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Selective catalytic reduction of NO_x with NH_3 over Cu-ZSM-5—The effect of changing the gas composition

Hanna Sjövall [a,b,*], Louise Olsson [a,b], Erik Fridell [b], Richard J. Blint [c]

[a] Chemical Reaction Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[b] Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
[c] General Motors R&D Center, Chemical and Environmental Sciences Laboratory, 30500 Mound Road, Warren, MI 48090-9055, United States

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Abstract

The selective catalytic reduction of nitrogen oxides (NO_x) with ammonia over ZSM-5 catalysts was studied with and without water vapor. The activity of H-, Na- and Cu-ZSM-5 was compared and the result showed that the activity was greatly enhanced by the introduction of copper ions. A comparison between Cu-ZSM-5 of different silica to alumina ratios was also performed. The highest NO conversion was observed over the sample with the lowest silica to alumina ratio and the highest copper content. Further studies were performed with the Cu-ZSM-5-27 (silica/alumina = 27) sample to investigate the effect of changes in the feed gas. Oxygen improves the activity at temperatures below 250 °C, but at higher temperatures O_2 decreases the activity. The presence of water enhances the NO reduction, especially at high temperature. It is important to use about equal amounts of nitrogen oxides and ammonia at 175 °C to avoid ammonia slip and a blocking effect, but also to have high enough concentration to reduce the NO_x. At high temperature higher NH_3 concentrations result in additional NO_x reduction since more NH_3 becomes available for the NO reduction. At these higher temperatures ammonia oxidation increases so that there is no ammonia slip. Exposing the catalyst to equimolecular amounts of NO and NO_2 increases the conversion of NO_x, but causes an increased formation of N_2O.

Keywords: Ammonia; Ammonia oxidation; Cu-ZSM-5; Nitrogen oxide; NO reduction; Selective catalytic reduction (SCR); Water; Zeolite

1. Introduction

One major source of nitrogen oxides (NO_x) is the combustion of fossil fuel. Nitrogen oxides may cause formation of ground-level ozone, production of acid rain and respiratory problems to mankind [1]. Oxides of nitrogen are difficult to reduce in the presence of excess oxygen that occurs in diesel exhaust. There is currently a need for a solution for NO_x abatement in light duty diesel engines. One possible approach for reduction of NO_x to N_2 is selective catalytic reduction (SCR) with urea or ammonia. The use of NH_3-SCR has been investigated for several years and is today a well established technique for DeNO$_x$ in stationary applications [2].

The catalysts studied in the literature for this reaction can be divided in three groups that are active at different temperatures [3]. Noble metals, like platinum, were first considered for the SCR of NO_x. They are active in the selective reduction of NO_x at low temperatures, but the selectivity is poor at higher temperatures [1]. The second type of catalysts is metal oxides. Among the various investigated metal oxide mixtures, those based on vanadia supported on titania are commonly used. The catalyst is active at 350–450 °C, at higher temperatures the catalyst loses selectivity due to enhanced oxidation of ammonia [4]. For application in a wider temperature range, zeolite based catalysts have been developed, which are active at high temperatures, to a maximum of about 600 °C [5]. Among these, copper exchanged zeolites such as Cu-ZSM-5 have been widely studied for SCR with ammonia and also for applications such as NO decomposition and selective catalytic reduction by hydrocarbons [6–9].

NO_x in the exhaust gas from a diesel engine is usually composed of more than 90% NO. The overall SCR reaction with ammonia is usually assumed to involve stoichiometric amounts of NO and NH_3 in presence of oxygen to produce nitrogen and water [10]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

* Corresponding author. Tel.: +46 31 7723028; fax: +46 31 7723035.
E-mail address: hanna.sjovall@chalmers.se (H. Sjövall).

