EFFECT OF SOLVENT AND TRANSITION-METAL OXIDE AND CHLORIDE ON CATALYST ACTIVITY IN PHENYL ISOCYANATE SYNTHESIS BY NITROBENZENE CARBONYLATION

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In the synthesis of isocyanates by the carbonylation of nitro compounds, the active forms of the Rh catalyst are monomeric $Rh(CO)_nCl_mPy_l$ complexes (where n is 1 or 2; m is 1 or 2; and l is 0, 1, or 2) [1], in the coordination sphere of which nitro reduction and isocyanate formation apparently take place:

$$\begin{tikzcd}
Rh(CO)_nCl_mPy_l \arrow[r, "+RNO_2"] & Rh(CO)_nCl_mPy_l(RNO_2) \arrow[dr, "-CO_2", "+CO"'] & \\
Rh(CO)_{n-1}Cl_mPy_l \arrow[u, "+CO"] & Rh(CO)_nCl_mPy_l(RN) \arrow[l, "-RNCO"] & Rh(CO)_nCl_mPy_l(RNO) \arrow[l, shift left, "+CO"', "-CO"]
\end{tikzcd}$$

It has been proposed several times [2-4] that the active forms of the Pd catalyst for this reaction are the analogous monomeric complexes $Pd(CO)_nCl_mPy_l$; in contrast to the rhodium compounds these cannot be isolated, because they are apparently stable only under CO pressure in the presence of excess CO, Cl, and pyridine ligands, and are in dynamic equilibrium with inactive forms of palladium.

Indeed, in the presence of pyridine we failed to stabilize the Pd complexes that are catalytically active in isocyanate synthesis; under 5.0-16.0 MPa pressure of CO at 413-473°K in pyridine or its 10% solution in chlorobenzene or dichlorobenzene, $PdCl_2$ is reduced to Pd black. The reaction mixture does not contain $PdPy_2Cl_2$, which is easily formed under these conditions in the absence of CO. Under the same conditions in chloro- or dichlorobenzene without pyridine, $PdCl_2$ is converted to the polymeric carbonyl chloride $[Pd(CO)Cl_n]$, the IR spectrum of which, according to [5], contains a characteristic absorption band $\nu CO = 1995$ cm^{-1}. In the presence of pyridine at 293°K and atmospheric pressure $[Pd(CO)Cl]_n$ quickly decomposes to Pd black. In the presence of a nitro compound and pyridine at 433-473°K, $PdCl_2$ is substantially unreduced by CO, and is dehalogenated to Pd black. Under these conditions Pd black and palladium and rhodium oxides, in contrast to their chlorides, are inactive as catalysts for the carbonylation of nitrobenzene (NB) (Table 1). Evidently, when dehalogenation of the Pd catalyst is possible, analogous to that of Rh [1], deactivation can occur; this agrees with the activating effect of excess halide ions on Rh and Pd catalysts previously discovered by us [1, 2].

It has been shown [4] that in phenyl isocyanate synthesis by NB carbonylation, some transition-metal oxides deactivate the $PdCl_2-Py$ catalyst; in the light of what has been said, this may be due to a considerable extent to the dehalogenating action of the oxides. It may be assumed that when oxides are replaced by chlorides, the deactivating effect must be reduced.

We studied the effect on Pd activity of some transition-metal chlorides and oxides, where the oxides either do not affect $PdCl_2-Py$ catalyst (Fe, Cr), or deactivate it (Co). The data in Table 1 show that $CoCl_2$ deactivates considerably less than do CoO and Co_3O_4, the strongest known inhibitors of this reaction: under identical conditions $CoCl_2$ reduces catalyst activity to 1/3.5 of its value, whereas CoO and Co_3O_4 reduce it to 1/15-1/16. Fe, Cr, and Cu chlorides increase the output of both $PdCl_2$ and $RhCl_3$ catalysts, and reduce the temperature of phenyl isocyanate (PI) synthesis by ~20° (see Table 1, Fig. 1).

The carbonylation of NB to PI is usually carried out in chlorobenzene medium [1-4]. But C_6H_5Cl is not always convenient to use as a solvent because of the difficulty of separating catalyst and isocyanate product

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TABLE 1. Effect of Some Transition-Metal Oxides and Chlorides on Phenyl Isocyanate Synthesis by Nitrobenzene Carbonylation (8 MPa CO)

