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CATALYTIC PROPERTIES OF GROUP VIII METAL COMPOUNDS ON POLYMER SUPPORTS

COMMUNICATION 1. PALLADIUM COMPLEXES ON SUPPORTS CONTAINING OXYGEN-BASED

COORDINATING GROUPS IN THE HYDROGENATION AND ISOMERIZATION OF ALLYL BENZENE

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Coordination complexes of transition metals immobilized on or in polymer supports have recently attracted considerable attention for use as catalysts in many chemical processes. For instance, NaBH_4 -treated PdCl_2 on polyvinylpyrrolidone and polymer-bound complexes of Ti, Zr, and Hf [1, 2] catalyze the hydrogenation of olefins, and gel-immobilized Ni-containing systems are active in the dimerization and polymerization of olefins [3, 4].

The present work is devoted to studying the hydrogenation and isomerization of allylbenzene (AB) in the presence of Pd complexes immobilized on polymer supports with O-containing coordinating groups, viz., $-\text{OPh}$, $-\text{COOH}$, and $-\text{OH}$.

EXPERIMENTAL

The starting materials for preparing the polymeric catalytic systems (PCS's) were poly-1,2-butadiene (PB-1,2), poly-1,4-butadiene (PB-1,4), and ethylene/propylene/diene terpolymer (EPD) synthetic rubber. These were first purified by precipitation from acetone. Acrylic acid (AA) and allyl alcohol (AOH) were grafted by radical copolymerization [3]. The polymer support containing OPh was prepared by iodinating the polymer and then treating it with NaOPh .

To prevent the PCS particles from becoming dispersed under the reaction conditions, the polymer supports were crosslinked in the presence of benzoyl peroxide. The supports were treated under static conditions in the swollen state with a solution of PdCl_2 in a dry solvent ($\text{C}_6\text{H}_6:\text{MeOH}$ 61:39). The resulting PCS's were carefully freed of excess uncomplexed PdCl_2 in a Soxhlet apparatus (monitored spectrophotometrically) and then dried under vacuum. The proportion of coordinating groups in the PCS's was 10%.

The conversion of AB in the presence of the PCS's was studied at 25°C and atmospheric H_2 pressure in a thermostatted long-necked hydrogenation flask. The experiments were performed using 0.1–0.2 g of the PCS ($1\text{--}2\cdot 10^{-5}$ g-atom of Pd), $1\cdot 10^{-2}$ mole of AB, and $5\text{--}10\cdot 10^{-3}$ mole of NaBH_4 . The reaction rate was assessed by the change in H_2 volume, and the composition of the reaction mixture was determined by GLC analysis of a sample of the catalysate using a Khrom-41 chromatograph with a flame-ionization detector and a column of length 2.5 m and diameter 3 mm containing a stationary liquid phase comprising 15% PEG 4000 and 0.5% KOH on Celite 545, the analysis being performed at 130°C using ethylbenzene as internal standard.

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TABLE 1. Physicochemical Properties and Catalytic Activity of Pd-Containing PCS's in the Hydrogenation and Isomerization of AB

Polymeric catalytic system	Polymer support	Swellability in C_6H_6 , ml/g	Solvent, C_6H_6 :MeOH	AB conversion rate, mole AB/g-atoms Pd per min			Propenyl-benzene cis:trans ratio	Pd content, %
				hydrogenation	isomerization	total		
1	PB-1,2-OPh	8	9:1	0,5	0,33	0,83	0,66	1,0
			5:5	1,27	1,33	2,6	0,51	
			1:9	0,65	0,92	1,57	0,41	
2	EPD-OH	6	9:1	1,0	1,33	2,33	0,33	1,0
			5:5	0,58	0,54	1,12	0,45	
			1:9	0,45	0,57	1,02	0,42	
3	EPD-AA	5,5	9:1	0,49	0,09	0,58	0,35	4,9
			5:5	0,37	0,11	0,48	0,38	
			1:9	0,2	0,35	0,55	0,48	

The activity of the PCS's was assessed on the basis of the number of moles of AB undergoing hydrogenation and isomerization per g-atom of Pd per min.

