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Sandro Brandenberger^a, Oliver Kröcher^a, Arno Tissler^b & Roderik Althoff^b

^a Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

^b Süd-Chemie AG, Bruckmühl, Germany

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The State of the Art in Selective Catalytic Reduction of NO_x by Ammonia Using Metal-Exchanged Zeolite Catalysts

Sandro Brandenberger,¹ Oliver Kröcher,¹ Arno Tissler,² and
Roderik Althoff²

¹Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

²Süd-Chemie AG, Bruckmühl, Germany

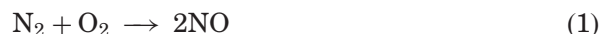
An overview is given of the selective catalytic reduction of NO_x by ammonia (NH₃-SCR) over metal-exchanged zeolites. The review gives a comprehensive overview of NH₃-SCR chemistry, including undesired side-reactions and aspects of the reaction mechanism over zeolites and the active sites involved. The review attempts to correlate catalyst activity and stability with the preparation method, the exchange metal, the exchange degree, and the zeolite topology. A comparison of Fe-ZSM-5 catalysts prepared by different methods and research groups shows that the preparation method is not a decisive factor in determining catalytic activity. It seems that decreased turnover frequency (TOF) is an oft-neglected effect of increasing Fe content, and this oversight may have led to the mistaken conclusion that certain production methods produce highly active catalysts. The available data indicate that both isolated and bridged iron species participate in the NH₃-SCR reaction over Fe-ZSM-5, with isolated species being the most active.

Keywords NH₃-SCR chemistry, Selective catalytic reduction of NO with ammonia, Metal-exchanged zeolites, Fe-ZSM-5, Active site, Hydrothermal aging, Preparation method, Exchange degree, Activity, Stability

Received 24 January 2008; accepted 25 March 2008.
Address correspondence to Oliver Kröcher, Paul Scherrer Institute, CH-5232 Villigen
PSI, Switzerland. E-mail: oliver.kroecher@psi.ch

INTRODUCTION

Nitrogen oxides (NO_x, x = 1, 2), which result from the combustion of fossil fuels, are a major source of air pollution (1, 2). Most of the NO_x (about 60% in Europe) is produced from combustion processes in engines (thermal NO_x) by the oxidation of atmospheric nitrogen at very high temperatures (1, 3):



NO_x formed by oxidation of organic nitrogen present in fuel is less significant nowadays, because the nitrogen content in gasoline and diesel has fallen significantly over the last 10 years. NO_x from diesel engines contributes about 75% of the total NO_x emissions of road traffic (3). Many efforts have been made to minimize NO_x emission either by combustion control or by post-combustion abatement technologies. While combustion control and engine management are adequate for compliance with current NO_x emission limits (4–6), legislation will become more stringent in the future, such that engine management alone will no longer be sufficient, and techniques to treat exhaust gas will become mandatory (4, 6).

Catalytic technologies are preferred for emission abatement because of their low costs and high efficiency (7). Although NO is thermodynamically unstable with respect to the decomposition to N₂ and O₂ (reverse of reaction 1), this reaction is kinetically very difficult to achieve, and to date no catalyst has been found that supports appreciable conversions under the conditions found in a vehicle (4, 8). Although NO_x from gasoline is very efficiently reduced by means of a three-way catalyst (8, 9), this technology cannot be applied in a diesel engine because it operates under oxygen excess. There exists, however, a very elegant reaction to remove nitrogen oxides from lean exhaust gases: the selective catalytic reduction with NH₃ to nitrogen (NH₃-SCR) (10). The special feature of this reaction is that a stoichiometric dosage of ammonia is sufficient for total NO_x conversion. The SCR process has been used for several decades to reduce NO_x emitted from stationary power plants (11, 12), and it has now matured enough to be applied to diesel vehicles as well (10, 13–15).

The abbreviation “SCR” is also widely used for the reduction of NO_x with hydrocarbons (HC-SCR) or hydrogen (H₂-SCR) (16, 17). This use of the label is misleading, however, since these reducing agents have to be applied in several-fold excess relative to the stoichiometry of underlying reaction equations, which should therefore not be called “selective.” Nevertheless, strenuous efforts have been made to develop these alternative NO_x reduction technologies, because the required reducing agents are either available as diesel fuel (HC-SCR) or may be easily produced from fuel by steam reforming (H₂-SCR). Another technology for the reduction of nitrogen oxides in lean exhaust gases is the NO_x storage and reduction (NSR) catalyst. It utilizes a

basic oxide (e.g., barium oxide), which stores NO_x in the form of nitrates during the normal, lean operation mode of the engine (18). For a short period, the exhaust is made rich, thereby allowing the desorption and reduction of NO_x with CO and hydrocarbons. In stationary SCR applications, ammonia is usually used as the reducing agent.

