CATALYTIC PROPERTIES OF GROUP VIII METAL COMPOUNDS SUPPORTED ON A POLYMERIC CARRIER.

3. NICKEL AND COBALT COMPLEXES SUPPORTED ON CARRIERS CONTAINING COORDINATION GROUPS BASED ON PHOSPHORUS IN THE HYDROGENATION AND ISOMERIZATION REACTIONS OF ALLYLBENZENE

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Palladium [1] and iron [2] complexes supported on polymeric carriers effectively catalyze the hydrogenation and isomerization of allylbenzene (AB). The present paper is devoted to the study of the catalytic properties of Ni and Co complexes supported on a polymeric carrier containing phosphonate or phosphinate groups in the hydrogenation and isomerization reactions of AB.

EXPERIMENTAL

Polybuta-1,2-diene previously purified by reprecipitation from acetone was used for the synthesis of the polymeric carrier (PC). The synthesis of PC containing phosphonate and phosphinate groups was carried out analogously to [2]. The obtained PC were treated under static conditions with a solution of $NiCl_2$ or $CoCl_2$ in a mixture of benzene:ethanol:water = 74:19:7. Pure $NiCl_2$ and $CoCl_2$ were obtained by the procedure described in [3]. The synthesized polymeric catalytic systems (PCS) were washed from the excess respective metal chloride not bound to the complex in a Soxhlet apparatus and then dried in vacuum. Hydrogenation of AB was carried out analogously to [2], and GLC analysis analogously to [1].

DISCUSSION OF RESULTS

The synthesized PCS (Table 1) after treatment with H_2 under normal conditions, with an alcohol solution of $NaBH_4$, or with a solution of diisobutylaluminum chloride in heptane did not display catalytic activity but displayed it after treatment with a solution of diisobutylaluminum hydride (DIBAH) in heptane. By this the particles of PCS became dark-brownish and colored the liquid phase. Preliminary data of ESR spectroscopy of Ni−PCS showed the absence of a metallic Ni phase in the PCS after its treatment with a solution of DIBAH, which indicated the retention of the metal-complex nature of the catalyst during the treatment. Coloring of the liquid phase, as for the Fe-PCS of [2], is probably explained by the formation of a complex of an organoaluminum compound with that portion of the ions of the corresponding metal which went into solution on treatment of the PCS. The colored liquid phase did not display catalytic activity.

It is evident from a comparison of the properties of the synthesized PCS that the Ni−PCS exceeded the Co−PCS 5-50 fold in its activity. PCS-II containing phosphonate coordinating groups were more active than the corresponding PCS-I containing phosphinate groups, while in the case of both PCS-I and PCS-II the highest value of the reaction rate for the hydrogenation and isomerization of AB was achieved when hydroxycyclohexyl was the substituent on the P atom (see catalyst 1 and catalyst 4).

As in the case of Fe−PCS [2], the electron-accepting properties of the substituent on the P atom and the presence of a phosphoryl oxygen atom have a strong influence on the magnitude of the catalytic activity of the Ni−PCS. Thus, in the case of PCS-I the rate of hydrogenation of AB was reduced from 2.94 to 0.6 and the rate of isomerization of AB to propenylbenzene (III) was reduced from 0.56 to 0.14, depending on the increase in electron-accepting properties of the substituent on the P atom in the series $OC_6H_{11} < OCH_2PH < OPh$.

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TABLE 1. Catalytic Properties of the Synthesized Ni- and Co−PCS

PCS	Catalyst*	Coordinating group	Content in catalyst, %		Reaction time, min	Conversion, %	Selectivity, † %			Reaction rate, mole AB/g·at·M·min	
			metal, (M)	P			(IV)	(III)		hydrogenation	isomerization
								trans	cis		
I	1	$P(OC_6H_{11})_2$	2,3	2,9	120	84	87,1	12	8,9	2,94	0,56
	2	$P(OCH_2Ph)_2$	1,1	2,1	126	90	100	–	–	2,5	–
	3	$P(OPh)_2$	1,9	3,1	540	80	89,4	7,5	3,1	0,6	0,14
II	4	$PO(OC_6H_{11})_2$	1,8	2,4	66	90	92,9	4,7	2,4	6,1	0,67
	5	$PO(OCH_2Ph)_2$	1,2	2,3	75	96	95,3	3,2	1,5	6,1	0,3
	6	$PO(OPh)_2$	1,3	2,1	84	93	95	3,3	1,6	5,15	0,38
III	7	$P(OPh)_2$	1,9	3,1	600	18	64,8	25,2	10	0,1	0,05
	8	$P(OC_6H_{11})_2$	1,8	2,9	1200	18	100	–	–	0,075	–

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* Catalysts 1-6 contained Ni; catalysts 7-8 contained Co.

† On conversion of AB.

It is necessary to record that the content of isomer (III) and the rate of its formation was determined by the ratio of the rates of isomerization of AB to (III) and the hydrogenation of (III) to propylbenzene (IV).

In the case of PCS-II also the rate of conversion of AB fell along the series catalyst-4 > catalyst-5 > catalyst-6, depending on the increase in electron-accepting properties of the substituent on the P atom in the series of substituents indicated above. However, in this case the drop in the rate of hydrogenation of AB was insignificant, evidently because of the presence of a phosphoryl O atom which smoothed out the influence of the electronic properties of the substituent on the P atom. A similar relationship was also observed for Fe−PCS in [2].

It should be recorded that no isomerization of AB to (III) was detected in the presence of the considered PCS in an atmosphere of Ar.

CONCLUSIONS

1. Nickel and cobalt complexes supported on a polymeric carrier containing phosphinate or phosphonate groups catalyze the hydrogenation and isomerization of allylbenzene. Nickel complexes were more active than cobalt complexes.

2. A reduction in the electron-accepting properties of the substituent on the phosphorus atom promoted an increase in the catalytic activity of the synthesized systems. Complexes containing a cyclohexyloxy substituent on the phosphorus atom displayed the greatest activity.

LITERATURE CITED

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