Selective catalytic reduction of NOx by hydrocarbons enhanced by hydrogen peroxide over silver/alumina catalysts

Petr Sazama[a] and Blanka Wichterlová*[b]

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It is shown that hydrogen peroxide enhances substantially selective reduction of NOx to nitrogen with hydrocarbons over Ag/alumina catalysts.

Ag/alumina is one of the promising catalysts for selective catalytic reduction of nitrogen oxides to nitrogen (SCR-NOx) by hydrocarbons, providing high and stable activity at temperatures >350 °C when using long-chain paraffins (the main components of diesel fuel) as reductants. However, at temperatures <350 °C the activity is low. A great improvement has been achieved by the discovery that hydrogen added to a hydrocarbon feed dramatically increases the conversion of NOx, especially at low temperatures and high gas space velocities.[1,2] Shibata *et al.*[3] suggested that the hydrogen effect stems from the enhanced rate of oxidation of propane to acetates, which are more reactive. UV-Vis and EXAFS measurements of the state of the silver has led to the conclusion that the presence of hydrogen causes the formation of small metallic charged Ag clusters,[4] which are the active sites responsible for the enhanced rate of the SCR-NOx reaction.

However, time-resolved monitoring of the effect of the addition of hydrogen to and its removal from the reactant stream on the NOx conversion and Ag cluster formation has not yielded evidence for their direct relationship.[5] Moreover, the presence of metallic Ag clusters on alumina was also detected in the SCR-NOx reaction performed in the absence of hydrogen.[5,6] These findings led us to the conclusion that hydrogen itself probably takes part in the SCR-NOx reaction.[5] This conclusion was supported by the observation that the presence of both CO and H_2 induced the formation of Ag clusters, but only hydrogen increased the conversion of NOx to nitrogen.[7]

Based on these results, but without providing any direct experimental evidence, we suggested in ref. 5 that the mechanism by which hydrogen functions could be explained by the formation of Ag hydride with subsequent formation of hydroperoxy and hydroxy radicals. These radicals then enhance the individual reaction steps of the SCR-NOx process as well as the observed NO–NO_2 oxidation.

In the present study we used hydrogen peroxide as a source of radicals that would enhance the rate of SCR-NOx, if the radical mechanism is operative in the hydrogen-co-assisted reaction. When using SCR-NOx, particularly for mobile diesel engines, a method employing hydrogen to increase the rate of SCR-NOx could entail considerable problems in storage of hydrogen or its preparation on board. Even though the application of hydrogen peroxide in SCR-NOx would also bring some difficulties the observed positive effect of hydrogen peroxide on NOx conversion to nitrogen over Ag/alumina described here could be considered in the reduction of NOx in the exhaust gases of lean-burn combustion processes.

A 2 wt.% Ag/alumina catalyst was prepared by the procedure described in ref. 8. Catalytic tests, performed in a quartz tubular micro-reactor, employed a reactant mixture modelling the exhaust gas composition, and consisting of 1000 ppm NO, 6.0% O_2, 12.0% H_2O, 600 ppm n-$C_{10}H_{22}$, 0 or 2000 ppm H_2O_2 and 0 or 2000 ppm H_2 and the rest helium. The gas components in the feed were controlled by mass-flow controllers, and *n*-decane was fed *via* saturators maintained at the desired temperature and using helium as a carrier gas. Water and hydrogen peroxide vapour were added by using a linear dosing device and aqueous solution of 3.2% H_2O_2. The flow of the gas mixture and the weight of catalyst corresponded to GHSV of 60 000 h^{-1}. The reaction products were analyzed under reaction steady-state conditions using an on-line connected NO/NOx chemiluminescence analyzer (Horiba CLA-355K) and gas chromatograph (Hewlett Packard 6090). Experimental details are given in ref. 5.

Conversion of NO in the reaction with *n*-decane at 470–520 K without co-fed hydrogen peroxide or hydrogen was low (Fig. 1a). The NO conversion was increased considerably by addition of hydrogen peroxide into the reactant stream. This was accompanied by higher conversion of *n*-decane and higher selectivity to CO_2 (Fig. 1b). Both molecular nitrogen and nitric dioxide were formed. The greatest enhancement of NO conversion was achieved at low temperatures.

