Supported Gallium, Indium and Tin Oxides as High Performance Catalysts for the HC-SCR Process: Influence of Loading and Support Acidity on Activity

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Introduction
First generation catalysts for the HC-SCR process, aimed at the reduction of NO\textsubscript{x} with hydrocarbons, are based on metal ion exchanged zeolites (in particular Cu or Co on MFI or beta structures [1,2]). Oxides of elements from periodic table groups 13 (Ga\textsubscript{2}O\textsubscript{3} and In\textsubscript{2}O\textsubscript{3}) and 14 (SnO\textsubscript{2}) are interesting active phases possessing high activity and selectivity in the HC-SCR process [3,4] and can be viewed as a second generation of SCR catalysts. In-depth information has to be collected in order to control the preparation of Ga-, In-, and Sn-containing catalysts with optimal activity. The aim of this paper is to study from the characterization and catalytic activity point of view a large series of catalysts containing Ga\textsubscript{2}O\textsubscript{3}, In\textsubscript{2}O\textsubscript{3}, and SnO\textsubscript{2} phases dispersed at various loadings (3-30 wt.%) on various oxide carriers (Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, SiO\textsubscript{2}, WO\textsubscript{3}, MgO, Nb\textsubscript{2}O\textsubscript{5}, ZrO\textsubscript{2}) covering a wide interval of acidity. The role played by the carrier in governing the surface structure, the acid-base properties, the red-ox properties, and the catalytic activity of the active phases, as well as the role played by the surface concentration of the active phase have been highlighted to provide relationships between properties of catalysts and activity.

Experimental
The Ga-, In-, and Sn-based catalysts were prepared by impregnating oxide supports with a wide range of acid-base properties with aqueous solutions of Ga(NO\textsubscript{3})\textsubscript{3}\cdot9H\textsubscript{2}O, In(NO\textsubscript{3})\textsubscript{3}\cdotH\textsubscript{2}O, and SnCl\textsubscript{4}\cdot5H\textsubscript{2}O, respectively. All the samples were dried overnight at 120 °C and further calcined in oxygen flow at 500 °C for 12h. For each support, at least two and at most six samples with different loadings of Ga\textsubscript{2}O\textsubscript{3} (on γ-Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2}, SiO\textsubscript{2}, WO\textsubscript{3}, and Nb\textsubscript{2}O\textsubscript{5}), In\textsubscript{2}O\textsubscript{3} (on Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, SiO\textsubscript{2}, and Nb\textsubscript{2}O\textsubscript{5}), and SnO\textsubscript{2} (on Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2}, SiO\textsubscript{2}, and MgO) were prepared. The oxide loadings varied from 3 wt.% to the theoretical monolayer.
The bulk and surface properties of the samples were investigated by ICP-AES, XRD, BET measurements, XPS, adsorption microcalorimetry of the appropriate probe molecules (NH\textsubscript{3} and SO\textsubscript{2}) and TPR/TPO measurements.
The catalytic activity for reduction of NO\textsubscript{x} with C\textsubscript{2}H\textsubscript{4} in excess O\textsubscript{2} was measured by using a fixed-bed flow microreactor. Typical feed gas mixtures contained from 0.3 to 0.5% of both NO and C\textsubscript{2}H\textsubscript{4} and from 4 to 9% of O\textsubscript{2} diluted in helium as balance gas. The reaction temperature was changed stepwise from 150 to 550°C and the contact time was 50,000 h\textsuperscript{-1} in terms of GHSV. The effluent gases were analyzed by an on-
line analytical apparatus: a gas chromatograph or a FT-IR spectrometer (Bio-Rad with DTGS detector) equipped with a gas cell (path length 2.4 m).

**Results and Discussion**

The surface areas of the different supports as determined by BET measurements slightly decreased when the amounts of active phase increased. Only Ga$_2$O$_3$, In$_2$O$_3$ and SnO$_2$ were detected by XPS on the surfaces, and a comparative scale of active phase dispersion was established. Well developed crystalline phases of deposited In$_2$O$_3$ and SnO$_2$ were identified by XRD, while Ga$_2$O$_3$ was amorphous. Adsorption microcalorimetry measurements of the acidity and basicity of the supported metal oxides and bare supports have shown that SnO$_2$ and Ga$_2$O$_3$ can be considered as amphoteric oxides, while In$_2$O$_3$ can be considered as mainly basic. Gallium oxide could not be reduced, while indium oxide and tin oxide were readily reduced and reversibly reoxidized.

The catalytic activity of the Ga-, In-, and Sn-based catalysts is dramatically dependent on the support rather than on the metal oxide loading. MgO, WO$_3$ and Nb$_2$O$_5$ could not impart any activity to SnO$_2$, Ga$_2$O$_3$ or In$_2$O$_3$ phases in the reduction of NO$_x$ by hydrocarbons. SiO$_2$ leads to catalysts with little activity, while, on the most acidic supports (ZrO$_2$, TiO$_2$, and Al$_2$O$_3$), the threeoxic phases display good activity. In particular the use of γ-Al$_2$O$_3$ gave rise to series of catalysts with very active and selective behavior in the HC-SCR reaction. The results obtained suggest that some supports, ZrO$_2$, TiO$_2$, and Al$_2$O$_3$, give rise to a strong metal oxide-support interaction that leads to well dispersed oxide phases possessing catalytic activity, in terms of NO$_x$ reduction. The other supports, MgO, WO$_3$, Nb$_2$O$_5$, and SiO$_2$, are not able to interact with the SnO$_2$, Ga$_2$O$_3$ or In$_2$O$_3$ oxides and no, or very little, catalytic activity occurred. Concerning the influence of the metal oxide loading, no general conclusion can be drawn. HC-SCR activity increased with Ga$_2$O$_3$ loading, while SnO$_2$ and In$_2$O$_3$ loading had very little influence on the activity. As a general trend, the maximum activity was not observed on the more concentrated samples, suggesting an important role of the active phase dispersion. The temperature of maximum activity in terms of N$_2$ formation was different for SnO$_2$ and In$_2$O$_3$ with respect to Ga$_2$O$_3$. The temperature of maximum NO$_x$ reduction to N$_2$ was 450° C for the SnO$_2$ phase, while Ga$_2$O$_3$ and In$_2$O$_3$ produced more N$_2$ at higher temperature (around 500° C). Comparing the best catalytic systems among those studied, it was possible to achieve about 70% of N$_2$ formation (ca. 1 mol$_{\text{N}_2}$/mol$_{\text{Ga}}$·s$^{-1}$) on Ga$_2$O$_3$/γ-Al$_2$O$_3$; 50% of N$_2$ formation (ca. 0.5 mol$_{\text{N}_2}$/mol$_{\text{Sn}}$·s$^{-1}$) on SnO$_2$/ZrO$_2$, and 35% of N$_2$ formation (ca. 0.6 mol$_{\text{N}_2}$/mol$_{\text{In}}$·s$^{-1}$) on the In$_2$O$_3$/Al$_2$O$_3$ system.

**References**