METAL-CARBON NANOCOMPOSITE SYSTEMS WITH ADJUSTABLE SELECTIVITY FOR CHLOROBENZENE TRANSFORMATIONS

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Hydrodechlorination is the only way to utilize chlorinated wastes without dioxins formation. This technique is environmentally safe, appropriate for wide range of chlorinated organic substances, makes it possible to recuperate hydrocarbon moiety or perform partial dechlorination to obtain desirable products. The development of the new selective catalysts for this process is the urgent task.

In this work contactless levitation melting together with hydrocarbon decomposition was used to produce nano-sized carbon-covered particles of Ni, Fe, Pd, and NiPd. The nanocomposites produced were investigated by TEM, XPA, DTA, TPR and magnetic methods and tested as the catalysts in vapor-phase continuous-flow transformations of chlorobenzene in fixed-bed reactor at 50-350°C.

Physical-chemical investigation have demonstrated that nanocomposites consist of metal particles covered by the shell of layered carbon. The particles are dispersed very uniformly, average diameter is in the range of 3-12 nm, depending on the metal nature. Carbon shell prevents metal nanoparticles from aggregation and oxidation during storage on air.

On the other side carbon shell doesn't hinder from the catalytic performance of nanocomposites. The row of activity in hydrodechlorination of chlorobenzene is Pd@C ≈ NiPd@C >Ni@C>5%Ni/UDD>Fe@C (T_{50} are <50, <50, 170, 260 and >350°C, respectively). On Pd@C the only product is cyclohexane at the T>75°C; on Ni@C at 50-300°C only benzene is formed, and in the presence of PdNi@C the selectivity changes as the reaction temperature raises: at 150-200°C the only product is cyclohexane, at higher and lower temperatures benzene predominates in effluent gas.

Ni nanocomposites demonstrate high stability: repeated three times temperature rise up to 350°C and decrease down to 50°C doesn't lead to the decrease in activity. Carbon shell remained in the composites after 3 temperature cycles.

Preliminary mechanism of the reaction is proposed, that includes activation of H_2 on metal core and chlorobenzene on carbon shell with spill-over of hydrogen moieties to the adsorbed chlorobenzene where reaction proceeds. The surface of metal core is enriched by Pd in PdNi@C nanocomposites, so the selectivity corresponds to Pd@C at low temperatures. Rising the temperature in HCl containing atmosphere leads to the enrichment of the core surface by Ni with simultaneous decrease of benzene adsorbtion strength, so benzene formation predominates at the middle temperatures.

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