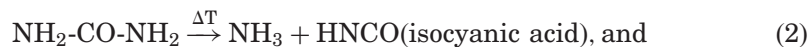
One of the first articles describing an SCR system to be applied in a vehicle was published by Held et al. (19), who suggested using non-toxic urea as the reducing agent, from which ammonia could be released under hydrothermal conditions. Urea-SCR is a rather complex technology due to the difficulties of using the right amount of urea as a function of constant changes in NO_x emissions, catalyst activity, and ammonia stored on the catalyst (6, 20). The process has been improved step by step in the last decade (13, 21, 22), and reduction efficiencies in the range of 80–90% or even higher have been demonstrated (14, 15, 23–25). The catalysts used for SCR in industry are based mainly on TiO_2 -supported V_2O_5 , promoted with WO_3 (26, 27). This catalyst type has also been used since 2005 for HD diesel vehicles in Europe (4). Although SCR technology based on vanadia catalysts has been introduced into the market for diesel vehicles, problems remain due to the high activity for oxidation of SO_2 to SO_3 , the rapid decrease in activity and selectivity at 550°C , and the toxicity of the vanadia species, which begin to volatilize above 650°C (24, 28, 29). Hence, researchers continue to work to develop new SCR catalysts; among these, metal-exchanged zeolites and pillared clays have received much attention in recent years. Zeolite types with narrow pores, such as MOR, FER, BEA, and ZSM-5 have proved to be especially suited for SCR applications.

In this study, we summarize the literature on NH_3 -SCR over metal-exchanged zeolites, focusing on mechanistic aspects and the influence of various parameters on the activity and stability of the catalysts.

CHEMISTRY OF THE SCR PROCESS AND MECHANISTIC ASPECTS

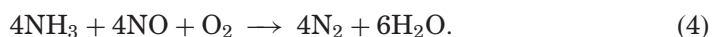
Basics of SCR Chemistry

The main feature of the SCR process is the use of a reducing agent to react specifically with nitrogen oxides, but not with the excess oxygen in the lean exhaust gas. N-containing compounds like ammonia or urea are well suited to this purpose. Because of its negligible toxicity, urea is used in diesel vehicles as a storage compound for ammonia. The decomposition reactions of urea in the presence of water are (30):

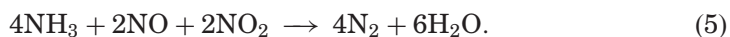


In the following discussion, we restrict ourselves to ammonia as the selective reducing agent, though all statements about the SCR mechanism can also be applied to urea, except for the preparation of the reducing agent.

It is well known that the exhaust gas of today's diesel engines contains nitrogen oxides mainly in the form of nitrogen monoxide (NO); only a minor fraction is nitrogen dioxide (NO₂) (20). Therefore, the basic reaction on SCR catalysts is (15, 20, 30):

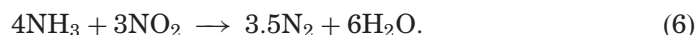


The reaction of a 1:1 mixture of NO and NO₂ is definitely faster than reaction (4) (15, 30, 31):



This reaction will become more important in future diesel engines, since new engine technologies, such as exhaust gas recycling (EGR) and especially the homogenous charge compression ignition (HCCI), will increase the NO₂ share of NO_x emissions.

If the NO₂/NO_x fraction exceeds 50%, an SCR reaction with pure NO₂ takes place (20, 30):



There is also an SCR reaction with NO in the absence of O₂, which changes the stoichiometry of NH₃:NO from the usual 1:1 ratio to 2:3 (20, 30):



The rate of reaction (7) is very slow and can be neglected in lean combustion gases (20).

Mechanistic Aspects of SCR Reactions

Experiments with isotopically labeled reactants using noble metals (32) and a Ba-Na-Y zeolite catalyst (33) have shown that N₂ takes one nitrogen atom from a molecule of NO_x and the other nitrogen from ammonia, which is in agreement with SCR reactions (4) and (5). However, the uniqueness of the SCR process over zeolites is that NO first has to be oxidized to NO₂, which is the rate-determining step of the mechanism (15, 28, 34–36). Thus, reaction (5) can be regarded as the actual and general SCR reaction over zeolites, and NO₂ has to be provided by the input gas or must be produced by the oxidation of NO. This is evident in the fact that H-ZSM5 shows negligible SCR activity if only NO is present, and high SCR activity after 50% NO₂ is added to the feed (15, 28, 37). On metal-exchanged zeolites the NO₂ is produced at the metal centers, while the SCR reaction itself takes place within the zeolite framework (15, 28). The NO₂ is consumed immediately after production in

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