# NEW WATER TOLERANT, HIGHLY ACTIVE CATALYST FOR THE SELECTIVE REDUCTION OF NITRIC OXIDE BY ALCOHOLS

*Istvan Halasz, Ravindra Datta*

ihalasz@blue.weeg.uiowa.edu; Phone: 319-335-0306; Fax: 319-335-1415
radatta@icaen.uiowa.edu; Phone: 319-335-1395; Fax: 319-335-1415
Department of Chemical and Biochemical Engineering
The University of Iowa, Iowa City, IA 52242

The selective catalytic reduction, SCR, of NO by hydrocarbons or oxygenated hydrocarbons is a promising technique for minimizing $NO_x$ emissions from oxygen rich exhausts of combustion sources at high space velocities [1, 2]. Some ZSM5 type zeolites are so far the most active SCR catalysts. However, the catalytic activity of most zeolites substantially decreases in presence of $H_2O$, which is always present in exhaust streams. Moreover, the low hydrothermal stability of zeolites is a concern.

Here we report the first observation of very high catalytic activity and good water tolerance of a new, indium based supported molten metal catalyst (In-SMMC) in the SCR of NO by alcohols at reaction conditions resembling those in the commercial catalytic converters for $NO_x$ abatement in coal combustion exhausts. In contrast to common supported metal catalysts composed of solid metal crystallines dispersed on porous supports, SMMCs contain micro droplets or thin films of non-transition low melting metals on refractory supports. These recently explored new heterogeneous catalysts have been found to be active for various dehydrogenation and selective oxidation processes [3].

Catalytic experiments were carried out with mixtures of (0.1% NO + 8% $O_2$ + x% $C_1$-$C_3$ alcohol + y% $H_2O$) in He carrier gas at temperatures from 300 to 600 $^oC$ and space velocities SV = 60,000 $h^{-1}$. To get comparative information about the catalytic performance of In-SMMC for the reduction of NO by various reductants, experiments were also done by using $H_2$, CO, and hydrocarbons instead of alcohols. The reaction steps were probed by using bi- and trimolecular feeds of (NO + $O_2$), (NO + alcohol) ($O_2$ + alcohol)and ($O_2$ + $H_2O$ + alcohol).

Results indicate that In-SMMC is more active for the SCR of NO by Et-OH in presence of excess $O_2$ and $H_2O$ than any other catalysts reported for this reaction including $In^{3+}$ or $In_2O_3$ promoted zeolite and non zeolite samples [4-8]. Catalyst

performance remained largely intact when catalytic tests were carried out at various reaction conditions for an extended period. Periodic oscillations were observed in the NO and $NO_2$ concentrations of the products. Unlike in SCR reactions with hydrocarbons [13], this is the first time that oscillations have been observed for oxygenated hydrocarbon reductants. Water affects both the amplitude and the frequency of these oscillations.

Oxidation of Et-OH is a likely initial reaction in the SCR process over the In-SMMC. As opposed to most other SCR catalysts [1, 9, 10], formation of $NO_2$ has presumably a secondary role over this catalyst. This non-conventional behavior might be due to the $SiO_2$ (controlled pore glass) support. While acidic supports, such as $Al_2O_3$ or $TiO_2$-$ZrO_2$, are typically good supports for non-zeolite SCR catalysts, $SiO_2$ has been found to be an unsuitable support for the best water tolerant catalysts, such as $In_2O_3$, $CoO_x$, or Ag [7, 8, 14]. Similar to the SCR of NO by $C_3H_6$ over $Mn_2O_3$/Sn-ZSM5 [12], $H_2O$ improves both the activity and the selectivity of In-SMMC. Homogeneous and heterogeneous radical reactions may be involved in the SCR process over this catalyst.

## References


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