

## ABSTRACT

The Selective Catalytic Reduction of nitrogen oxides (SCR-NO<sub>x</sub>) is nowadays a very relevant process for reducing NO<sub>x</sub> emissions in diesel vehicles, which must comply with increasingly restrictive European regulations. In this thesis the reaction mechanism and active centers in Cu-zeolite catalysts with different structures has been investigated. For his purpose two *in situ* spectroscopic techniques were mainly used, being Nuclear Magnetic Resonance NMR and Electron Paramagnetic Resonance EPR, which allowed the detection of reaction intermediates and identification of Cu active species.

In particular we have studied the SCR-NO<sub>x</sub> reaction using NH<sub>3</sub> as the reducing agent and Cu-zeolites catalysts with the chabazite structure. The preliminary study of the interaction of the catalysts with NH<sub>3</sub> has shown the formation of several Cu-NH<sub>3</sub> complexes with different stability. At SCR typical reaction temperatures (~250 ° C), ammonia forms NH<sub>4</sub><sup>+</sup> ions in Brønsted acids centers of the zeolite and stable Cu<sup>+</sup>-(NH<sub>3</sub>) complexes, while Cu<sup>2+</sup> remains isolated at the 6R plane, which is precisely the active site. However, when studying species formed on Cu-zeolites in the presence of the reaction mixture NH<sub>3</sub>/NO/O<sub>2</sub>, it appears that NH<sub>4</sub><sup>+</sup> ions are consumed during reaction and the formation of various intermediates including nitrite/nitrate species that decompose at T ≥ 250 ° C to the reaction products (N<sub>2</sub> and H<sub>2</sub>O).

We also investigated the mechanism of the SCR-NO<sub>x</sub> reaction using C<sub>3</sub>H<sub>8</sub> as the reducing agent and Cu-zeolites of different topology with medium and large pore systems. The results show the formation of a hydrocarbon activated species in the Cu<sup>2+</sup> which is related to the catalytic activity. Furthermore, isolated Cu<sup>2+</sup> is an active site that is reduced to Cu<sup>+</sup> during reaction, and then re-oxidized to Cu<sup>2+</sup> in the presence of O<sub>2</sub>.

Finally, the hydrothermal stability of Cu-zeolites has been studied, since it is a prerequisite for its application as SCR catalysts, comparing the very hydrothermally stable Cu-SSZ-13 zeolite and the Cu-ZSM-5 which is completely disabled after hydrothermal treatment. The findings suggest the origin of the deactivation to be a change in the coordination of isolated Cu<sup>2+</sup> in the Cu-ZSM-5 type to form CuAlO<sub>x</sub> species which are inactive in the SCR-NO<sub>x</sub> reaction.