

Novel Pd-Hydrotalcite Clays as Highly Selective Catalysts in Alkyne Semihydrogenation under Mild Conditions

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Introduction

There is a growing interest in the preparation methods of noble metal nanoparticles distributed inside layered-structure host materials such as hydrotalcite-type (HT) clays [1,2]. The structure of the HT compounds consists of a positively charged brucite-like octahedral layer and a negatively charged interlayer containing inorganic anions and water molecules [3]. The pronounced anion-exchange capacity of HT-like materials allows replacement of the interlamellar anions by others, including long-chain organic anions [4,5]. The current study describes a novel synthetic method for the preparation of finely dispersed Pd particles, stabilized by anionic surfactant molecules, in a HT clay host. The Pd-HT samples were tested as catalysts for the liquid-phase hydrogenations of substituted alkynes.

Experimental

Surfactant-stabilized Pd nanoparticles were prepared via solubilization of the precursor Pd(acac)₂ by the anionic surfactant sodium dodecyl sulfate (Na⁺DS⁻) and its subsequent reduction by aqueous hydrazine. On addition of this Pd hydrosol to an aqueous suspension of HT⁺NO₃⁻ under stirring, a hydrophobic clay-organocomplex was formed through anion exchange and the released Pd particles were incorporated in the organoclay host. The above procedure ensured the formation of low-loaded Pd-organoclays, of which two samples (Pd-HT1 and Pd-HT2, with metal contents of 0.1% and 0.4%, respectively) were subjected to further investigations. The characterization of Pd-HTs was performed by XRD and TEM measurements. Hydrogenations for the reactants phenylacetylene, 4-octyne and 1-phenyl-1-pentyne were carried out in an automated liquid-phase vibration reactor at 298 K and 10⁵ Pa.

Results and discussion

The increased basal spacings of Pd-HTs as compared with that of the pristine organoclay suggested that part of the Pd content was intercalated between the clay lamellae. TEM images revealed the formation of quasi-spherical, monodispersed Pd nanoparticles for both samples and the mean particle diameters for Pd-HT1 and Pd-HT2 were 2.3 nm and 3.4 nm, respectively. The size and the shape of the substrate were of crucial importance in determining the activity of the Pd-HT samples. The apparent substrate size dependence, possibly related to steric effects of reactant adsorption, may be attributed to the presence of intercalated Pd

crystallites. For all reactants, the catalytic activity of Pd-HT1 proved to be superior to that of Pd-HT2.

For the transformation of phenylacetylene, a marked catalytic activity on Pd-HT1 was experienced. The reactant was hydrogenated to styrene with 100% selectivity up to a conversion of 90%, when ethylbenzene formation was first observed. Investigation of the solvent effect revealed that the best catalytic performances could be obtained by applying the solvents THF, toluene or n-hexane.

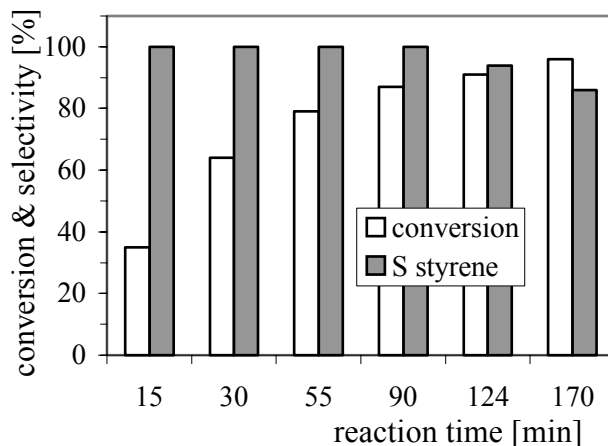


Figure 1. Hydrogenation of phenylacetylene on Pd-HT1

For the reactants 4-octyne and 1-phenyl-1-pentyne, stereoselective semihydrogenation took place on Pd-HTs, with the predominant formation of the *cis*-alkene stereoisomers. The catalytic activities for the hydrogenation of 4-octyne were considerably higher than those obtained for the aromatic alkyne, which suggested the participation of intercalated Pd particles in the above reactions. Overhydrogenation of 1-phenyl-1-pentyne was found to be more pronounced than that of 4-octyne. For the latter, the selectivity of octane was rather low (3-4%), irrespective of the reaction time. Further, no *trans*-alkene formation on Pd-HT1 could be observed. In the transformations of 1-phenyl-1-pentyne and 4-octyne, the *cis*-alkene stereoselectivities were in the range 86-93% and 94-97%, respectively. The novel Pd-HT samples may therefore be regarded as highly stereoselective catalysts.

References

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