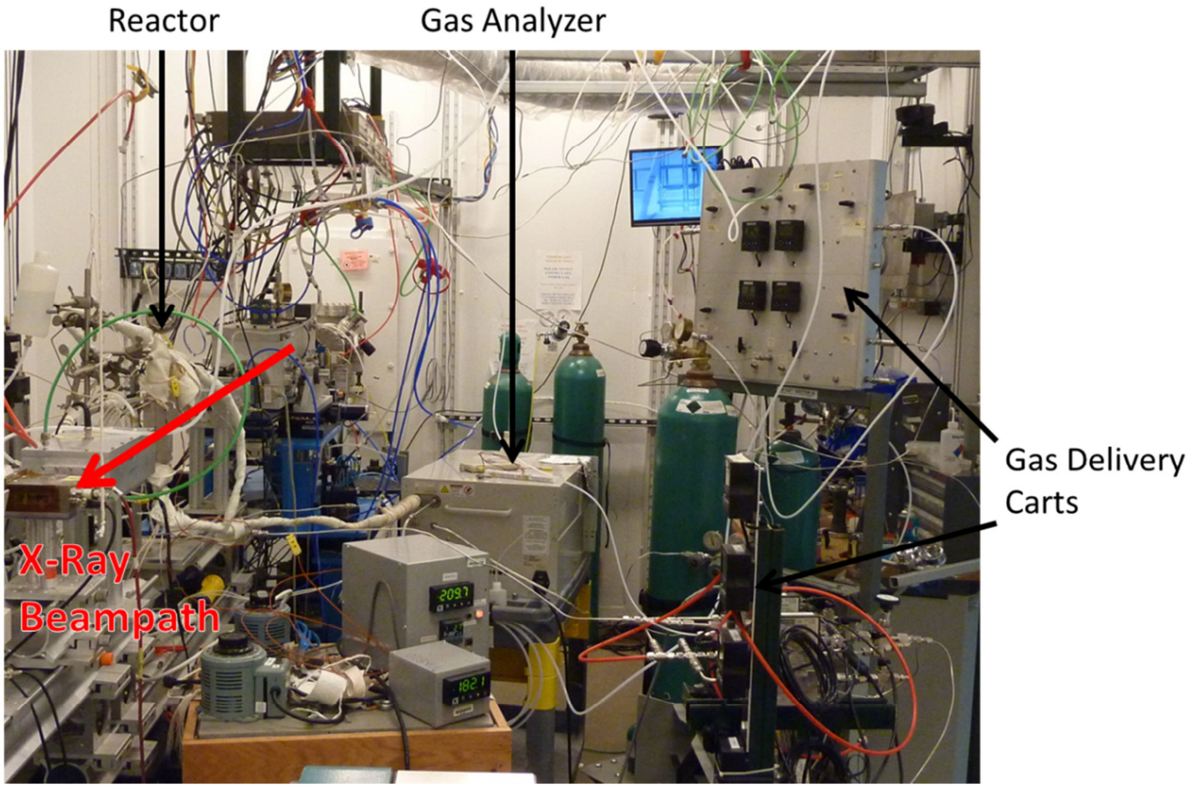

Figure S1. Expanded view of the *operando* reactor setup in the hutch at MRCAT, Sector 10-ID.