Table 1 shows a comparison of decane-SCR-NO co-assisted by hydrogen peroxide over Al_2O_3 and Ag/Al_2O_3 at 523 K. The activity of alumina itself in the absence of hydrogen peroxide in the feed was negligible and the effect of the added hydrogen peroxide was remarkable. The NO conversion to nitrogen was significantly higher over Ag/alumina as well as in the reaction co-assisted by hydrogen peroxide. The positive effect of hydrogen on CH-SCR-NO has been observed only with silver on alumina or Ag-zeolite catalysts.[9] Analogously to hydrogen, with Cu- and Fe-ZSM-5 catalysts the increase in NOx conversion in the presence of hydrogen peroxide was not observed.

When hydrogen was employed as an additive over Ag/alumina, the conversion of NO to NO_2 was lower and the yield of N_2 was higher compared to the reaction using hydrogen peroxide (Table 2). Thus, in comparison with hydrogen, in addition to improving the reduction of NO to N_2, hydrogen peroxide enhances NO oxidation to NO_2 much more. This effect is more pronounced at low

[a]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague 8, 182 23, Czech Republic. E-mail: petr.sazama@jh-inst.cas.cz; Fax: +420 286582307; Tel: +420 26605 3325
[b]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague 8, 182 23, Czech Republic. E-mail: wichterl@jh-inst.cas.cz; Fax: +420 286582307; Tel: +420 26605 3595

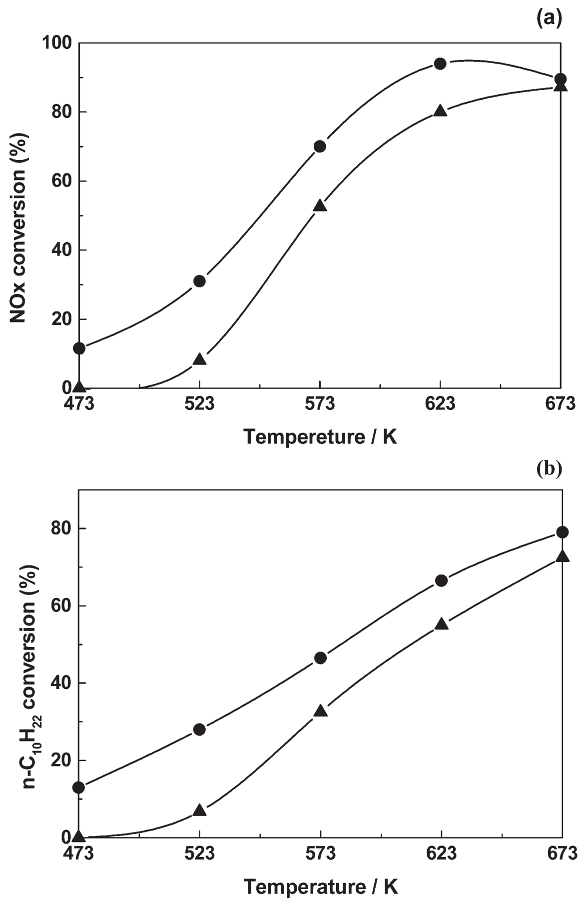

Fig. 1 The effect of hydrogen peroxide on the conversion of NO to N_2 (a) and decane to COx (b) in $C_{10}H_{22}$–SCR–NO over Ag/Al_2O_3 at different temperatures. Feed: 1000 ppm NO, 600 ppm $C_{10}H_{22}$, 6% O_2, 12% H_2O and 0 ppm H_2O_2 (▲) or 2000 ppm H_2O_2 (●).

Table 1 Comparison of the activity of Al_2O_3 and Ag/Al_2O_3 in the $C_{10}H_{22}$-SCR-NO reaction, co-assisted by hydrogen peroxide at 523 K

	Al_2O_3		Ag/Al_2O_3	
	0 ppm H_2O_2	2000 ppm H_2O_2	0 ppm H_2O_2	2000 ppm H_2O_2
xNO[a]	0.2	43.7	28.2	58.6
Yield of N_2	0.1	15.7	8.0	32.1
Yield of NO_2	0.1	28.0	20.2	26.6

[a] Conversion of NO to nitrogen and nitrogen dioxide.

temperatures (*cf.* Table 1 and 2), where the SCR-NOx reaction contributes less to the overall transformations.

