

SUPPORTING INFORMATION

The Comparison of Copper and Acid Site Zeolites for the Production of Nitric Oxide for Biomedical Applications

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Zeolite Syntheses

Ferrierite: Water (25.8 g), sodium hydroxide (0.14 g, 3.5 mmol) and sodium aluminate (0.66 g, 8.0 mmol) were stirred together in a beaker until dissolved. In a separate beaker, Ludox AS-30 colloidal silica (9.29 g, 0.046 mol) and ethylenediamine (3.66 g, 0.061 mol) were mixed. The two solutions were combined in a 50 mL autoclave providing a molar composition of $1.85 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 15.2 \text{ SiO}_2 : 592 \text{ H}_2\text{O} : 19.7$ ethylenediamine. The gel was placed in the oven at 175 °C for 10 days. The resulting crystals were recovered by vacuum filtration, washed with water and allowed to dry.

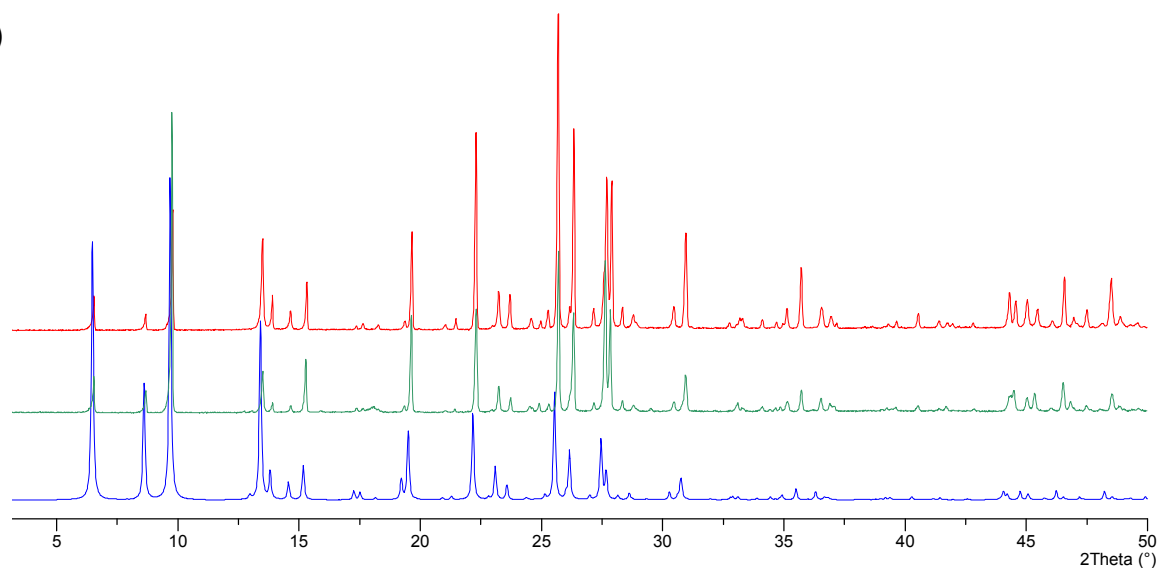
Mordenite (acid sites): Water (6.6 g), sodium hydroxide (0.76 g, 0.019 mol) and sodium aluminate (0.37 g, 4.5 mmol) were stirred in a teflon liner until dissolved. Water (20.5 g) was added and stirred followed by the addition of silica solution (3.93 g). The silica solution was prepared with fumed silica (3.62 g, 0.060 mol) and water (0.31 g). The resulting molar composition was $6 \text{ Na}_2\text{O} : 30 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 780 \text{ H}_2\text{O}$. A small sample of mordenite (0.25 g) was added as a seed to encourage the crystallisation of the synthesis gel. The autoclave was placed into the oven at 175 °C for 2 days.

Mordenite (copper sites): Water (23.17 g), sodium hydroxide (2.66 g, 0.067 mol) and aluminium nitrate (4.16 g, 0.011 mol) were stirred in the autoclave teflon liner until dissolved. Ludox AS-30 colloidal silica (16.67 g, 0.278 mol) was added to the teflon with high speed stirring to ensure complete mixing. The molar composition of the resulting gel was $12 \text{ Na}_2\text{O} : 100 \text{ SiO}_2 : 2 \text{ Al}_2\text{O}_3 : 500 \text{ H}_2\text{O}$. The mixture was aged at room temperature for 20 hours before being placed in the oven at 175 °C for 5 days.