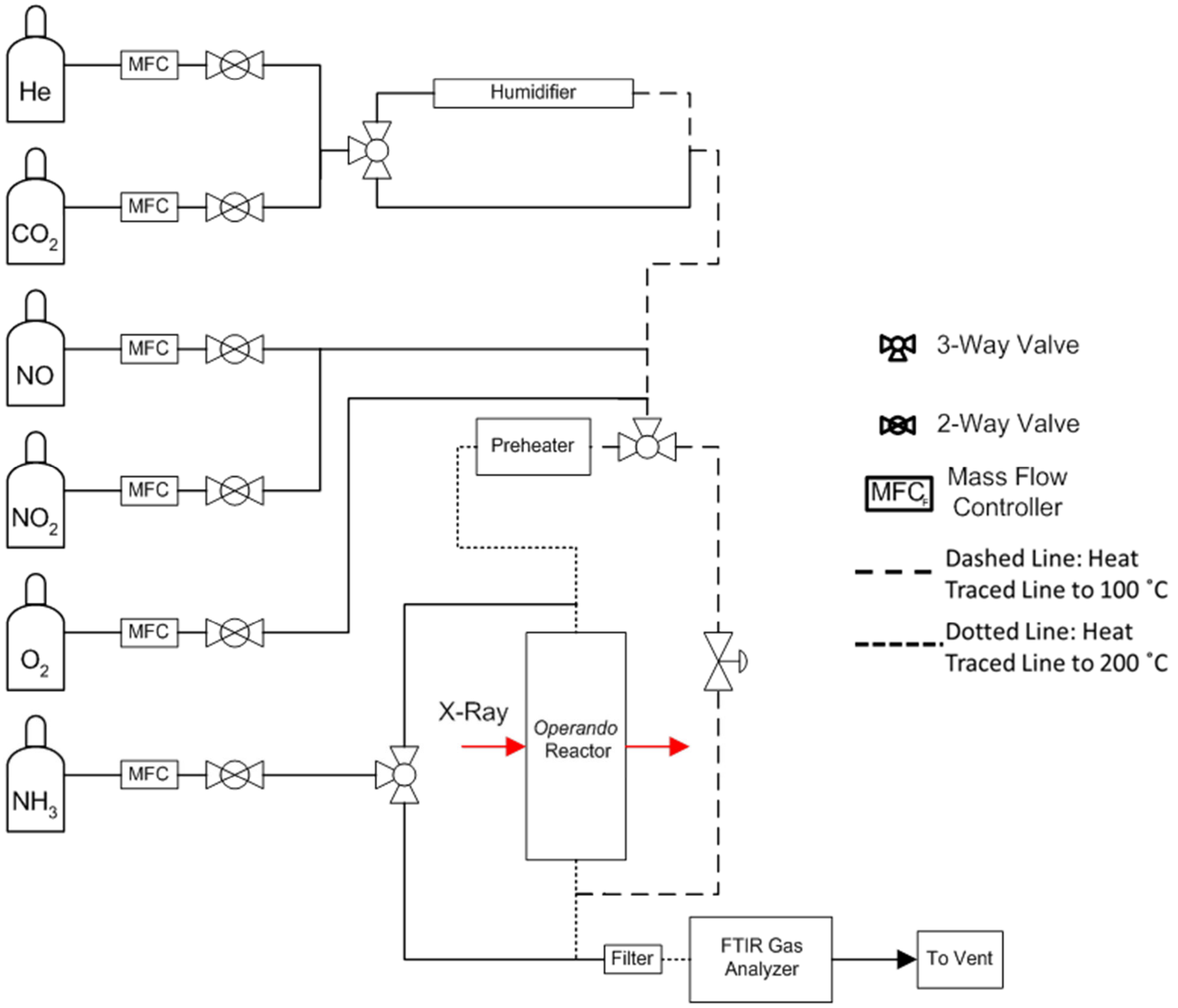

Figure S2. Schematic drawing of the *operando* experimental setup.

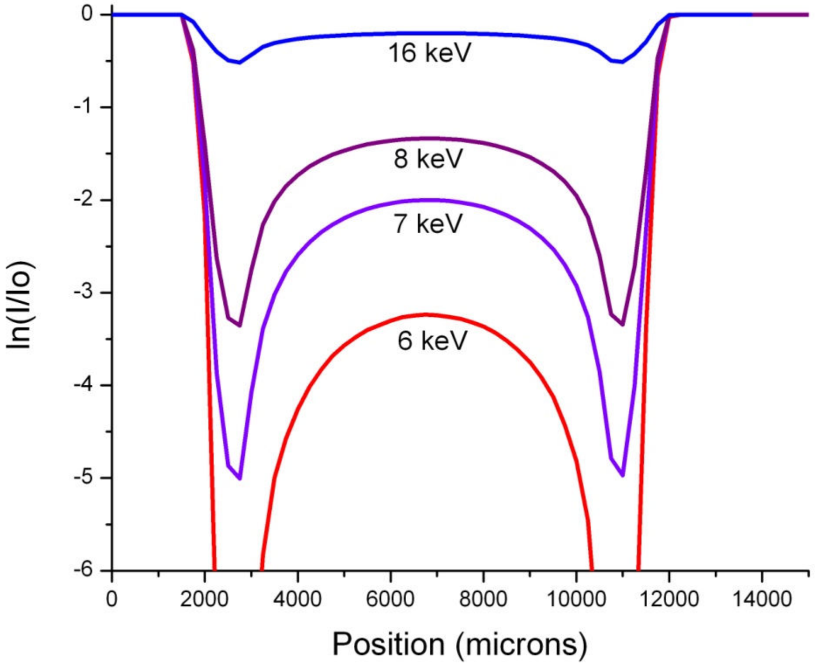

Figure S3. Transmission signal through an empty thin walled 10 mm OD x 8 mm ID vitreous carbon tube at different bending magnet beam energies.

