

Structure-performance relationships of Cu based porous catalysts for selective catalytic reduction (SCR) of NO_x gases from diesel exhausts

The aim of this project is to obtain a fundamental understanding of Ammonia-Selective Catalytic Reduction (NH₃-SCR) systems commonly used for emission abatement in heavy duty diesel vehicles. An important aspect of the work involves synthesis of various copper exchanged zeolites using different preparation techniques. The catalysts are pre-characterized using conventional laboratory techniques such as UV-Vis spectroscopy and X-ray diffraction. The materials are further tested for their catalytic activity using an in-house built catalytic rig under plug-flow conditions. The output gasses are analysed online using infra-red spectroscopy and a Hiden Analytical, HPR-20 QIC bench top gas analysis system. Fast and continuous monitoring of the output gasses allows for the determination of activity/selectivity profiles of catalysts in question.

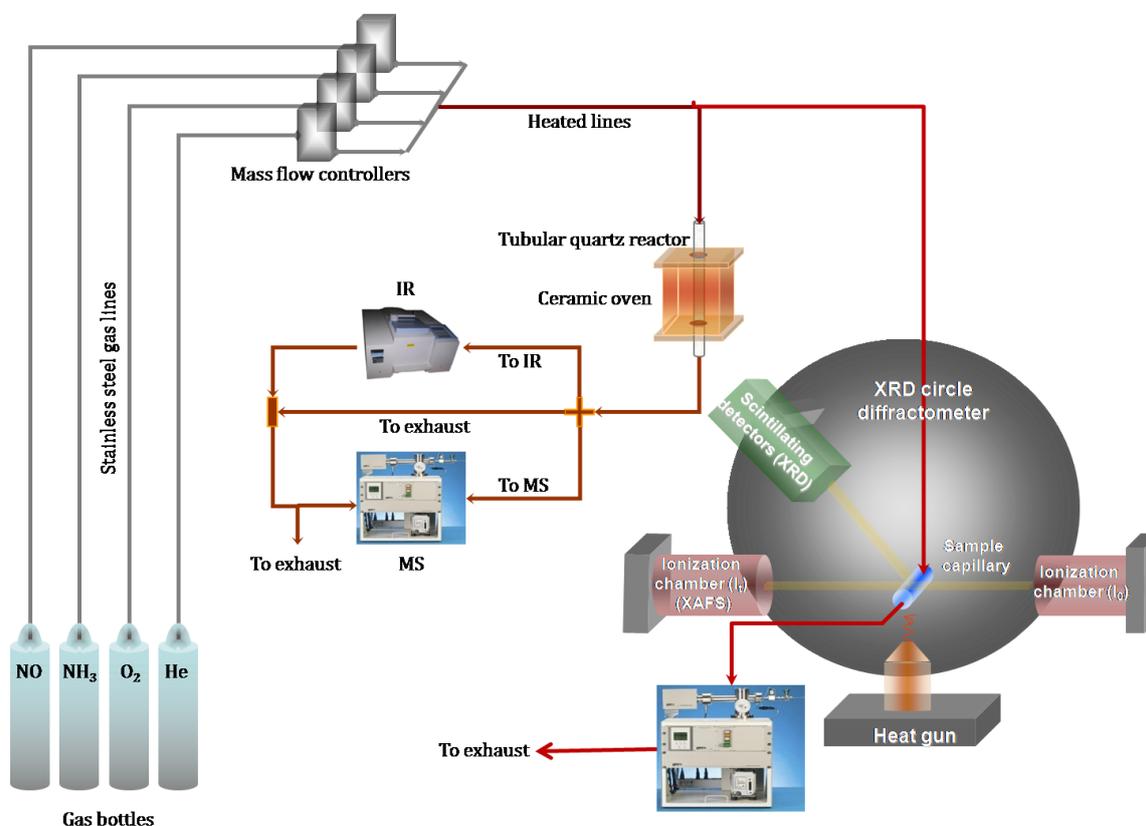


Figure 1: Simplified schematic illustration of the in-house built catalytic rig used to mimic exhaust conditions and perform selective catalytic reduction of NO in the presence of NH₃. All gas lines used were stainless steel grade. All (red colored) lines between the MFCs and analysis instruments (via the reactor) were heated using electrical heat tracing and insulated using quartz wool bands. The electronics, including controls for the MFC units, heating for the gas lines and oven are excluded for clarity. The whole setup can be interfaced into one computer using commercially available lab-view software for automation of the running process. The analytical instruments can work as stand-alone (as in this case) for ease of individual software use, or can be interfaced together with the rest of the setup. Towards the right bottom is an extended illustration of the use of a similar setup at synchrotron beamlines for performing in situ/operando type experiments. Samples can be placed in a capillary (to mimic plug-flow conditions), and connected to a MS at the end for online product analysis. X-ray absorption/X-ray diffraction data can be collected in sequence as a function of reaction conditions.

The catalysts are further analysed using synchrotron light sources under in situ NH₃-SCR reaction conditions. Catalysts are loaded into quartz capillaries connected to a pre-set gas rig. The output gasses are continuously monitored using mass spectrometry to obtain accurate information on the conversion profiles. The pre-determined positions of cations within zeolites

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make it possible to combine both long and short range probing techniques to yield information on the structure and co-ordination of the active sites. To that end, combined X-ray absorption and X-ray diffraction data are collected at different temperatures under SCR conditions which help elucidate the local Cu environment in these catalysts.

In this particular case-study, an attempt was made at tailoring the active sites in Cu-CHA based catalysts. Three different synthetic routes were adapted to achieve this goal: two methods are based on post-synthetic treatment of the zeolite material (via aqueous or vapour phase) and a third one involving the direct synthesis of a Cu-loaded SAPO-34. Product analysis under SCR conditions revealed that whilst the catalyst materials prepared via wet chemical routes show excellent deNO_x activity and high selectivity to N₂, the one prepared via chemical vapour deposition gave the undesired product N₂O in significant quantities. Isolated mononuclear Cu²⁺ ions in the vicinity of six-membered rings (*6mrs*, part of the *d6r* sub-units of CHA) were found to be active sites in both catalyst materials prepared via the wet chemical approaches. In contrast, the catalyst prepared via chemical vapour deposition possesses Cu in two different environments: isolated Cu²⁺ cations and CuAlO₂-type species. Catalytic experiments revealed a strong correlation between the number of isolated mononuclear Cu²⁺ in or near the plane of the *6m* rings and N₂ production, whereas the presence of CuAlO₂ species appears to promote the formation of undesired N₂O.

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