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HYDROGENATION OF BENZENE TO CYCLOHEXANE CATALYZED
BY RHODIUM(I) COMPLEX SUPPORTED ON
MONTMORILLONITE CLAY

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$[\text{Rh}(\text{I})\text{PPh}_3]^+$ intercalated in the interlamellars of montmorillonite clay catalyzes the hydrogenation of benzene to cyclohexane at 70°C and 20 atm hydrogen pressure.

$[\text{Rh}(\text{I})\text{PPh}_3]^+$, добавленный к прослойкам глины монтмориллонита, катализирует гидрирование бензола до циклогексана при 70°C и давлении водорода - 20 атм.

INTRODUCTION

Hydrogenation of benzene to give cyclohexane selectively is an industrially important problem. Cyclohexane is used in making caprolactam, a nylon precursor, and is mainly obtained by the hydrogenation of benzene using catalysts based on nickel, palladium or platinum at 20-30 atm pressure and 300-350°C [1, 2]. High temperature hydrogenation of benzene in liquid or vapor phase does not provide pure cyclohexane as the temperature is above 200°C and in this process the equilibrium is shifted in

favor of formation of benzene and the isomerization product methyl cyclopentane, which becomes critical in meeting a typical specification of less than 500 ppm benzene content in the final products. Therefore, the problems faced in the conventional process of benzene hydrogenation necessitated to develop new catalyst systems based on transition metal complexes, which have been proved to be effective catalysts giving selective products in many reactions under milder conditions.

Hydrogenation of aromatic cyclic arenes such as benzene, naphthalene and anthracene were found to be catalyzed under milder reaction conditions by soluble rhodium and ruthenium complexes to give the corresponding monocyclic arenes [3, 4]. However, benzene hydrogenation to give cyclohexane catalyzed by complexes supported on montmorillonite clay has not been reported in the literature.

In this Laboratory, the ruthenium complex $\text{RuCl}_3(\text{AsPh}_3)_2$ MeOH supported on montmorillonite clay by adsorption method was found to be an effective heterogeneous catalyst for the hydrogenation of jojoba and castor oils under ambient conditions [5]. Similarly, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ adsorbed on montmorillonite clay catalyst was prepared, and spectroscopic characterization by NMR, XPS and EPR revealed that this species is intercalated in the interlamellar layers of the clay [6]. Therefore, we investigated $[\text{Rh}(\text{I})(\text{PPh}_3)_3]^+$ /montmorillonite for its catalytic activity in the liquid phase hydrogenation of benzene to give cyclohexane at 70°C and 20 atm hydrogen pressure. The turnover number was 2.0 mol of cyclohexane per mol of catalyst per hour.

EXPERIMENTAL

Montmorillonite clay obtained from Fluka A.G. had the chemical composition (wt.%) SiO_2 (70%), Al_2O_3 (15%), Fe_2O_3 (1.5%), CaO (2.5%) MgO (3.0%), Na_2O (0.5%), K_2O (1.5%), loss on ignition (6%). It was used in preparing the $[\text{Rh}(\text{I})(\text{PPh}_3)_3]^+$ loaded catalyst. The method described elsewhere [6] was followed to prepare the loaded catalyst. It was found by the gravimetric estimation of Cl^- released from $\text{RhCl}(\text{PPh}_3)_3$ as AgCl that

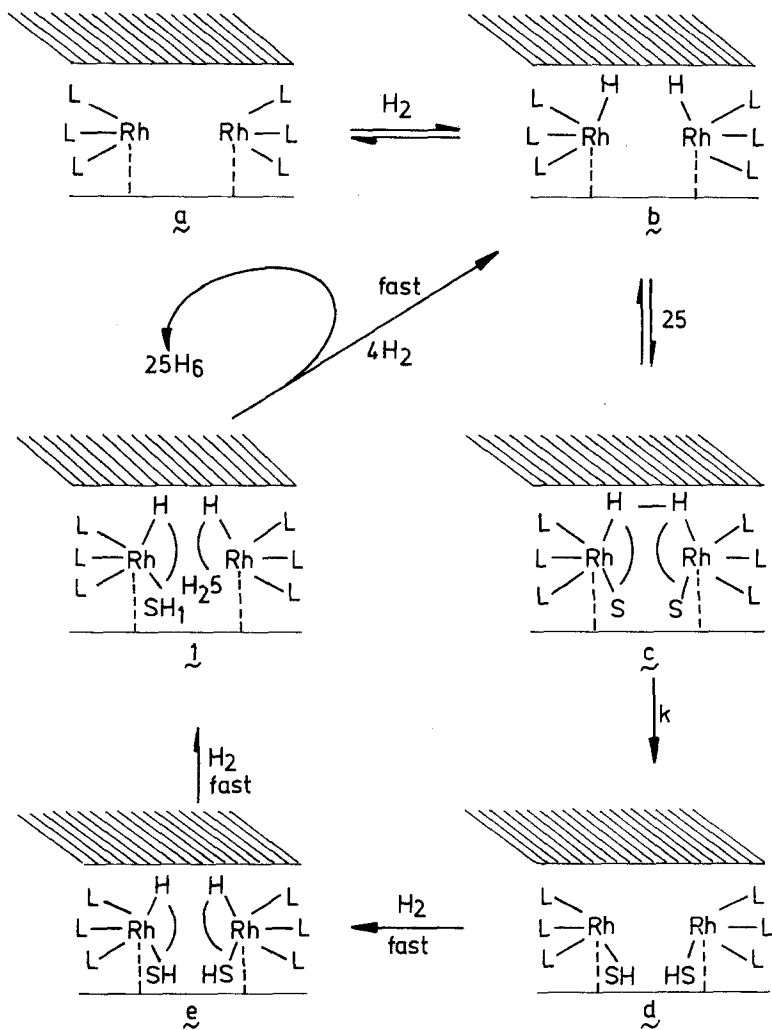
85 mg of complex was present per gram of clay. The powdered X-ray diffraction pattern of the intercalated complex showed based region expansion (001) from 9.5 to 17.65 Å of dehydrated montmorillonite. The complex adsorbed in the hydration layers of the clay as the cationic species $[\text{Rh(I)}(\text{PPh}_3)]^+$ was confirmed by NMR, XPS and EPR spectroscopy [6].

