CATALYTIC PROPERTIES OF GROUP VIII METAL COMPOUNDS ON POLYMER SUPPORTS

COMMUNICATION 2. IRON COMPLEXES ON SUPPORTS CONTAINING PHOSPHORUS-BASED COORDINATING GROUPS IN THE HYDROGENATION AND ISOMERIZATION OF ALLYBENZENE

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Complexes of Pd [1] and Fe, Ni, and Co [2, 3] immobilized on polymer supports effectively catalyze the hydrogenation and isomerization of allylbenzene (AB). The present work is devoted to studying the catalytic properties of Fe complexes on polymer supports containing phosphonate and phosphinite groups in the hydrogenation of AB.

EXPERIMENTAL

The starting materials for preparing the polymer supports were poly-1,2-butadiene (PB-1,2), poly-1,4-butadiene (PB-1,4), ethylene/proplyene/diene (EPD) terpolymer synthetic rubber, and their copolymers. These were first purified by reprecipitation from acetone.

The supports containing phosphinite groups were prepared by radical addition of PCl_3 to the double bonds of the polymer [4], and those containing phosphonate groups were prepared by treating the polymer with PCl_5 [5], after which the chlorine atoms were replaced by alkoxy groups. The supports were treated under static conditions in the swollen state with a solution of $FeCl_3$ in dry benzene. Anhydrous $FeCl_3$ was prepared as described in [6]. The resulting polymeric catalytic systems (PCS's) were freed of excess uncomplexed $FeCl_3$ in a Soxhlet apparatus (monitored by KSCN assay) and then dried under vacuum. In the case of the PCS's containing phosphinite groups, special care was taken to make sure that no oxidizing agents were present in the reaction medium. All reactions were performed in an Ar atmosphere and the solvents and liquid reagents used were first flushed with Ar.

The AB hydrogenation experiments were performed in a thermostatted long-necked hydrogenation flask at 25°C under an H_2 pressure at 1 atm. The flask was charged with 0.1-0.2 g

TABLE 1. Physicochemical Properties of PCS's and Their Catalytic Activity in the Hydrogenation of AB (solvent benzene)

Polymeric catalytic system	Catalyst	Polymer support		Content, %		Swellability in C_6H_6, ml/g	Al:Fe atomic ratio	Reaction rate, mole AB/g-atom Fe per min	
		polymer	coordinating group	P	Fe			hydrogenation	isomerization
I	1	EPD/PB-1,4	$P(OMe)_2$	2,3	1,7	12,2	29	0,05	–
	2		$P(O\text{-}i\text{-}Pr)_2$	4,0	3,4	10,5	17	0,37	–
	3		$P(O\text{-}t\text{-}Bu)_2$	3,4	3,3	10,8	13	0,2	–
	4		$P(OC_6H_{11})_2$	2,3	2,7	8,4	15	0,83	–
	5	EPD/PB-1,2	$P(OC_6H_{11})_2$	2,4	1,1	4,0	41	0,89	–
	6	EPD/PB-1,4	$P(OPh)_2$	2,4	3,4	12,0	14	0,18	–
II	7		$PO(OEt)_2$	2,1	1,2	12,0	43	0,5	–
	8		$PO(O\text{-}i\text{-}Pr)_2$	1,1	1,1	13,5	34	0,72	–
	9		$PO(OC_6H_{11})_2$	0,4	0,6	7,3	98	5,45	1,03
	10		$PO(OCH_2Ph)_2$	0,3	0,7	7,8	120	5,92	1,35
	11		$PO(OPh)_2$	0,4	0,5	11,5	66	4,75	1,42
	12	PB -1,2	--CH=CH–	—	1,1	6,0	12	0,78	–
	13	PB -1,2	OPh	—	1,1	9,0	14	1,23	–
	9*						52	1,05	0,07
	10*						53	4,21	1,32
	11*						51	3,33	0,76

*Reaction performed in absolute heptane.

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of the PCS (1-$5 \cdot 10^{-5}$ g-atom of Fe) and 10 ml of dry C_6H_6 or C_7H_{16}, and air was displaced by repeated flushing with H_2. The PCS granules were swollen from 0.5-1 h and then treated with a 15% solution of diisobutylaluminum hydride (DIBAH) in abs. C_7H_{16}, which was injected by means of a syringe previously flushed with Ar (see Table 1 for Al:Fe ratios). After 0.5-1 h, the flask was charged with $1 \cdot 10^{-2}$ mole of AB in admixture with ethylbenzene (internal standard). The reaction rate was determined from the amount of H_2 absorbed, and the composition of the reaction mixture was determined by GLC analysis of samples of the mixture [1].

DISCUSSION OF RESULTS

Yhe PCS's (see Table 1) exhibited no catalytic activity after treatment with H_2 under normal conditions, after treatment with an alcohol solution of $NaBH_4$, or after treatment with a solution of diisobutylaluminum chloride, in C_7H_{16}. Only after treatment with DIBAH was hydrogenation of AB observed, the color of the PCS particles becoming dark-brown and the liquid phase becoming colored. An extract of the colored liquid phase exhibited no catalytic activity, but the activated PCS remaining in the reactor retained its catalytic properties. A mechanical mixture of the polymer support, $FeCl_3$, and DIBAH exhibited no catalytic activity under otherwise identical conditions.