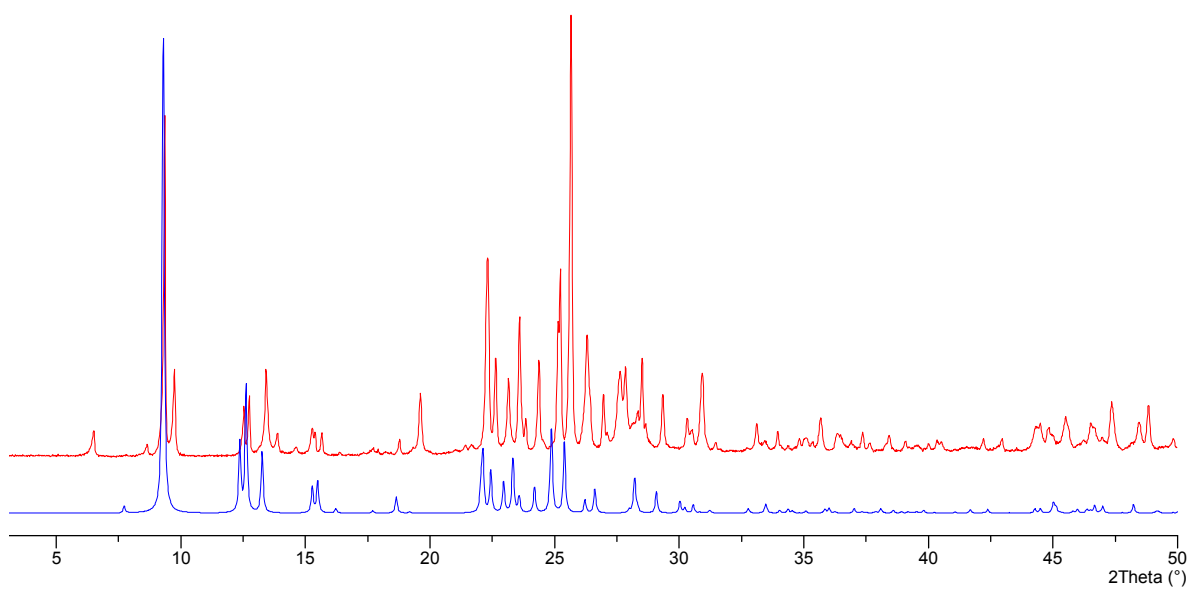
Powder X-Ray Diffraction Patterns

Figure S1: Calculated (blue) and experimental (red, green) PXRD patterns for (a) mordenite, (b) ferrierite, (c) ZSM-5 and (d) SSZ-13. Ferrierite (b) purity confirmed by comparison with data from “Verified Syntheses of Zeolitic Materials 2001”.¹

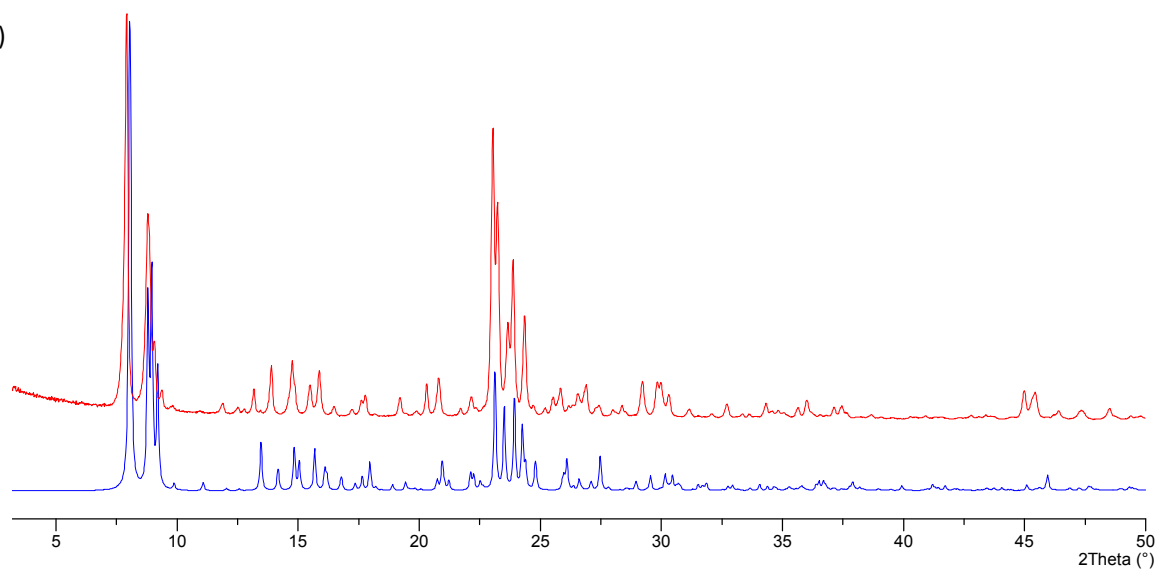
a)



