ACTIVATION OF HETEROGENEOUS CATALYSTS BY ORGANOALUMINIUM COMPOUNDS

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The catalytic (benzene hydrogenation) and adsorption (O\textsubscript{2}, CO) properties of NiO/Al\textsubscript{2}O\textsubscript{3} and Ni(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} reduced by trimethylaluminium and hydrogen have been studied. Significant differences in their catalytic and adsorption properties have been observed. The increased hydrogenation activity of catalysts reduced by trimethylaluminium is due to the increased reduction degree and dispersity of the active component.

It has been established previously /1/ that heterogeneous complex organometallic catalysts, whose specific activity is not lower than those of their homogeneous analogues /2/, are significantly more stable in the hydrogenation of aromatic hydrocarbons.

The aim of this work is to study the nature of activation of heterogeneous hydrogenation catalysts by aluminium alkyls. NiO/\gamma-Al\textsubscript{2}O\textsubscript{3} and Ni(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} in combination with Al(CH\textsubscript{3})\textsubscript{3} were chosen as the objects of investigation. The properties of these catalysts are compared with those obtained through reduction of Ni by H\textsubscript{2}.
The samples will be referred to as follows:

- Sample 1 - NiO/Al₂O₃ reduced by hydrogen;
- Sample 2 - NiO/Al₂O₃ treated by Al(CH₃)₃;
- Sample 3 - Ni(C₅H₇O₂)₂/Al₂O₃ reduced by hydrogen;
- Sample 4 - Ni(C₅H₇O₂)₂/Al₂O₃ treated by Al(CH₃)₃;
- Samples 5 and 6 - Al₂O₃ treated by 3.4x10⁻³ and 1.5x10⁻³ mol Al(CH₃)₃, respectively. The content of nickel in samples 1, 2 and 3, 4 equals 5.1 and 2.2 wt%, respectively.

The preparation of catalysts for the study of O₂ and CO adsorption and the specific activity was carried out in a device permitting gas volumetric measurements too.

1 g NiO/Al₂O₃ catalyst (8.5x10⁻⁴ mol Ni) or Ni(C₅H₇O₂)₂/Al₂O₃ catalyst (5.7x10⁻⁴ mol Ni) was placed into an argon-flushed reaction vessel, then 10 ml benzene and heptane solutions of Al(CH₃)₃ (3.4x10⁻³ and 1.5x10⁻³ mol Al(CH₃)₃ for NiO/Al₂O₃ and Ni(C₅H₇O₂)₂/Al₂O₃, respectively) were added.

The reaction mixture was agitated for 20 min, the liquid phase separated, and the sample dried (150°C, 1 hr). Then the volume of gas evolved (V₁, see Table 1) was determined, the liquid was transferred to another vessel and decomposed by alcohol to determine the number of methyl groups V₂ (see Table 1) and the concentration of the organoaluminium compounds in the solution.

The quantity of Al(CH₃)₃ that reacted with the carrier hydroxyl groups, the nickel compounds and the adsorbed catalysts was determined from the difference between the quantity of Al(CH₃)₃ taken and that of Al(CH₃)₃ found in the liquid phase.

The number of methyl groups bonded with the organoaluminium compound on the catalyst surface was determined from the volume of methane, V₃, formed during treatment of the catalyst with 20% NaOH solution (see Table 1). The total balance...