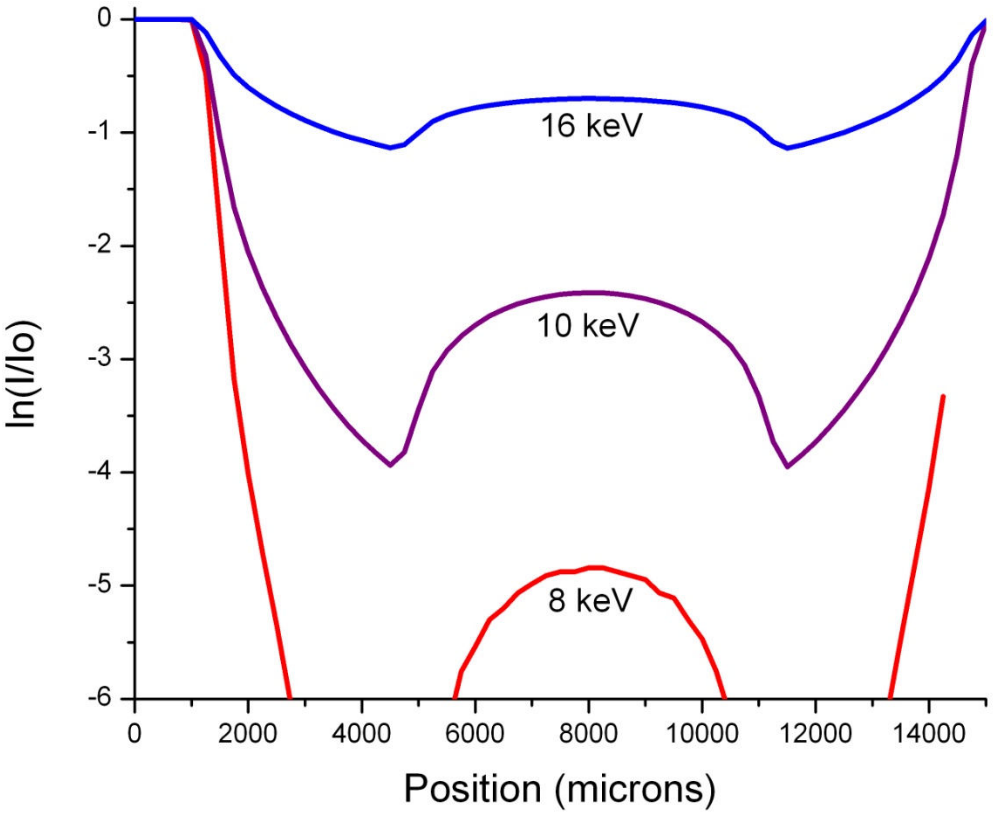

Figure S4. Transmission signal through an empty, large, thick walled 13.6 mm OD x 6.45 mm ID (large thick walled) vitreous carbon tube at different bending magnet beam energies.

