NEW ASPECTS OF DOPED OXIDES AS SUPPORTS FOR CATALYSTS

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Doped oxides are common supports for catalysts, but the connections between dopants, materials properties of the support, and catalytic reactions, are not always clear. We will discuss new aspects of Al$^{3+}$ ions in zeolite ZSM-5 and Ti$^{4+}$ ions in aluminas.

Zeolite ZSM-5 is an aluminum doped, porous silica. The SiO$_2$ : Al$_2$O$_3$ ratio of the original blend is the common way to denote the Al$^{3+}$ concentration. Al$^{3+}$ ions are accompanied by a charge imbalance which is neutralized by NH$_4^+$, H$^+$ or even NO$_2^-$ [1]. Metal ions may replace these species in exchange reactions under appropriate conditions, with respect to pH and ion concentrations [2]. The lattice-ion interaction is electrostatic and mutual, which means that di- or tri-valent ions are more tightly bound than mono-valent ions and also enhances the stability of the framework. A high Al$^{3+}$ concentration makes a more flexible lattice. This flexibility eventually leads to de-alumination unless counter measures are taken, but lattice movements are also an essential part of the unique catalytic properties of zeolite ZSM-5. Modelling have often focussed on the narrow channels of ZSM-5 and the accompanying strong electrostatic field from charged groups at the inner walls, but we have suggested a 'dynamic' picture, where lattice movements, enhanced by Al$^{3+}$ doping, destabilizes species adsorbed on active sites [3].

Ti$^{4+}$ ions in alumina induce sites with enhanced acidity, and textbooks tell that weakly bound protons are directly involved in dehydrogenation reactions. This function is probably significant in TWC and HC-SCR catalysts for nitrogen oxide abatement, but dehydrogenation will also lead to carbonaceous residues. Titanium carbides, formed on the alumina under reducing conditions, are very reactive for nitrogen oxide dissociation, following a path similar to that of CO$_2$ in coal gasification [4]. Titanium ions are also common in supports for hydrogenation catalysts, based on sulfided metal catalysts. Sites with enhanced acidity act as dispersion agents and anchor metal sulfide particles [5], akin to the well documented role of Sn$^{2+}$ ions in the surface of alumina supported Pt.

REFERENCES
4. Paul J. et al., manuscript
5. Oehman L.O., Paul J., manuscript; 5. Safak S. and Paul J., manuscript

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