NO_x Abatement in Exhaust from Lean-Burn Combustion Engines by Reduction of NO_2 over Silver-Containing Zeolite Catalysts**

Johan A. Martens,* Anne Cauvel, Agna Francis, Chris Hermans, François Jayat, Marc Remy, Michael Keung, Jan Lievens, and Pierre A. Jacobs

Lean-burn gasoline and diesel engines operated with excess air offer the most efficient power source for transportation known today,[1] but their nitrogen oxide ($NO_x = NO + NO_2$) emissions remain unacceptably high.[2] Although selective catalytic reduction of NO_x with hydrocarbons from the exhaust or the fuel under oxidizing conditions (lean DeNOx) has been extensively studied,[3–7] a breakthrough of this technology is hindered by the low activity, narrow temperature window, and insufficient durability of the catalysts.[8] Here we report that silver/proton-exchanged zeolites represent a unique redox system that outperforms the known catalysts for reduction of NO_2 and is devoid of their disadvantages. In the presence of an excess of oxygen, silver is the only transition metal ion that does not segregate from the zeolite;[9] hence, the stability of the catalyst depends entirely upon the steam stability of the H zeolite. The zeolite framework, its Brønsted acidity, and the specific redox behavior of silver in association with the zeolite are the three key catalyst functions that cooperate to form nitrogen from NO_2 via intermediate nitro, amino, and diazonium compounds.

Below 400 °C, silver catalysts are rather inactive for reducing NO in lean-burn exhaust, unless oxygenated hydrocarbons are added as reducing agents.[10] For the reduction of NO with hydrocarbons, silver zeolites do not have any advantages over copper or cobalt zeolites.[11] We used a synthetic gas mixture that mimicks the exhaust composition of a lean-burn engine with NO_2 as the NO_x component. The gas mixture was passed over a fixed bed of catalyst at high gas velocity. Curves for the reduction of NO_x to N_2 at different reaction temperatures over ferrierite (FER) and mordenite (MOR) zeolites loaded with transition metal ions are shown in Figure 1. The silver zeolites are highly active at all temperatures. In particular, the Ag/H-FER catalyst transforms more than 60% of the NO_x into N_2 between 250 and 450 °C.

When used as lean DeNOx catalysts, many transition metal exchanged zeolites, of which Cu-ZSM-5[2, 3, 7] and Co-ZSM-5[5, 6] are representative examples, are deactivated in the presence of water vapor due to segregation of the metal oxide from the zeolite phase.[12] The Ag/H-FER catalyst does not show any deactivation below 600 °C (Figure 1) and retains 80% of its original activity after 16 h of continuous operation at 660 °C; the limiting factor is the hydrothermal stability of the Brønsted acid sites of the zeolite. The excellent lean DeNOx performance of the Ag/H zeolites even remained unaffected by the presence of 150 ppm of sulfur dioxide. Under reaction conditions, the silver is not converted into nitrate species, and no nitrogen deficiency was observed in the mass balance or detected by in situ IR spectroscopy (absence in all instances of a peak at 1385 cm^{-1}). Since silver cations in zeolites have a low tendency to undergo hydrolysis and silver oxide particles are thermally unstable, this remarkable catalytic stability is a unique feature of Ag zeolites. Irrespective of the position or degree of sintering of the metallic silver clusters formed by reduction, the zeolite can be restored to its original form by oxidation[9] [Eq. (1)].

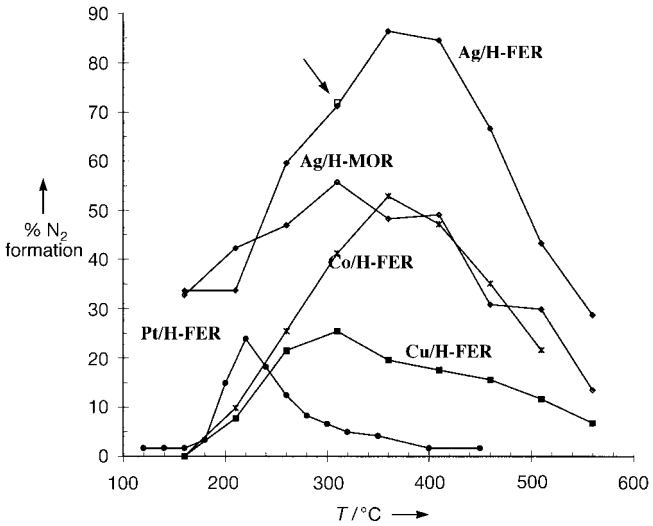

Figure 1. Nitrogen formation over H-MOR and H-FER zeolites with a loading of 5 wt% of silver, copper, or cobalt ions, or 1 wt% of platinum ions as a function of reaction temperature. The arrow on the curve for Ag/H-FER indicates a sample that was subjected to fast ageing (24 h at 560 °C under normal reaction conditions).

