

## Aspects of Propane, Isopropylamine and NH<sub>3</sub> as Reducing Agent for NO<sub>x</sub> over H-ZSM-5 in oxygen excess

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### Introduction

Combustion in excess oxygen, as in diesel- and lean-burn engines, significantly improves the fuel economy, *i.e.* reducing the CO<sub>2</sub> emissions. However, the lean environment in the exhaust gas obstructs the NO<sub>x</sub> reduction ability of the three-way catalyst, thus emphasizing the need for alternative techniques, where one promising is selective catalytic reduction with hydrocarbons (HC-SCR). A vast amount of research has been devoted to the mechanisms of this concept. For zeolite materials, three main reaction pathways have been suggested and debated in the literature [1,2]. That is catalytic decomposition of NO to nitrogen, oxidation of NO to NO<sub>2</sub>, and partial oxidation of the hydrocarbon forming oxygen- and/or nitrogen-containing intermediate species.

In previous studies we discuss the reaction pathway for the lean NO [3] and NO<sub>2</sub> [4-6] reduction by propane over H-ZSM-5. The mechanism involves formation of NO<sup>+</sup> species and activation of the hydrocarbon, likely through interaction with the Brønsted acid sites, forming carbenium ion adsorbates and alkenes. These two types of species are then proposed to react and form isocyanate species, which may be hydrolyzed to amine species that further react forming N<sub>2</sub>. In this work the reaction mechanism for propane-SCR over H-ZSM-5 is studied for NO and NO<sub>2</sub> as NO<sub>x</sub> source and the results are discussed in relation to isopropylamine and ammonia as reducing agents. In particular the role of possible reaction intermediates, *e.g.* formation of amine species, will be highlighted for the different systems.

### Materials and Methods

The catalyst used in this study was H-ZSM-5 (Akzo Nobel Catalysts BV) with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 40. Textural data, acidic characterization and preparation of the sample have been reported previously [5]. *In-situ* DRIFT (diffuse reflection infrared fourier transform) spectroscopy measurements were carried out using a BioRad FTS 6000 spectrometer. The powder sample was exposed to 1000 ppm NO<sub>x</sub> (as NO, NO<sub>2</sub> or 50:50 NO:NO<sub>2</sub>), 1000 ppm NH<sub>3</sub>, 1500 ppm propane, isopropylamine and 10% O<sub>2</sub> (Ar bal.). The evolution of surface species during transient experiments at 450°C was followed by DRIFTS (2 scans/min at a resolution of 1 cm<sup>-1</sup>).

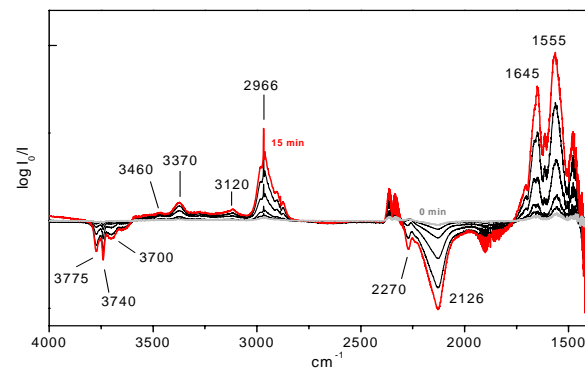
### Results and Discussion

The reactants are most likely adsorbed surface species for which the functional group (isocyanate, amine *etc.*) is the key in the reaction. The exact nature of the adsorbed molecule is less certain and most probably also of minor importance for the overall reaction

pathway. However, the same type of NH species, likely organic amines, is formed for either propane or isopropylamine as reducing agent for NO. On the contrary, for NH<sub>3</sub> as reductant, NH<sub>4</sub><sup>+</sup> is the dominating NH surface species during reaction. The difference in where these groups are formed, *i.e.* on different acidic sites, strongly suggests that they are different. Furthermore, the choice of NO<sub>x</sub>-source is crucial for the reaction. Using NO<sub>2</sub>, the reaction likely proceeds fast via direct reduction of NO<sub>2</sub> to N<sub>2</sub>, while for NO, oxidation to NO<sub>2</sub> is probably required before reduction takes place. In either case NH species play a vital role in the SCR reaction and organic amines are likely key-intermediates in the SCR with saturated hydrocarbons over H-ZSM-5.

### Significance

An increased and detailed understanding of catalytic key-processes is essential in development of new and efficient techniques for emission control systems.



**Figure 1.** Evolution of surface species adsorbed on H-ZSM-5 40 zeolite in presence of 10% O<sub>2</sub> and 1500 ppm propane in Ar, after removal of NO from the feed. Complete reaction conditions are used as background.

### References

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