The dramatically enhanced rate of oxidation of NO and decane by addition of hydrogen peroxide supports the suggestion that the initial step in the mechanistic pathways of the activation of SCR-NO by hydrogen peroxide consists in the generation of highly reactive hydroxy and hydroperoxy radical species. Hydrogen peroxide decomposition is a well-known process generating hydroxy and hydroperoxy radicals; however, competition between H_2O_2 consumption in the oxidation reactions and its non-productive decomposition could be expected in the SCR-NOx process. Hydroperoxy radicals can readily react with NO to form NO_2 and hydroxy radicals[10] according to the reaction

$$HO_2 + NO \rightarrow NO_2 + OH$$

The reactions of hydrocarbons and hydroxy radicals result in the formation of hydroxy alkyl radical species.[11,12] However, the simultaneous presence of nitrogen oxides and hydrocarbons in the SCR-NOx reaction lead to greater complexity of the oxidation process, with formation of various oxo/nitro species.[12] Cyanide (–CN) and isocyanate (–NCO) species were found to be important intermediates in the formation of molecular nitrogen in the SCR process over Ag/alumina.[13] Thus, the function of H_2O_2 in the SCR-NOx reaction is specifically based on the activation of relatively stable reactants as well as intermediates.

Table 2 Comparison of the effect of hydrogen and hydrogen peroxide on the $C_{10}H_{22}$-SCR-NO reaction over Ag/Al_2O_3 at 473 K

	Reducing agent		
	Decane	Decane + H_2O_2	Decane + H_2
xNO[a]	2.5	60.0	49.5
Yield of N_2	0	11.8	21.0
Yield of NO_2	2.5	48.2	28.5

[a] Conversion of NO to nitrogen and nitrogen dioxide.

Therefore, the enhanced conversion of NO to NO_2 and N_2, accompanied by the increase in the decane oxidation, caused by the addition of hydrogen peroxide to the SCR-NOx reactants, supports our previous suggestion[5] that the initial step and the role of hydrogen in the mechanistic pathways of the H_2/CH-SCR-NO reaction might consist in generation of the highly reactive hydroxy and hydroperoxy radical species. If hydrogen peroxide is used as a co-reactant with hydrocarbons, higher yields of NO_2 are obtained compared to the reaction in which hydrogen is used. It should be mentioned that the increased formation of NO_2 does not increase the degree of reduction of NOx to nitrogen over Ag/alumina, but that the opposite effect was found.[5]

The positive effect of hydrogen peroxide could be utilized to boost the SCR-NOx process; this is especially important in applications for reducing emissions in the exhaust gases of mobile diesel engines.

Notes and references

1 B. Krutzsch, Ch. Goerigk, S. Kurze, G. Wenninger, W. Boegner and F. Wirbeleit, *US Patent*, 5,921,076, 1999.
2 S. Satokawa, *Chem. Lett.*, 2000, 294.
3 J. Shibata, K. Shimizu, S. Satokawa, A. Satsuma and T. Hattori, *Phys.Chem. Chem. Phys.*, 2003, **5**, 2154.
4 J. Shibata, K. Shimidzu, Y. Takada, A. Shichi, H. Yoshida, S. Satokawa, A. Satsuma and T. Hattori, *J. Catal.*, 2004, **227**, 367.
5 P. Sazama, L. Čapek, H. Drobná, Z. Sobalík, J. Dědeček, K. Arve and B. Wichterlová, *J. Catal.*, 2005, **232**, 302.
6 J. P. Breen, R. Burch, C. Hardacre and C. J. Hill, *J. Phys. Chem. B*, 2005, **109**, 4805.
7 B. Wichterlová, P. Sazama, J. P. Breen, R. Burch, C. J. Hill, J. Čapek and Z. Sobalík, *J. Catal.*, submitted.
8 K. Eränen, L.-E. Lindfors, A. Niemi, P. Elfving and L. Cider, *SAE paper 2000-01-2813*, 2000.
9 S. Satokawa, J. Shibata, K. Shimizu, A. Satsuma and T. Hattori, *Appl. Catal. B*, 2003, **42**, 179.
10 J. Park, C. G. Jongsma, R. Zhang and S. W. North, *J. Phys. Chem. A*, 2004, **108**, 10688.
11 J. Smith, J. Phillips, A. Graham, R. Steele, A. Redondo and J. Coons, *J. Phys. Chem. A*, 1997, **101**, 9157.
12 J. Zhang, T. Dransfield and N. M. Donahue, *J. Phys. Chem. A*, 2004, **108**, 9082.
13 N. Bion, J. Saussey, M. Haneda and M. Daturi, *J. Catal.*, 2003, **217**, 47.