DISCUSSION OF RESULTS

The PCS's (Table 1) did not exhibit catalytic activity after treatment with H_2 under normal conditions, but did exhibit such activity after treatment with a solution of $NaBH_4$ in MeOH, the color of the PCS particles changing from light-yellow or light-brown to dark-brown. The complex nature of the Pd-containing PCS's is confirmed by the fact that addition of thiophene (thiophene:Pd = 20:1) does not reduce their catalytic activity and that the hydrogenation of AB is accompanied by isomerization, whereas only insignificant isomerization of AB takes place in the presence of Pd black under the same conditions and the addition of thiophene completely suppresses the hydrogenation of AB [5].

It can be seen from Table 1 that the activity and selectivity of the PCS's are strongly influenced by the nature of the grafted coordinating groups and by the nature of the solvent. The Pd atoms in the PCS's may be coordinated by residual double bonds in the polymer support, by the electron-donor atoms of the grafted coordinating groups, or by a combination of these coordination centers. On the basis of the experimental data obtained, we may conclude that coordination takes place by the third variant in all the PCS's in the present case, since a change in the nature of the grafted coordinating groups results in a change in the catalytic properties of the PCS. Thus, the relative AB conversion rates (solvent C_6H_6 :MeOH = 5:5) in the series PCS-1, PCS-2, and PCS-3 are respectively 1, 0.41, and 0.18.

It is known that in the course of the catalytic act the metal atom undergoes a change in degree of oxidation due to additional coordination of the substrate molecule. By virtue of this, the ligands forming the coordination bond with the metal must play a dual role; they must exhibit electron-donor properties in order to coordinate the metal atom in its high oxidation state (especially Pd^{2+}), and they must exhibit electron-acceptor properties in order to stabilize the metal in its lower oxidation state. It may be supposed that PCS-1, which contains a -OPh group, will be capable of both supplying electrons to the Pd atom and withdrawing electrons from it on account of the phenyl substituent on the O atom coordinated to the Pd atom, thereby stabilizing it in its higher and lower oxidation states. As can be seen from Table 1, such a dependence does indeed occur in a solvent containing $\geq 50\%$ MeOH: the relative AB conversion rates decrease in the order PCS-1 > PCS-2 > PCS-3, with values of 1, 0.46, and 0.29, respectively, for hydrogenation and 1, 0.4, and 0.08, respectively, for isomerization. This sequence fits in well with the order in which the OPh, OH, and COOH groups are arranged with respect to their ability to exhibit simultaneously electron-donor and electron-acceptor properties.

Changes in solvent composition have different effects on the catalytic properties of the PCS's. Thus, when the MeOH content is increased from 0.1 to 0.5, the AB conversion rates on PCS-1 increase by a factor of 2.5 for hydrogenation and 4 for isomerization. Any further increase in MeOH content results in a decrease in the rates of both reactions. In the case of PCS-2, the maximum AB conversion rate in both reactions is reached at the minimum MeOH

content in admixture with C_6H_6 . Increasing the MeOH content to 0.5 sharply decreases the rates of both reactions by a factor of 2-2.5, and further increasing the MeOH content to 0.9 has practically no effect on the rates. In the case of PCS-3, increasing the MeOH content from 0.1 to 0.9 gradually decreases the hydrogenation rate and increases the isomerization rate, the overall AB conversion rate remaining practically constant.

All three PCS's are trans-stereospecific in isomerization: the trans-propenylbenzene content is 1.3-3 times that of the cis isomer, and the cis:trans ratio does not reach the equilibrium value (0.23 [6]). It is to be expected that the solvent composition will have considerably less influence on the ratio of the isomerization products than on the ratio of the hydrogenation and isomerization rates.

It should be pointed out that no isomerization of AB is observed in the absence of H_2 . This indicates that both reactions occur at the same centers, proceeding by a mechanism involving stepwise addition of an H_2 molecule [7].

CONCLUSIONS

1. Palladium complexes immobilized on a polymer support have been synthesized and their catalytic properties in the hydrogenation and isomerization of allylbenzene have been investigated.

2. The activity and selectivity of the polymer-containing catalytic systems are influenced by the electron-donor properties of the coordinating groups and by the nature of the solvent.

3. The isomerization of allylbenzene to propenylbenzene proceeds with preferential formation of the trans isomer in the presence of all the catalytic systems synthesized.

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