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Synthesis, Characterisation and Activity Testing of Titanium-Containing Zeolite Systems of the MFI-type

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The successful design of titanium silicalite, TS-1, by Enichem as an oxidation catalyst for environmentally benign industrial oxidation reactions with hydrogen peroxide, comprises one of the most important innovations in heterogeneous catalysis over the last thirty years. The unique performance of this MFI-type zeolite catalyst, which is isomorphous with the ZSM-5 zeolite and silicalite-1, is attributable to the specific features of isolated Ti^{4+} active sites incorporated in the silica structure of the zeolite framework.

This paper, describes the synthesis, characterization and activity-testing of a series of Ti-silicalite catalysts (TS-1) using the hydroxylation of phenol as the test reaction. In addition, high-silica ZSM-5 zeolites and silicalite-1, comprising isomorphous zeolite systems were also produced and characterized and their textural and structural properties were compared with those of the TS-1 zeolite. For characterization, the zeolite nano catalysts were analyzed with XRD, SEM, TEM, FTIR, and UV-vis. The spatial distribution of the titanium and silicon in the TS-1 micro particles was studied with EDS. The rate of Si:Ti in the TS-1 was 24. Finally, N_2-adsorption isotherms were obtained, in order to determine the textural properties of the nano catalysts. The TS-1 catalysts designed and tested by our team demonstrated significant catalytic activity and high selectivity for the hydroxylation reaction of phenol to hydroquinone and catechol. The selectivities obtained were dependent on the solvent used.

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Ch-Phosphorylation of Aromatic Substrates Involving Redox-activated Co, Ag, Mn, Fe, Ni and Their Complexes

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The aim of this work is to find new reactions capable to activate and transform catalytically inert C-H bonds in organic molecules to carbon-phosphorus functional groups using redox -activated metals Co, Mn, Fe, Ni and their complexes.

Within this work it was shown that the electrochemical activation of metal complex to M (III) oxidation state (apart from Ag) allows to add the dialkylphosphite to the aromatic substrates (benzene, pyridine, coumarine) successfully. Silver nitrate yields to monoalkylphosphonate in th same electrochemical conditions.

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Metalcomplex Catalysis in Synthesis of Biological Active Esters of the Isovaleric Acid

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Hydroalkoxycarbonylation of isobutylene with carbon monoxide and alcohols in the presence of catalytic systems based on Palladium Phosphin Complexes was applied for preparing of biological active isovaleric acid esters: l-menthylisovalerate (main active component of the spasmolytic medicine “Novovalidolum”), ethylisovalerate (intermediate product for obtaining sedative and spasmolytic medicines “Ethyl ether of α-bromisoveleric acid” (EEBIA) and “Corvololum-K”), cyclohexylisovalerate (bactericide and antifungus activity), benzylisovalerate (bactericide activity) and monoglyceryde of isovaleric acid (bactericide and antifungus activity).

Hydroalkoxycarbonylation reaction of isobutulene with carbon monoxide and alcohols (ethanol, cyclohexanol, l-menthol, benzyl alcohol, glycerol) in the presence Palladium Phosphin Complexes carried out at conditions: temperature 100^0C; CO pressure 2,0 MPa; reaction time 4 h. [1-3]. The yields of the products were 57,0-96,0%. The selectivity in linear reaction products was 100%. Such a high regioselectivity is apparently provided both by the structure of the starting alkene (isobutylene) and by the reaction mechanism. The most probable is a hydride mechanism.

New efficient technologies for preparation of drugs (Novovalidolum, EEBIA and Corvalolum-K) are based on isovaleric acid esters were worked out. Due to the more advanced technology of production the Medicines will have better qualitative characteristics. The cost of production of the Medicines with the use of new technologies is 2-3 times lower as compared to the medicines produced by existing at the present traditional technologies.

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Selective Hydrogenation of Hexanoic Acid to Hexanol under Mild Conditions over Titania-based Pt-Re Catalyst

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The Pt-ReO$_x$ species ($x \leq 1$) of atomic dispersion were formed and stabilized on the titania surface. Their size, charge and chemical composition were characterized by means of HRTEM/STEM with EDX mapping, XPS, FTIR. It was shown these centers with Re:Pt = 2 are highly active and selective in hydrogenation of carboxylic acid to alcohol under very mild conditions (T = 110°C, P = 50 bar). The reaction rate constant for hydrogenation of hexanoic acid increased linearly with Pt content. As for *Ru-NPy* pair in homogeneous pincer-type complexes, the neighboring *Pt-O* atoms form a similar pair capable to dissociate H_2 heterolytically with generation of Pt hydride to hydrogenate the carbonyl group of acid. Indeed, the TOF (40 h^{-1}) and selectivity (99%) are approaching those of homogeneous catalyst. The first order kinetic model described well the kinetic data obtained in a wide range of reaction conditions.