

# TRANSITION METAL OXIDES SUPPORTED ON ACTIVE CARBONS AS CATALYSTS FOR THE SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE WITH AMMONIA

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## Introduction

Nitrogen oxides from stationary combustion facilities such as power plants contribute a considerable part of total NO<sub>x</sub> emitted to the atmosphere. The emission standards are already quite strict and they will be stricter in future. Therefore, the selective catalytic reduction of NO<sub>x</sub> using ammonia as reducing agent forming environmentally nonpoisonous reaction products (N<sub>2</sub> and H<sub>2</sub>O) was extensively studied within the recent 20 years. It has become a technologically important process for NO<sub>x</sub>-removal. Industrially, the SCR-process uses V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalysts and there are many publications on that topic dealing with kinetic investigations as well (e.g. 1-5). Additionally, many different catalysts like noble metals, other transition metal oxides than V<sub>2</sub>O<sub>5</sub>, zeolites and pillared clays have been tested in this reaction (6).

There exist, however, many applications for which lower reaction temperatures and possibly cheaper catalysts would be preferable, e.g. the removal of nitric oxide after desulfuration. Transition metal oxides supported on active carbons are a cheaper alternative working at lower temperatures than the available catalysts (7).

In order to develop more efficient low temperature catalysts for SCR the catalytic behavior of several transition metal oxide loaded active carbons with varying ash contents was investigated in absence and presence of O<sub>2</sub>.

## Experimental

Active carbons with different ash contents (0.2 - 7.1%) were activated either by heating in concentrated nitric acid at 90°C for 1h (designated A90) or by exposing to a stream of air at 400°C for 2h (A400). The activation in air was performed in situ. The catalysts were loaded with Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and CuO by impregnation with solutions of the corresponding nitrates and their subsequent decomposition in a stream of helium at 350°C for 2h. The SCR-reaction was performed in a microcatalytic fixed bed reactor in the temperature range from 100 - 500°C for experiments in absence of oxygen and from 100 - 340°C during reactions using an excess of oxygen. The reactor effluent was analyzed gaschromatographically by a Shimadzu GC equipped with a TCD. For separation of the

reaction products (N<sub>2</sub> + O<sub>2</sub>), CO<sub>2</sub> and N<sub>2</sub>O and for unreacted NO two packed columns of Porapak Q and Porapak R were used in combination. O<sub>2</sub> and N<sub>2</sub> were separated with a molecular sieve 5A column. Data acquisition and experiments were run using a computer aided process control. In order to avoid ammonia slip stoichiometric ratios of NO/NH<sub>3</sub> were used in absence as well as in presence of O<sub>2</sub>. The space velocity was about 7000h<sup>-1</sup>.

The characterization of the catalysts comprised the determination of the above mentioned different ash contents and their chemical compositions, the investigation of textural properties and the study of oxygen containing groups on the surface of the catalysts. These groups were investigated by TPD-experiments and acidity measurements. Additionally, XPS-, EPR- and SEM-investigations were performed.

## Results and Discussion

The catalytic measurements were not influenced by transport limitation phenomena. The pretreatment of active carbons with concentrated nitric acid resulted in a higher catalytic activity in SCR than the pretreatment by oxidation in air. In absence of O<sub>2</sub> in the reaction mixture no effect of the ash content of the active carbons (from 0.2 to 7.1%) on the catalytic activity was observed below 300°C. However, in presence of oxygen an increasing ash content resulted in increasing activities. Transition metal oxide loaded supports were more active in SCR than their unloaded equivalents, especially in absence of oxygen. An increase in transition metal content from 1 to 10 wt.-% improved the catalytic activity as well. Fig. 1 illustrates this catalytic behavior.

During measurements in absence of oxygen the selectivity towards N<sub>2</sub> the main product of the SCR-reaction was significantly lowered in the same temperature range in which NO-conversion was drastically enhanced (200-300°C). Simultaneously, the selectivity towards N<sub>2</sub>O ran through a maximum indicating according to literature (8) that N<sub>2</sub>O was a reaction intermediate of the SCR-process on Fe containing active carbons in absence of oxygen.