To study the stability of the PCS's we performed four successive experiments in which, after complete conversion of the AB, the whole reaction mixture was removed from the reactor, the PCS was washed with pure solvent, 10 ml of C_6H_6 was again added, and the experiment was repeated as above. It can be seen from Fig. 1 that the activity of the PCS decreases by a factor of two after the first experiment, after which it functions stably. It should be noted that the liquid phase is discolored only after the first treatment of the PCS with DIBAH and does not change color on successive treatments. Evidently, when the polymer support is treated with the $FeCl_3$ solution, the Fe^{3+} undergoes energetically nonequivalent coordination with at least two coordination centers. In the case of the present PCS's, these centers may be the grafted phosphonate and phosphinite groups as well as $-PO(OH)_2$ residues formed by partial hydrolysis of the grafted PCl_2 and PCl_4 groups (elementary analysis data show that the Cl:P molar ratio for all the polymer supports is 5-10% less than the calculated value). When the PCS is treated with the DIBAH solution, the Fe^{3+} is reduced to a lower oxidation state, whereby weakly bonded Fe ions will transfer into the liquid phase (which is probably the reason for the coloration of the liquid phase, possibly due to the formation of complexes with organoaluminum compounds). The remaining Fe ions have the most favorable coordination and stabilization and retain their catalytic activity in subsequent experiments. It may well be that Fe atoms originally coordinated to centers of the second type are transferred into the liquid phase.

A study of the influence of the activation conditions of the PCS's on their catalytic properties showed that they begin to display activity only when the Al:Fe molar ratio is >10, the maximum value of this ratio being different for different PCS's (see Table 1). The somewhat increased Al:Fe molar ratio in the PCS's compared with the nonheterogenized homogeneous Fe complexes of [7] may be explained by the fact that part of the DIBAH is consumed by direct reaction with free functional groups in the polymer support.

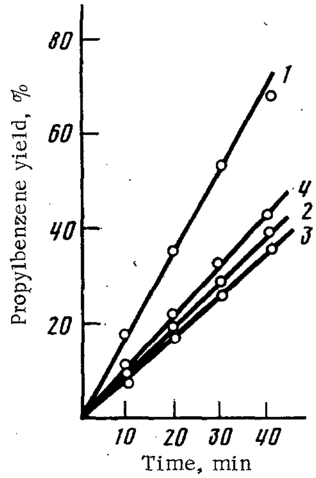

Fig. 1. Four successive experiments of the hydrogenation of allylbenzene in the presence of the same sample of Cat 11.

It can be seen from the data in Table 1 that the catalytic activity is strongly dependent on the electron-donor properties of the substituent attached to the P atom and on the presence of a phosphoryl O atom. In the case of PCS-I, for example, the catalytic activity decreases from 0.83 to 0.05 in the order Cat 4 > Cat 3 > Cat 2 > Cat 1 as the electron-donor power of the substituent attached to P increases in the order OMe > O-i-Pr > OC_6H_{11}. The departure of t-Bu from the sequence is probably due to steric hindrance caused by the ligand during coordination of the AB in the sphere of the metal complex. Similarly in the case of PCS-II, the catalytic activity decreases in the order Cat 9 > Cat 10 > Cat 11 as the electron-donor power of the substituent attached to P increases in the order OPh > OCH_2Ph > OC_6H_{11}. It should be noted, however, that the presence of a phosphoryl O atom obliterates the influence of the electronic properties of the substituent attached to P. In this case, the hydrogenation rate decreases only by 13% in the series Cat 9, Cat 10, and Cat 11. It should be noted that the highest activity, both in PCS-I and PCS-II, is observed when the substituent attached to P is an OC_6H_{11} group (see Cat 4 and Cat 9). This is evidently due to the fact that in the case of the OC_6H_{11} radical the positive charge giving the optimum stabilization of the metal is localized on the P atom.

It is interesting to note that all the catalysts containing phosphinite groups (Cat 1–Cat 6), those containing phosphonate groups with nonbulky substituents (Cat 7 and Cat 8), and also those not containing phosphorus (Cat 12 and Cat 13), are highly selective and do not isomerize the AB. In the case of PCS-II (Cat 9-Cat 11), with bulky substituents attached to the P atom, hydrogenation and isomerization proceed in parallel, the cis:trans ratio of the propenylbenzenes being close to equilibrium. Replacement of C_6H_6 by C_7H_{16} decreases the activity of Cat 9; in particular, it reduces the hydrogenation rate by a factor of five and the isomerization rate by a factor of 15. In the case of Cat 10 and Cat 11, the reaction rate decreases by a factor of less than two.

CONCLUSIONS

1. Iron complexes immobilized on polymer supports containing phosphinite and phosphonate groups catalyze the hydrogenation and isomerization of allylbenzene, the catalytic activity increasing as the electron-donor power of the substituent attached to the phosphorus atom decreases.

2. The catalysts containing phosphinite groups are highly selective with respect to hydrogenation but are less active than those containing phosphonate groups.

LITERATURE CITED

1. L. N. Sukhobok, G. P. Potapov, V. G. Luksha, V. N. Krutii, and B. D. Polkovnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2307 (1982).
2. V. N. Krutii, L. N. Sukhobok, B. D. Polkovnikov, V. G. Luksha, and G. P. Potapov, Inventor's Certificate No. 770523 (1980); Byull. Izobret., No. 38, 18 (1980).
3. L. N. Sukhobok, V. N. Krutii, B. D. Polkovnikov, V. G. Luksha, and G. P. Potapov, Catalysts Containing Supported Complexes [in Russian], Part II, Novosibirsk (1980), p. 95.
4. M. S. Kharash, E. V. Jensen, and W. H. Urry, J. Am. Chem. Soc., 67, 1864 (1945).
5. G. K. Fedorova, R. N. Ruban, and A. V. Kirsanov, Zh. Obshch. Khim., 39, 1471 (1969).
6. Yu. V. Karyakin and I. I. Angelov, Pure Chemicals [in Russian], Khimiya, Moscow (1974), p. 108.
7. M. F. Sloan, A. S. Matlack, and D. S. Breslow, J. Am. Chem. Soc., 85, 4014 (1963).