High pressure benzene hydrogenation experiments were conducted in a 300 ml Parr pressure reactor. 1 g of loaded catalyst containing 85 mg of rhodium complex suspended in 50 ml benzene (A.R. grade) was placed in the reactor. The bomb was pressurized to the desired hydrogen pressure when the temperature attained 70°C. The progress of the reaction was monitored by estimating the amount of cyclohexane formed by ^{13}C NMR and GC measurements in time. The amount of benzene converted into cyclohexane after 12 h was 4.2%, resulting in a turnover frequency of 2.0 mol product per mol catalyst per hour.

RESULTS AND DISCUSSION

The mechanism proposed for the hydrogenation of benzene catalyzed by $[\text{Rh(I)}(\text{PPh}_3)_3]^+$ /montmorillonite catalyst to give selectively cyclohexane is as shown in Scheme 1.

Complex 1 interacts with H_2 in a preequilibrium step to form a monohydrido Rh^{II} complex b. The formation of the cationic Rh(II) hydrido complex $[\text{Rh}^{\text{II}}(\text{PPh}_3)_3\text{H}]$ (b), which is the actual catalytic species was confirmed by its IR and EPR spectra. The IR spectra of b showed a single peak at 2028 cm^{-1} , confirming (Fig. 1) the formation of a monohydrido complex. The EPR spectrum of b at room temperature gave a broad signal centered at $g_{\text{iso}}=2.3$. However, at 77 K, the compound gave a signal resolved into three components $g_1=2.49$, $g_2=2.34$ and $g_3=2.2$. The EPR of Rh(II) observed [5] for the $\text{Rh(II)}-\mu$ -peroxo complex in montmorillonite clay gave $g_{\perp}=2.03$, $g_{\parallel}=1.98$ with $g_{\text{av}}=2.01$. From this one can conclude that hydrogen reacts with a in the clay lattice to form the $\text{Rh(II)}-\text{H}$ species b. The Rh^{II} hydride b interacts with the substrate benzene to form a mixed ligand



where L = triphenylphosphine
 S = benzene, SH₂ = cyclohexadiene
 SH₄ = cyclohexene, SH₆ = cyclohexane.

Scheme 1

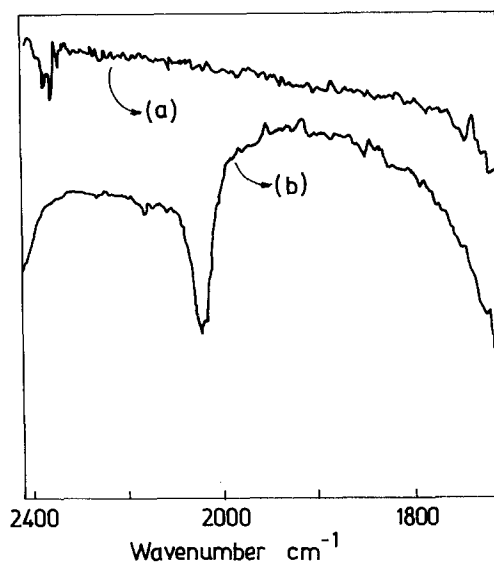


Fig. 1.

metal-olefin-hydrido complex c. Hydride transfer the metal-olefin bond takes place in the rate-determining step to give intermediate complex d. Species d reacts with molecular hydrogen in a fast step to give intermediate dihydrido mixed ligand complex e. The intermolecular hydride transfer and intramolecular hydride addition in the presence of molecular hydrogen takes place in a fast step to give metal-olefin (SH_2 =cyclohexadiene) dihydrido intermediate complex f. The complex f being unstable, it rapidly undergoes transformation into catalytically active species h by interacting with four moles of molecular hydrogen to give one mole of cyclohexane. Stoichiometrically 1 mol of benzene requires 3 mol of hydrogen to give 1 mol of cyclohexane.

The turnover number obtained for hydrogenation of benzene using $[\text{Rh}(\text{I})(\text{PPh}_3)_3]^+$ /montmorillonite catalyst at 70°C and 20 atm of H_2 is 2.0 mol of cyclohexane per mol of catalyst per hour, which is less in comparison with similar homogeneous catalyst systems. The homogeneous rhodium catalyst $[\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ catalyzed the hydrogenation of deuterated benzene to the corresponding cyclohexane in the presence of triethylamine at

50°C and 5 atm with a turnover number of 6 [4]. The ruthenium complex $[\eta^6\text{-C}_6\text{Me}_6]\text{Ru}(\text{H})(\text{Cl})(\text{PPh}_3)$ catalyzed the hydrogenation of benzene to give cyclohexane at 46 atm H_2 and 50°C with a turnover number of 5 mol product per mol catalyst per hour [7]. Supported catalyst system is more attractive from the commercial viewpoint due to the easy separation of the catalyst from the reaction product and facile handling of the system.

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