Hydrodechlorination of polychloro-benzenes and polychlorinated aliphatic compounds under mild conditions by Pd and Rh ions or their complexes intercalated in γ-zirconium phosphate

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The catalytic activity of γ-zirconium hydrogen phosphate (γ-ZrP) containing either naked ions (γ-ZrP-M; M =Pd, Rh), or the metal N,N'-diamine complexes (γ-ZrP-M-L; L = 2,2'-bipyridil, 1,10-phenantroline), or also intercalated octadecyltrimethylammonium ions (γ-ZrP-M-C18) in the hydrodechlorination of monochloro- and polychloro-benzenes and polychlorinated aliphatic and aromatic compounds was studied. The influence of the reaction conditions on the catalytic activity as well as on the stability and recycling of different materials over time is reported and discussed.

Results and discussion

The above mentioned materials effectively catalyse the hydrodechlorination of polychlorinated compounds (reaction 1) under mild condition (T=30-70°C; P_{H2}= 1 atm) in methanol or in aqueous solution containing an organic or inorganic base

$$C_6H_{(6-x)}Cl_x + xH_2 \longrightarrow C_6H_6 + xHCl \qquad (1)$$

The halogenation process was quite effective with 100% conversion.

The progress of the reactions was monitored both by gas-chromatography and by the volume of reacted hydrogen. The titration of formed HCl confirmed the stoichiometry of the reaction

The catalytic activity depends on the added base and the metal system intercalated. The best results were obtained using NEt_3 as base and Pd-system.

Materials containing palladium naked ions exhibit an high catalytic activity at the start of the reaction, all others γ-ZrP-systems, including those containing palladium co-ordinated to intercalated ligands, show an activity that increases over time and reaches a maximum within 3-5 h. This trend is in agreement with the fact that the catalytically active sites are not the initial intercalated metal ions, but their reduced species produced by interaction with molecular hydrogen (reactions 2-4)

$$\gamma\text{-ZrPd(II)}_x\text{H}_{(2-2x)}(\text{PO}_4)_2 + x\text{H}_2 \longrightarrow \gamma\text{-ZrPd(0)}_x\text{H}_2(\text{PO}_4)_2 \qquad (2)$$

$$\gamma\text{-ZrRh(III)}_x\text{H}_{(2-3x)}(\text{PO}_4)_2 + x\text{H}_2 \longrightarrow \gamma\text{-ZrRh(I)}_x\text{H}_{(2-x)}(\text{PO}_4)_2 \qquad (3)$$

$$\gamma\text{-ZrRh(I)}_x\text{H}_{(2-x)}(\text{PO}_4)_2 + 1/2x\text{H}_2 \longrightarrow \gamma\text{-ZrRh(0)}_x\text{H}_2(\text{PO}_4)_2 \qquad (4)$$

The protons generated in the reductive process remain in the matrix bonded to PO_4 groups for the electroneutrality of the materials. The resulting HPO_4 groups could interact with reduced metal centres, Pd° or Rh°, with formation of an hydrido species.

Palladium materials were much more active than the corresponding rhodium compounds. This different reactivity could be attributed to the greater versatility of palladium compounds to promote the cleavage of carbon –chlorine bond, as the hydrodechlorination process would involve the oxidative addition of chloro compounds to the reduced form of metal, followed by reductive elimination upon interaction with molecular H_2.

The presence of intercalated ligands, dipy or phen, causes a decrease of catalytic activity both for palladium and rhodium materials but improves their stability.

The stability of compounds was monitored following the TOF, expressed as mol of choro-carbon reacted per mol^{-1} of metal per h^{-1}, over time and after recycling of catalysts. The results show that the activity remains almost constant within the first 3 cycles, then a decrease occurs which intensity depends on the metal and intercalated ligand. The decrease was higher for Pd-materials. After seven cycles the TOF was about 55% lower than the initial, for materials contained Pd-naked ions, while a decrease of about 40% was observed for the corresponding Rh-materials. With bipy and phen ligands the decrease of activity was reduced and resulted to be 40% for γ-ZrPPd-bipy and by 30% for γ-ZrPPd-phen.

For the analogue Rh-compounds the observed decrease of activity after seven cycles was 30% for γ-ZrPRh-bipy and by 20% for γ-ZrPRh-phen.

The reactivity of materials with intercalated octadecyltrimethylammonium ion was quite different. Their initial activity was lower than that of the corresponding materials with naked ions but higher than that with intercalated dipy and phen..

We have also recorded the XPS-spectra before and after the use of materials in order to have information about the oxidative state of metal, that allowed to establish that the catalytic active sites are metal centres in a reduced state.

Acknowledgement s - The authors wish to thank MURST (Progetto di Interesse Nazionale MM0327791- 2000) and INCA (Project L. 488) for financial support .