Zirconia-based inorganic oxide catalysts for the abatement of highly toxic agrochemicals and chemical warfare agent simulants

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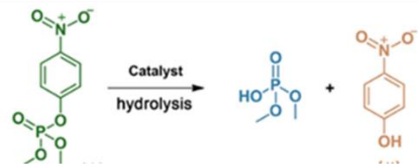
Zr-containing inorganic oxides and metal-organic frameworks are attracting an ever-growing interest as heterogeneous catalysts for the degradation and abatement of highly hazardous organophosphorus compounds, that are toxic ingredients of polluting obsolete agrochemicals (*e.g.*, paraoxon, parathion, malathion) and anticholinergic nerve chemical warfare agents (*e.g.*, sarin, soman).[1]

The ability of Zr-O-Zr surface domains to effectively degrade organophosphorus esters is widely attributed to a hydrolytic capability similar to the Zn(II) multinuclear metal sites in phosphatase enzymes.[2] Thanks to a fine tuning of the arrangement and distribution of Zr centers at the inorganic oxide surface, it is possible to optimize the rapid and safe degradation and decontamination of hazardous organophosphates.

The present study aims at investigating how the density of exposed and accessible Zr(IV) species at the surface of a mesoporous zirconia-silica mixed oxide solid affects the capability to degrade the pesticide paraoxon (diethyl 4-nitrophenyl phosphate, obsolete agrochemical and nerve agent simulant) into non-noxious products, under very mild conditions, at ambient temperature and pressure. A set of ZrO_2-SiO_2 non-ordered mesoporous mixed oxide materials was prepared with a variable percentage of zirconia, namely, 100, 90, 70 and 50 (wt.%). Pure ZrO_2 (100%) was used in two forms: a tailor-made mesoporous high specific surface area and a reference low surface area bulk oxide obtained from commerce (Merck). The solids were fully characterized in terms of porosimetric, morphologic and physico-chemical properties. In particular, the acid and basic sites on the surface were thoroughly evaluated and quantified by means of in-situ FT-IR characterization by probe molecules.[3]

The catalysts (40 mg) were tested in the hydrolytic degradation of paraoxon (220 ppm solution) in liquid-phase batch reactor, in ethyl acetate as a solvent, at 20°C and 1 bar. Phosphoric acid derivatives and p-nitrophenol were the main observed products (Fig. 1).



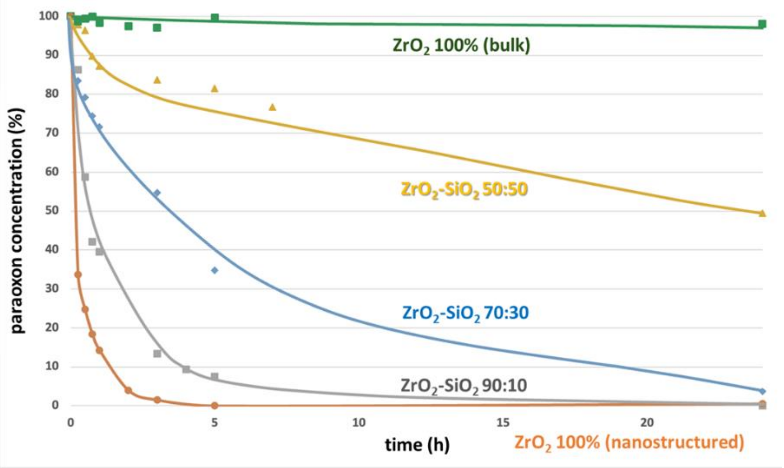


Fig. 1. Hydrolytic degradation of paraoxon over Zr-Si mixed oxides Reaction conditions: 220 ppm paraoxon; 40 mg catalyst; anhydrous AcOEt; 293 K; 1 bar

Nanostructured catalysts with high contents in ZrO_2 showed optimal performance and paraoxon was completely and selectively degraded into non-noxious derivatives with half-life times in the order of 15-30 min. Commercial bulk ZrO_2 showed virtually no activity under the same conditions. The most active ZrO_2 catalyst was successfully recovered and reused in a new catalytic cycle up to 3 times, with a full recovery of its performance after a mild rinsing in polar solvents.

A clear correlation between the conversion of the pollutant and the amount of surface acid + basic sites on the catalysts was observed. The results evidenced a remarkable joint action of acid and, especially, basic sites in organophosphate hydrolysis. This study paves the path to a better understanding of the role of surface Zr-O-Zr-like aggregates at the surface of zirconia-containing oxides and the synergistic effect of both acid and basic sites in the catalytic safe and sustainable degradation of organophosphorus pollutants and contaminants.

References

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