$$n(Ag^+\text{-}Z^-) \xrightleftharpoons[n/2\ H_2O \quad n/4\ O_2]{n H^0} n(Ag^0)/n(H^+\text{-}Z^-) \qquad (1)$$

The mechanism of the lean DeNOx reaction was investigated with several organic compounds as reducing agents. At 250 °C, the rate of NO_2 reduction over Ag/H-MOR decreases in the following order: propene (55%) > nitropropane, cyclopentanone, octane (45%) >> propane, acetic acid, carbon monoxide (5%). The more active reducing agents have a higher tendency to undergo radical oxidation by O_2.[13] Pronounced activity peaks occur when the catalyst temperature is increased in steps (Figure 2). These activity peaks are not due to the spontaneous reaction of NO_x that has accumulated in the catalyst (storage effect) since the independently determined NO_x conversion and N_2 formation were in agreement. This behavior was also exhibited by other zeolitic catalyst carriers (MOR, ZSM-5, FER) with NO_2-containing exhaust, irrespective of the nature of the charge-

[*] Prof. Dr. Ir. J. A. Martens, Dr. A. Cauvel, Dr. A Francis, Ir. C. Hermans, Dr. Ir. F. Jayat, Dr. M. Remy, Dr. M. Keung, Dr. Ir. J. Lievens, Prof. Dr. Ir. P. A. Jacobs
Centrum voor Oppervlaktechemie en Katalyse
Departement Interfasechemie, K.U. Leuven
Kardinaal Mercierlaan 92, B-3001 Heverlee (Belgium)
Fax: (+32) 16-321998
E-mail: johan.martens@agr.kuleuven.ac.be

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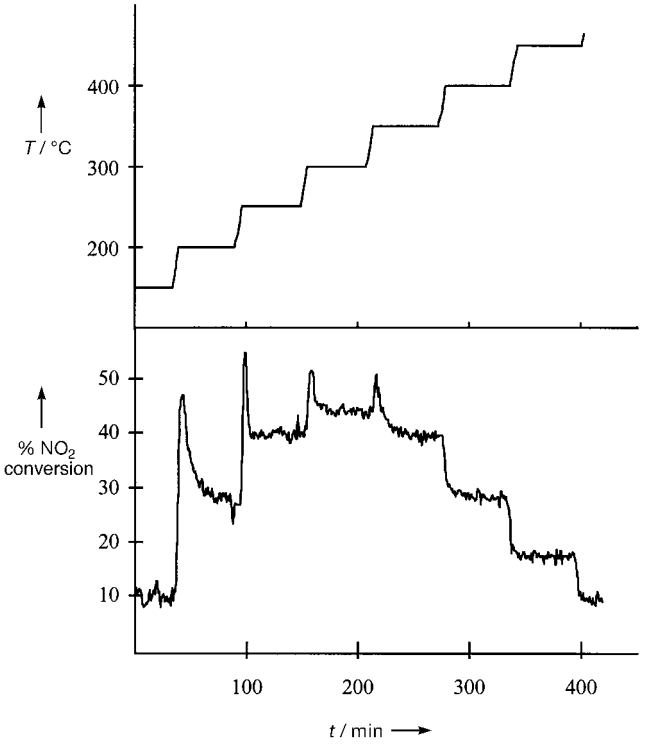


Figure 2. Nitrogen formation over Ag/H-MOR with stepwise increase of the reaction temperature ($8\,^{\circ}C\,min^{-1}$).

compensating metal ion (Cu, Co, Pt, Ce, Na) in the zeolite or of the hydrocarbon reducing agent. This indicates that a zeolite-induced radical reaction takes place. Below 300 °C NO_2 does not react in the absence of propene, and vice versa; this suggests that the two compounds react with one another.