The presence of oxygen in the reaction mixture enhanced the conversion of nitric oxide especially in the low-temperature-range between 100 and 200°C. Activity

and selectivity of the respective catalysts were influenced by the type of metal oxide: In presence of oxygen catalysts with 10 wt.-% Fe were the most active and selective ones as shown in Fig. 2 (800 ppm N<sub>2</sub> represent 100% conversion of NO to N<sub>2</sub>). The decreasing N<sub>2</sub> formation of the Cr containing support with increasing temperature was due to the simultaneous formation of N<sub>2</sub>O which was in contrast to the measurements in absence of O<sub>2</sub> not formed as a reaction intermediate but as an undesired side product.

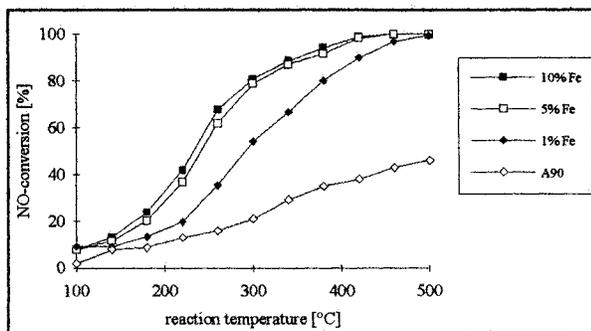


Fig. 1 NO-conversion of unloaded active carbon A90 and of support A90 loaded with 1, 5 and 10 wt.-% Fe

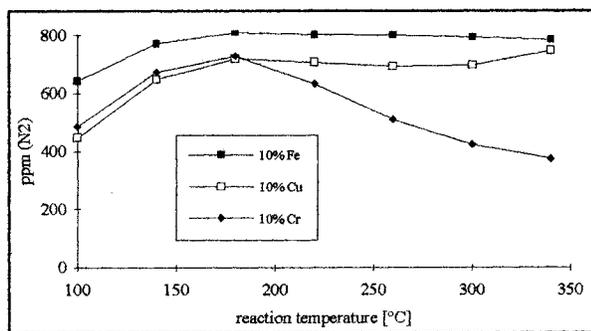


Fig. 2 N<sub>2</sub>-formation of active carbon A90 loaded with 10 wt.-% Fe, Cu and Cr as a function of reaction temperature

Kinetic measurements in absence and presence of oxygen revealed completely different reaction orders for NO. In absence of oxygen the effective reaction rate was lowered with increasing partial pressure of NO whereas in presence of oxygen the influence of NO was strongly positive. However, further investigations will be necessary to understand the mechanism completely, especially with respect to the role of oxygen.

Fig. 3 shows CO<sub>2</sub>-TPD-profiles of active carbon supports A, A90 and A90 loaded with 10 wt.-% Fe. All catalysts revealed CO<sub>2</sub>-formation at temperatures above 100°C which can be explained by the burn-off of the active carbon support and by the desorption of CO<sub>2</sub> from oxygen containing surface groups such as e.g. carboxylic groups, aldehydes or anhydrides. The latter was much stronger after pretreatment with nitric acid showing several single peaks and shoulders which indicate a more

heterogeneous structure of the surface. Such a surface is assumed to improve the dispersion of the transition metal oxide deposited and the catalytic activity itself. After deposition of Fe<sub>2</sub>O<sub>3</sub> a sharp desorption signal at 690°C arised. According to literature (9) it can be put down to the reduction of Fe oxid with Fe<sup>3+</sup> to Fe oxid with Fe<sup>2+</sup> or even to elementary Fe. The strong desorption maxima at lower temperatures observed in the case of A90 disappeared. This is due to an extensive coverage of the carbon surface with Fe-Oxid which was observed with scanning electron microscopy as well.

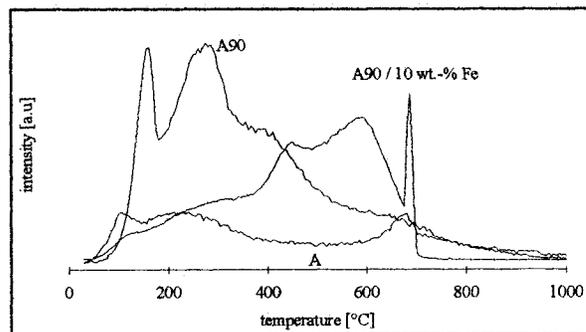


Fig. 3 CO<sub>2</sub>-desorption profiles of active carbon supports A, A90 and A90 loaded with 10 wt.-% Fe, Cr and Cu

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