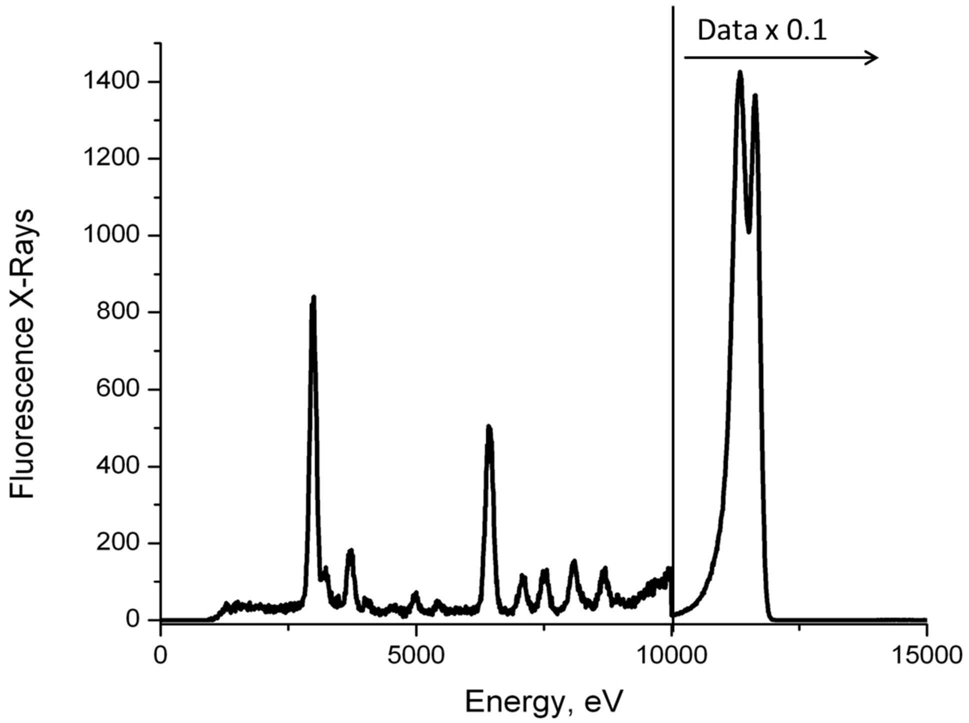

Figure S5. Fluorescence spectrum, collected at a beam energy of 11.8 keV, to identify metal impurities. The peaks at 2970 and 3200 eV are the K-alpha and K-beta fluorescence from Ar in air. The remaining peaks represent the following impurities: Ca, Ti, V, Fe, Co, Ni, Cu, and Zn.

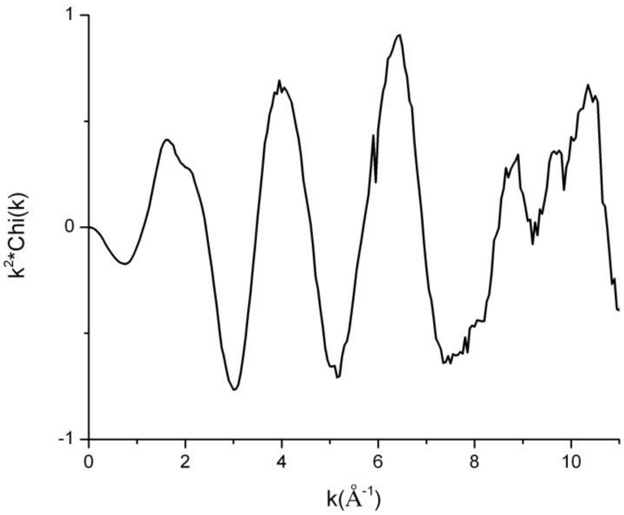

Figure S6. Example k-space spectrum of the 2.1 wt.% Cu/SSZ-13 catalyst under standard SCR gas conditions. EXAFS data was usually fit from k = 2.7 to ~11 Å^{-1}.

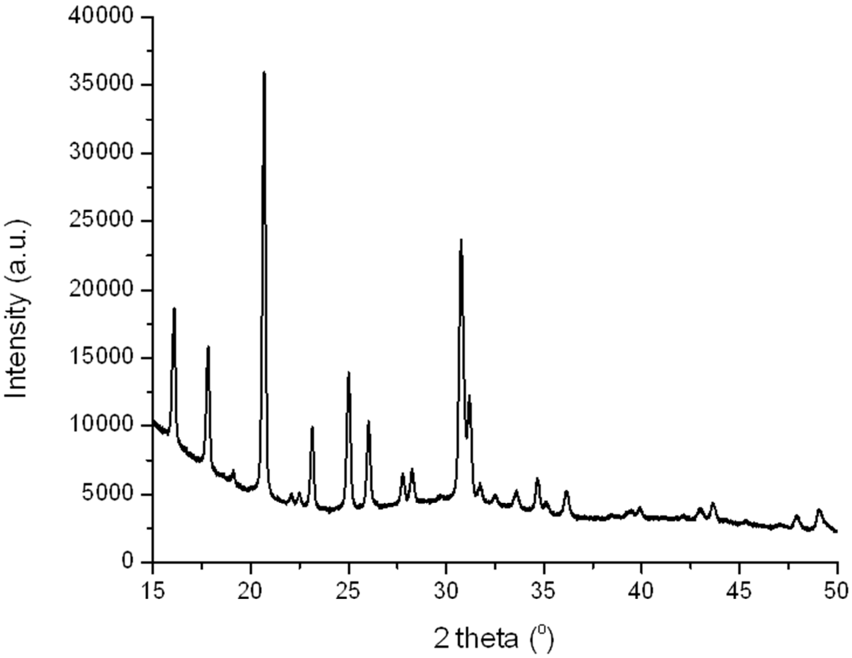

Figure S7. XRD of calcined SSZ-13 catalyst collected at a scan rate of 2deg min^{-1}.