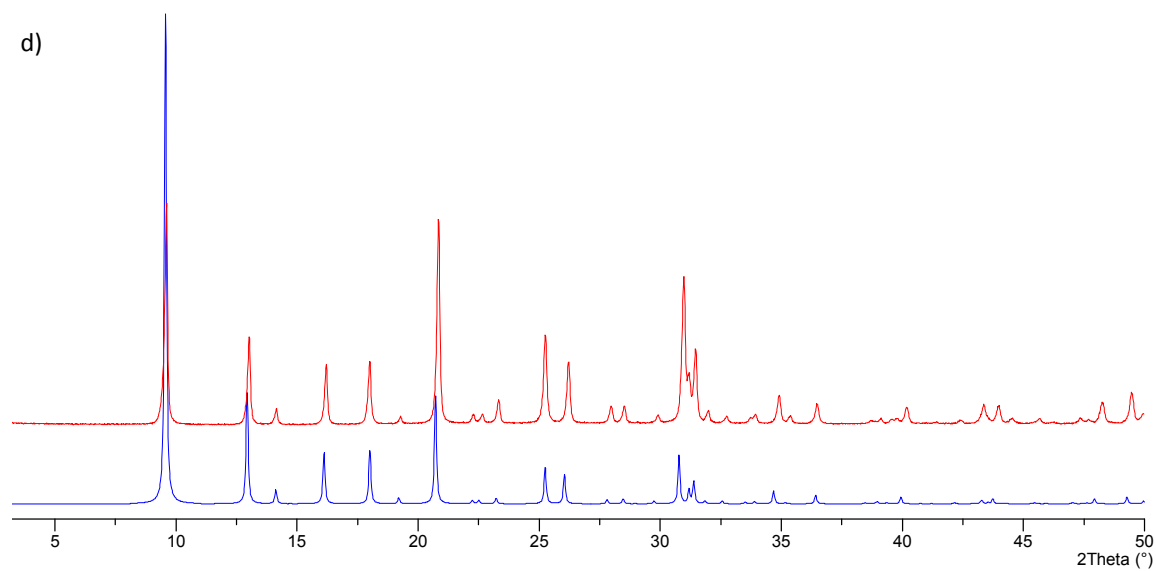
b)



c)

