SYNTHESIS AND PROPERTIES OF COMPOSITE CATALYSTS CONTAINING Pd AND Ho₂O₃ PARTICLES IN PORES OF CARBON CARRIER

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Received October 15, 1990
Accepted January 10, 1991

Specific activity (TOF) of the catalysts prepared through the interaction of C₃H₅PdC₅H₅ with the surface of evacuated Ho₂O₃/C is two orders of magnitude higher compared to that of Pd/C in the synthesis of both CH₃OH and CH₄. Deactivation data suggest that CH₃OH and CH₄ are formed on different active sites.

Lanthanide oxides (LnₓOᵧ) are known to be the most favorable supports for Pd catalysts for CO hydrogenation, since they permit to increase both specific activity (turnover frequency TOF, s⁻¹) and selectivity of CH₃OH synthesis [1]. But an essential disadvantage of LnₓOᵧ is their low surface area (3-30 m²/g) and insufficient stability to sintering [2,3]. In recent times convincing evidence has been obtained from experimental data for the hypothesis that CH₃OH formation on Pd/LnₓOᵧ takes place on heteroatomic active sites on the metal-support interface [2-7]. The concentration of these sites would, apparently, in-
crease with increasing dispersity of both metal and support.

As is known, the highest promoting effect on Pd/SiO₂ activity in the synthesis of CH₃OH is observed for lanthanides localized approximately in the middle of each half-period, namely Pr and Ho ions [6]. To stabilize the highly dispersed state of Ho₂O₃, we have used a carbon support whose surface has chemical properties radically differing from those of oxides. Catalysts were prepared through the interaction of C₃H₅PdC₅H₅ with Ho₂O₃/C.

EXPERIMENTAL

Mesoporous carbon material with graphite-like structure, Ar adsorption surface area 600 m²/g, predominant pore radius 400 Å, pore volume 0.8 cm³/g and ash content below 0.5 wt.% [8] was used as a support.

Ho₂O₃/C samples were prepared by the incipient wetness method through the impregnation of the carrier with a water solution of HoCl₃·6H₂O, subsequent sedimentation of Ho(OH)₃ in the support pores by excess aqueous NH₄OH, washing and drying at 373 K. Then Ho₂O₃/C were evacuated at 673-973 K up to 10⁻⁴ torr.

Pd/Ho₂O₃/C catalysts were obtained through the interaction of C₃H₅PdC₅H₅ in pentane with the surface of Ho₂O₃/C with subsequent washing and drying in vacuum. Then catalysts were reduced by H₂ at 573 K or treated by air at 573 K for the complete removal of organic ligands with subsequent reduction by H₂ at 573 K. For comparison, a 2.1% Pd/C catalyst was obtained through C₃H₅PdC₅H₅ interaction with the surface of carbon support like in Ref. [7].

Palladium dispersity was measured in a flow pulse installation by chromatographic analysis, using hydrogen titration (HT) at 373 K, assuming the stoichiometry of HT = 3 [9].

Ethane hydrogenolysis was carried out in a static circulation reactor at T = 573-623 K, P_C₂H₆ = 50 torr, P_H₂ = 150 torr like in Ref. [4].

CO hydrogenation was performed in a copper flow reactor at