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The overall reaction of a mixture composed of equimolecular amounts of NO and NO_2 may also be important, since it is suggested to occur much faster than the main reaction [2]:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (2)$$

At high temperatures the oxidation of ammonia may lead to formation of additional NO over the catalyst [11]:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (3)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (4)$$

Other reactions may be taking place over the catalyst that could result in the reduction of NO_2 without concurrent NO reduction. In addition, formation of other products such as nitrous oxide and ammonium nitrate may be occurring.

The importance of the different reactions above varies with both gas composition and temperature. Due to the transient conditions in vehicle application it is important to investigate the SCR activity at several settings to reach a high average NO_x conversion and to avoid ammonia slip. There are several studies that investigate zeolites such as Cu-ZSM-5 and their catalytic behavior in ammonia SCR [11–17]. However, neither of them investigates changes in the feed composition in order to evaluate the possible reactions that occur over coated monoliths. In this study, Cu-ZSM-5 coated catalysts of three different silica/alumina ratios have been evaluated. The catalyst that produced the highest conversion has been studied further. The aim is to investigate the catalytic activity at various concentrations of oxygen, ammonia, nitrogen oxides and water to provide knowledge about the different reactions that occur at the surface of a Cu-ZSM-5 catalyst.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared from zeolite powder of three different SiO_2/Al_2O_3 ratios obtained from Alsi-Penta. The starting material for the zeolites with SiO_2/Al_2O_3 ratios of 27 and 55 was H-ZSM-5 and the starting material for the zeolite with ratio 300 was Na-ZSM-5. Five different catalysts, H-ZSM-5-27, Na-ZSM-5-27, Cu-ZSM-5-27, Cu-ZSM-5-55 and Cu-ZSM-5-300, were prepared according to the method described below.

To ion exchange the H-ZSM-5 powder, a 108 mM $NaNO_3$ solution was stirred for 30 min and the pH was adjusted by adding NH_3. The zeolite was then added. This ion exchange was performed twice. The total amount of Na^+ in the slurries was two times the number of aluminum in the zeolite. The Na-ZSM-5 was placed in an oven and dried for 1 h at 80 °C, followed by a second drying at 125 °C for 30 min. The copper was introduced into the zeolite by exchange in an 11 mM $Cu(CH_3COO)_2$ solution at ambient temperature and the pH was adjusted with ammonia. The slurry was stirred for 14 h, followed by a second (8 h) exchange and then a third (14 h) exchange. The total amount of Cu^{2+} in the slurries was one and a half times the number of aluminum in the zeolite. After the last exchange, the powder was filtered and washed with 1 l distilled water. The Cu-ZSM-5 was placed in an oven and dried for 1 h at 80 °C, followed by a second drying at 125 °C for 5 h. For detailed information of the different catalysts, see Tables 1A and 1B.

The zeolite powder was washcoated on monoliths. The respective slurry was composed of a liquid phase of equal amounts of distilled water and ethanol and a solid phase of

Table 1A
Information about the ion exchange from H^+ to Na^+. The volume of $NaNO_3$ solution used in the ion exchange was determined from the number of Al present in the zeolite. The ion exchange was performed twice

SiO_2/Al_2O_3	Zeolite weight (g)	Volume, $NaNO_3$ solution (ml)	Concentration, $NaNO_3$ (mM)	Time (h)	pH
27	45.2	485	108	0.5	7.06
		485	108	0.5	6.90
55	31.6	170	108	0.5	7.10
		170	108	0.5	7.06

Table 1B
Information about the ion exchange from Na^+ to Cu^{2+}. The volume of $Cu(Ac)_2$ solution used in the ion exchange was determined from the number of Al present in the zeolite. The ion exchange was performed three times

SiO_2/Al_2O_3	Zeolite weight (g)	Volume, $Cu(Ac)_2$ solution (ml)	Concentration, $Cu(Ac)_2$ (mM)	Time (h)	pH
27	31.2	1643	11	14	5.64
		1643	11	8	5.75
		1643	11	14	5.73
55	23.2	618	11	14	5.80
		618	11	8	5.84
		618	11	14	5.85
300	31.1	151	11	14	5.80
		151	11	8	5.70
		151	11	14	5.80