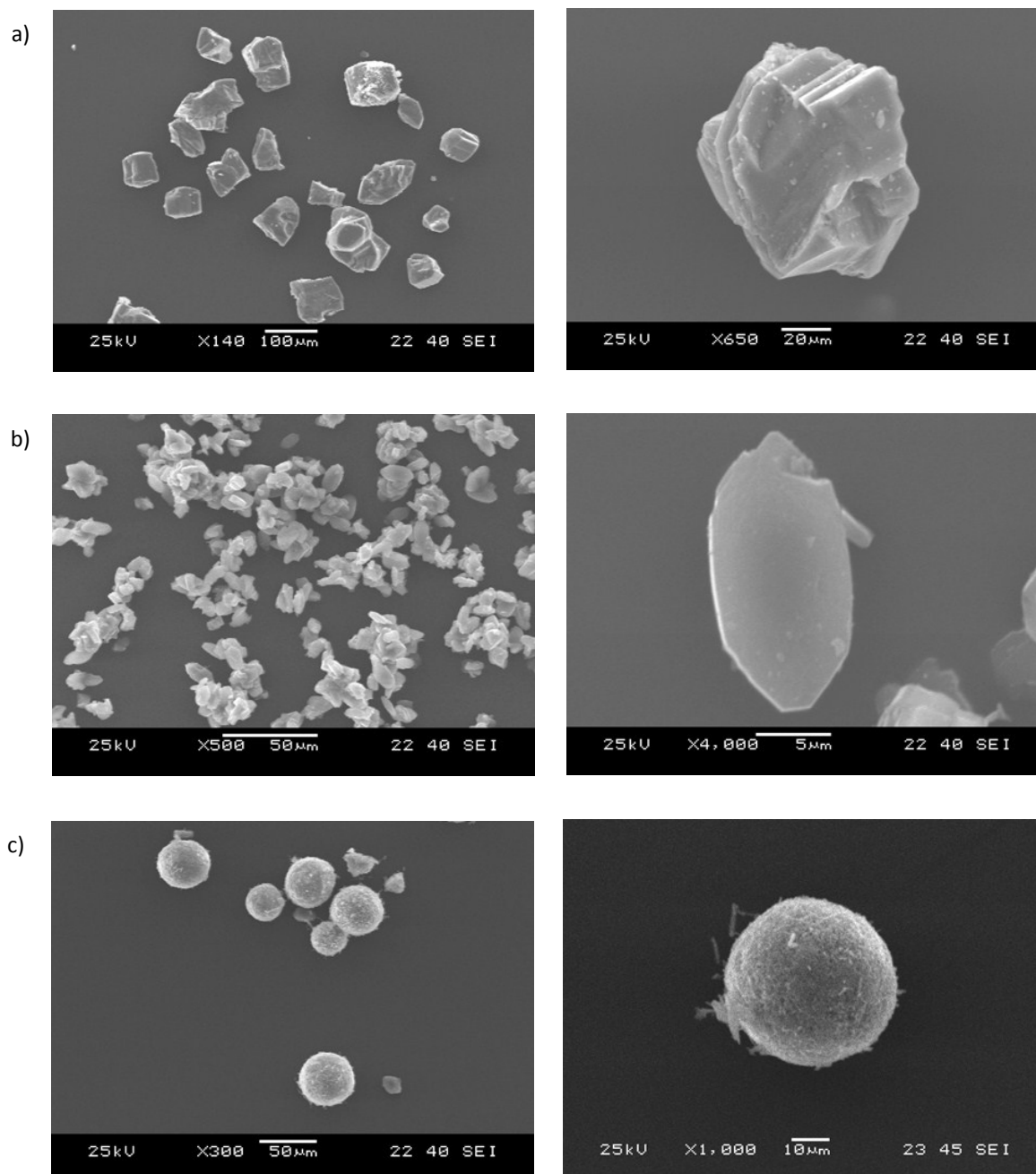


d)



Scanning Electron Microscopy Images

Figure S2: SEM images of starting material for (a) mordenite for Cu-MOR, (b) mordenite for H-MOR and (c) ferrierite



Energy Dispersive X-Ray Spectroscopy (EDX) Data

The calculated EDX data for the copper zeolites after copper ion exchange are shown below. The minor difference in Si/Al ratio in comparison to the values stated in the paper can be attributed to small variations in composition of different crystals. The values however still lie within the degree of error.

Table S1: The composition of Cu-MOR.				
Atom	Silicon %	Aluminium %	Oxygen %	Copper %
Average	22.76	3.63	71.71	1.90
Standard Deviation	± 4.11	± 0.66	± 5.23	± 0.64

Table S2: The composition of Cu-FER.				
Atom	Silicon %	Aluminium %	Oxygen %	Copper %
Average	19.59	2.89	76.05	1.47
Standard Deviation	± 1.40	± 0.33	± 1.66	± 0.56

Table S3: The composition of Cu-SSZ-13.				
Atom	Silicon %	Aluminium %	Oxygen %	Copper %
Average	24.54	1.52	73.24	0.70
Standard Deviation	± 1.68	± 0.12	± 1.89	± 0.13

Table S4: The composition of Cu-ZSM-5.				
Atom	Silicon %	Aluminium %	Oxygen %	Copper %
Average	19.72	1.39	78.10	0.80
Standard Deviation	± 1.47	± 0.14	± 1.55	± 0.19

Full Protocol of Copper Cytotoxicity Testing

The cytotoxicity activity of zeolites was investigated using CellTiter 96® Aqueous Non-Radioactive Cell Proliferation Assay (Promega, UK). The day before the experiment, the cells were seeded in to a 96 well-plate at a density of 5×10^3 cells per well. Prior to the treatments, the cells were washed twice with PBS (phosphate-buffered saline). The different zeolites concentrations were dispersed in complete medium, then 100 µL were added to each well and incubated for 24 h at 37 °C with 5% CO₂. To measure the toxicity, the cells were washed extensively to remove the solids, the medium was replaced with 100 µl of fresh complete growth medium and 20 µl of MTS/PMS (in a proportion 20:1) solution and the plate was incubated for 1 h and 15 min at 37 °C with 5% CO₂. The plates were then read by UV/Vis spectroscopy (Spectro Star^{Nano}, BMG Labtech) at 490 nm.

Complete media: Dulbecco's modified Eagle's Medium (DMEM, with phenol red) supplemented with 10% (v/v) Fetal Bovine Serum (FBS), 2 mM L-glutamine, 100 units/mL penicillin and 100 µg/mL streptomycin.

References

1. H. Robson, *Verified Syntheses of Zeolitic Materials*, 2001, 168.