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Hydrodechlorination of organic compounds over modified palladium catalysts

Abstract

Catalytic hydrodechlorination is economically and environmentally attractive method of transformation of halogenated hydrocarbons to useful chemicals. Among metals, palladium seems to play the most important role in Cl removal from organic compounds. However, high reactivity of hydrogen on these catalysts usually leads to formation of less desired from economical point of view, of fully hydrogenated products. The thesis describes various effects of addition of Pt, Co, Cu, Au, Ni and Si to palladium catalysts on the catalytic activity and selectivity to C_2H_4 and CH_2F_2 in 1,2-dichloroethane and dichlorodifluoromethane hydrodechlorination, respectively.

The theoretical part of the thesis contains:

- Description of the physicochemical properties and toxicity of the most important halogenated organic compounds
- Different aspects of the hydrodechlorination of volatile organic compounds
- Short characteristic of the methods used for the characterization of catalysts.

The experimental part of the thesis contains the preparation of silica-, alumina- and active carbon-supported catalysts and the methods applied to characterise the catalysts: temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), TPHD, temperature-programmed hydrogenation (TPH) and chemisorption.

It was confirmed that modification of supported palladium catalysts by addition of a second metal such as 9(VIII B)–Co, 10(VIII B)–Ni and Pt, 11(II B)–Au and Cu, 14(IV A)–Si changed their catalytic activity and/or selectivity. Doping palladium with those metals brought about several synergistic effects. For example it was discovered that Pd-based catalysts after addition of Cu were the most efficient in hydrodechlorination of 1,2-dichloroethane. The very high selectivity to C_2H_4 on copper- rich bimetallic catalysts was correlated with the effect of copper surface segregation and affinity to chlorine.

The addition of the small amounts of platinum to 1%Pd/ Al_2O_3 leads to increase of catalytic activity in 1,2-dichloroethane and dichlorodifluoromethane hydrodechlorination, respectively. The Pd-Pt catalysts were also more selective to CH_2F_2 which is desired reaction product.

Sibunit carbon-supported nickel catalysts proved to be an active, stable and selective in conversion of 1,2-dichloroethane to ethene at low temperatures of reaction ($\leq 230^\circ C$). The highest ethylene selectivities ($\sim 100\%$) were observed for the catalyst prepared from nickel nitrate. The overall behavior of the above mentioned catalysts creates suitable objects for further low temperature hydrodechlorination studies in order to improve the selectivity to more desired unsaturated compounds.