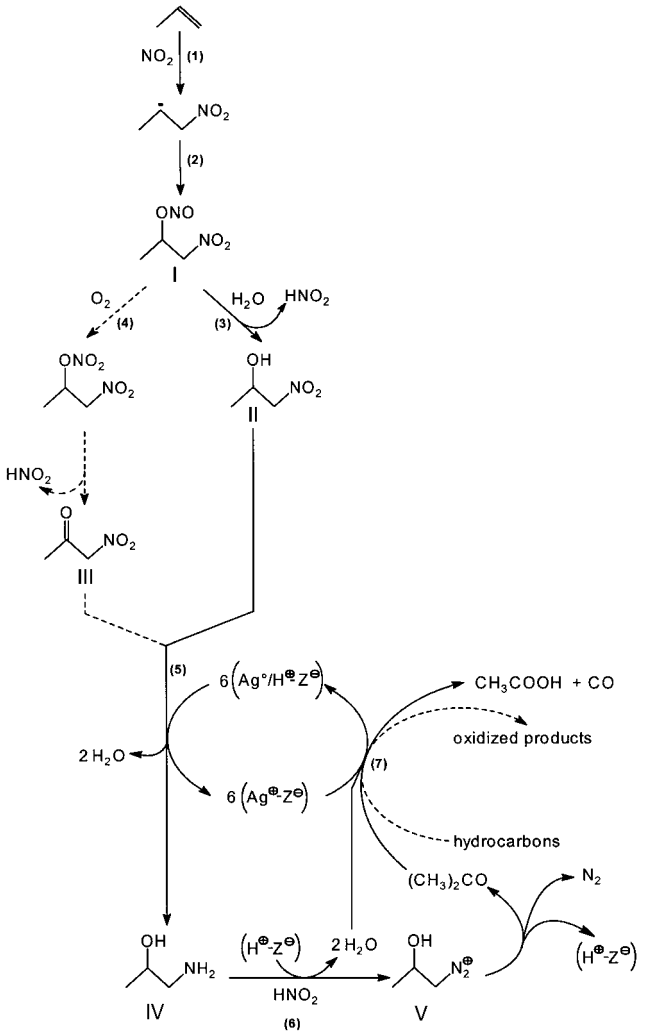
Below 270 °C in the absence of organic compounds, prereduced Ag/H-MOR does not catalyze the conversion of the exhaust gas. Upon injection of propene, the conversion passes through a peak value before reaching a steady state. This shows that metallic silver, although involved in the mechanism, is unable to reduce NO_2 in the absence of alkene, and suggests that the pairing of N atoms in the DeNOx reaction occurs via an organic nitrogen species rather than by disproportionation[14] of NO on the metal ions. Experiments performed at 220 °C gave further clues as to the nature of these intermediates: 1) the lower reactivity of H-MOR is enhanced to the level of Ag/H-MOR when nitropropane is replaced by, for example, propylamine as reducing agent; 2) a MOR zeolite exchanged with ammonium ions has excellent DeNOx activity until all ammonium ions are consumed.

Optimization of the exhaust gas composition allowed product stoichiometries at low reaction temperatures (below 200 °C) to be determined. One CO molecule is obtained per N_2 molecule formed, and two NO_2 molecules can be reduced with one molecule of propene. Almost equimolar amounts of acetic acid, nitrogen, and carbon monoxide were detected together with traces of acetone. Consequently, the overall stoichiometry of the NO_2 reduction with propene corresponds to Equation (2). At higher reaction temperatures, all inter

$$2\,NO_2 + C_3H_6 \longrightarrow N_2 + CO + H_2O + CH_3COOH \qquad (2)$$

mediates undergo complete oxidation. The catalyst is active in the absence of water, dioxygen, or both, but is most active in the presence of the typical concentrations of these compounds.

A mechanism for the reduction of NO_2 with propene that is consistent with all of these experimental observations is presented in Scheme 1. The initial step (1, 2; first catalyst



Scheme 1. Reaction mechanism of NO_2 reduction with propene on Ag/H zeolites.

function) is a zeolite-catalyzed radical nitro–nitrosooxy addition[16] of two NO_2 molecules to the olefin,[17] a reaction already invoked for Ce-ZSM-5.[18] β-Nitropropyl nitrate (**I**) can react with water (3) to give β-hydroxynitropropane (**II**) and nitrous acid.[19] The nitro group is subsequently reduced (5) by the reduced catalyst (second catalyst function) to β-hydroxypropylamine (**IV**). On zeolitic Brønsted acid sites, amines react with nitrous acid (6, third catalyst function) to form unstable diazonium salts (**V**),[20] which decompose rapidly to nitrogen, carbon monoxide, and acetic acid (7), the typical autoxidation product of acetone. Acidic zeolites presumably operate according to the same mechanism, whereby the catalytic function of silver is performed less efficiently by carbonaceous deposits. This reaction scheme is

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also valid for saturated hydrocarbons with labile hydrogen atoms.

