

Verification of hierarchical porosity in CuSAPO-34 by *in situ* XAS, N₂ adsorption measurements and NOx removal

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Removal of NOx from combustion processes made headlines in 2015 following the so-called “diesel-gate”, showing that new development and research concerning deNOx technology is still highly topical¹. Copper containing, microporous SAPO-34 has shown great activity concerning selective reduction of NOx (NH₃-SCR and HC-SCR) and may be thought of as a new possible catalyst for NOx removal from internal combustion engines²⁻⁶. These catalysts are known to suffer from instability concerning copper addition and deactivation due to coking. The goal of this project is to solve these challenges by introducing mesopores to create so-called hierarchical CuSAPO-34 to relieve the mass transfer issues.

Different structure directing agents have been used to obtain hierarchical CuSAPO-34 and comparisons have been made with the conventional microporous analogue. *In-situ* XAS data has been recorded at the Swiss-Norwegian Beam Lines (SNBL, BM 31) at the ESRF in Grenoble, France in order to obtain information about the reducibility and size of copper clusters in the samples. Multivariate curve resolution (MCR) analysis has been utilised to obtain reduction profiles of copper. Results from *in situ* XAS analysis have been correlated with BET surface area and BJH pore size distribution measurements. In the presence of copper, the structure directing agent (SDA)-pair diethylamine (DEA) + tetraethylenepentamine (TEPA) yields a high degree of mesoporosity in CuSAPO-34, whereas the SDA-constellation morpholine (MOR) + TEPA + cetyltrimethylammonium hydroxide (CTAOH) yields mostly micropores. The pore distribution show a large number of mesopores ranging from 30 – 200 Å in the former, correlating with 100 m²/g external/meso area from the t-plot, not present in the sample made with CTAOH. The introduction of mesopores greatly affects the reducibility of copper during temperature programmed reduction (TPR) by H₂ (75%), as copper is completely reduced at 490°C in the sample containing mesopores, but 20% Cu^I-O remains in the microporous sample, even at 700°C. The introduction of mesopores is again reflected in the obtained copper particle sizes from EXAFS analysis, as the mesoporous CuSAPO-34 hosts clusters of 14 Å (N_{Cu-Cu} = 8) whereas they are found to be 9 Å (N_{Cu-Cu} = 6) in the sample with mainly micropores (the method of corrected multiplicities were employed for the latter sample).

Employing HC-SCR deNOx as a model reaction, the introduction of mesopores greatly improves the NOx conversion over the whole temperature range (275- 500°C), but especially in the low temperature range (<375°C). Whereas the hierarchical CuSAPO-34 made with DEA-TEPA becomes active at 325°C reaching maximum conversion of 67% at 400°C, the microporous

becomes active at 375°C and reaches maximum conversion of 52% at 450°C. Clearly, altering the porosity of CuSAPO-34 has great impact on chemical and catalytic behaviour of the zeotype.

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