As exhaust from lean-burn engines contains NO as the main NO_x component, the present knowledge could be technically implemented as a dual-catalyst system.[21] On an oxidation catalyst such as Pt-ZSM-5, NO_x from a lean-burn exhaust stream can be converted into NO_2, which in turn is converted over an Ag/H zeolite catalyst. Injection of sufficient reducing agent between the two catalysts is required.

Experimental Section

In the experiment of Figure 1, the synthetic exhaust gas was composed of 400 ppm NO_2, 350 ppm propene, 350 ppm CO, 10% CO_2, 10% O_2, and 12% H_2O, balance helium. The volumetric hourly space velocity (VHSV) and the weight hourly space velocity (WHSV) were 160000 h^{-1} and 320000 h^{-1}, respectively. NO, N_2O, and NO_2 were monitored by chemiluminescence and IR detectors. N_2 was monitored by gas chromatography.

In the experiment of Figure 2, the synthetic exhaust gas was composed of 450 ppm NO_2, 50 ppm NO, 175 ppm propene, 175 ppm propane, 350 ppm CO, 10% CO_2, 6% O_2, 12% water, balance helium. The VHSV was 60000 h^{-1}.

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Determination of the Orientation of a Distant Bond Vector in a Molecular Reference Frame by Cross-Correlated Relaxation of Nuclear Spins**

Bernd Reif, Henning Steinhagen, Bernd Junker, Michael Reggelin, and Christian Griesinger*

Dedicated to Professor Richard R. Ernst on the occasion of his 65th birthday

Recently, a new class of structural restraints has been introduced that allows the measurement of projection angles between internuclear vectors from relaxation rates of double-quantum (DQ) and zero-quantum (ZQ) coherences.[1] This relaxation mechanism is induced by cross-correlation of two individual dipolar coupling tensors. Angular restraints can also be obtained by the measurement of relaxation rates of DQ and ZQ coherences that are induced by the cross-correlation of one dipolar coupling and a chemical shift tensor.[2,3] So far applications have addressed only the measurement of such rates in fully $^{13}C/^{15}N$-labeled biomacromolecules. We show here by comparison with a crystal structure that angles between H – H and C – H bond vectors that are separated in space by 7 Å in a small organic molecule can be determined with an accuracy of a few degrees. It is further shown that by measuring two such relaxation rates it is possible to determine the orientation of one vector in the frame of reference of the two other vectors. For sensitivity reasons we had to introduce ^{13}C labeling in part of the molecule. The accuracy and precision of the measurement established in this publication will be used in a forthcoming paper to derive long-range structural information for a catalytic intermediate that cannot be crystallized.

In two pairs of nuclei ($A^1 - A^2$ and $B^1 - B^2$) cross-correlated relaxation rates $\Gamma^{c}_{A^1A^2,B^1B^2}$ of DQ and ZQ coherences between nuclei A^1 and B^1 can be measured provided the DQ and ZQ coherence between these nuclei can be excited, the scalar coupling between A^1 and A^2 as well as between B^1 and B^2 is resolved, and the main relaxation source for A^1 (B^1) is the dipolar coupling to A^2 (B^2). If we identify the nuclei A^1, A^2, B^1, and B^2 according to Table 1 and Figure 1 with $(A^1,A^2) = (H^{26},H^{25})$ or (H^{23},H^{24}) and $(B^1,B^2) = (C^3,H^3)$ all the above requirements are fulfilled by the η^3-allylpalladium complex **1**.

[*] Prof. Dr. C. Griesinger, Dr. B. Reif, Dipl.-Chem. B. Junker, Priv.-Doz. Dr. M. Reggelin
Fachbereich Chemie der Universität
Marie-Curie-Strasse 11, D-60439 Frankfurt/Main (Germany)
Fax: (+49) 69-7982-9128
E-mail: cigr@krypton.org.chemie.uni-frankfurt.de (C.G.)
re@krypton.org.chemie.uni-frankfurt.de (M.R.)
Dr. H. Steinhagen
Institut für Organische Chemie der Universität Heidelberg (Germany)

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