Catalyst	Additive, mole per mole of Pd or Rh	Temp., °K	τ, min	Output, g isocyanate/g catalyst · h	Selectivity, %
Pd Black	–	463	60	0	–
8% PdO/Al_2O_3 *	–	473	60	0	–
5% Rh_2O_3/Al_2O_3 †	–	433	60	0	–
$PdCl_2$	–	473	60	38	79
»	Fe_2O_3	473	60	38	80
»	Cr_2O_3	473	60	38	77
»	CoO	473	60	2,3	96
»	Co_3O_4	473	60	2,6	90
»	$CoCl_2$	473	60	11	90
»	–	413	30	0	–
»	Cr_2O_3	413	30	0	–
»	$CrCl_3$	413	30	2,1	85
»	Fe_2O_3	413	30	0	–
»	$FeCl_3$	413	30	4,2	87
»	CuO	413	30	0	–
»	$CuCl_2$	413	30	2,6	40
»	–	433	30	5,8	80
»	Cr_2O_3	433	30	5,0	80
»	$CrCl_3$	433	30	10,4	86
»	$CuCl_2$	433	30	12,1	40
$RhCl_3 \cdot 3H_2O$	–	443	30	1,0	84
»	Fe_2O_3	443	30	1,0	84
»	$FeCl_3$	443	30	5,4	90
»	–	463	30	10,3	85
»	$FeCl_3$	463	30	20,1	91

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*200 mg catalyst.

†260 mg catalyst.

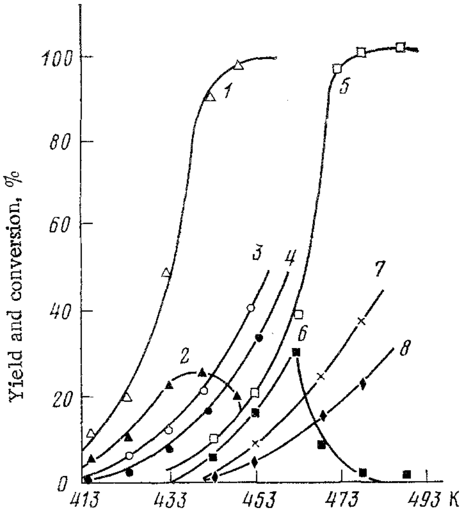

Fig. 1. Effect of reaction temperature on (1, 3, 5, 7) nitrobenzene conversion and (2, 4, 6, 8) phenyl isocyanate yield in presence of (3, 4) $PdCl_2$, (1, 2) $PdCl_2 + CuCl_2$, (7, 8) $RhCl_3 \cdot 3H_2O$, and (5, 6) $RhCl_3 \cdot 3H_2O + FeCl_3$ catalyst at 8 MPa CO and 0.5 h.

from the reaction mixture. The information on the use of other solvents in the synthesis, particularly aliphatic and aromatic hydrocarbons and nitriles, is contradictory. Thus, according to patents [6, 7] CH_3CN can be used as reaction medium; and the addition of o- or p-benzodinitriles to C_6H_5Cl activates the Pd catalyst. On the other hand, it was shown in [8] that CH_3CN and C_6H_5CN have a deactivating effect on $PdCl_2$ that is overcome in the presence of pyridine.

We tested aliphatic and aromatic hydrocarbons, nitriles, and halohydrocarbons as solvents in isocyanate synthesis. The study was carried out on NB carbonylation with $PdPy_2Cl_2$ as catalysts, because in the presence of excess ligand the PdL_2Cl_2 complexes (where L is pyridine, 2-methylpyridine, or 3,5-dimethylpyridine) show similar results in the synthesis of various monoisocyanates (Table 2).

As Table 3 shows, when the reaction is carried out in $CHCl_3$, in contrast to C_6H_5Cl the conversion of NB rises to 90%, but no PI is formed. The addition of $CHCl_3$ to C_6H_5Cl increases NB conversion but completely inhibits PI formation. CCl_4 has an even greater inhibiting effect; when added to C_6H_5Cl it even decreases NB conversion.

TABLE 2. Aromatic Isocyanate Synthesis with $PdCl_2$ Pyridine Complexes in Chlorobenzene (473°K, 10 MPa CO, 1 h reaction time)

Starting nitro compound	Conversion, %	Isocyanate formed	Selectivity, %	Output, moles isocyanate/g-atom Pd·h
		$PdPy_2Cl_2$ catalyst *		
Nitrobenzene	71	Phenyl isocyanate	66	22
2-Nitrotoluene	76	2-Methylphenyl isocyanate	92	25
3-Nitrotoluene	52	3-Methylphenyl isocyanate	79	16
2-Chloronitrobenzene	79	2-Chlorophenyl isocyanate	68	26
		Pd(2-methylpyridine)$_2$Cl$_2$ catalyst*		
Nitrobenzene	75	Phenyl isocyanate	73	25
2-Chloronitrobenzene	80	2-Chlorophenyl isocyanate	70	26
		Pd(3,5-dimethylpyridine)$_2$Cl$_2$ catalyst*		
Nitrobenzene	89	Phenyl isocyanate	80	29
2-Nitrotoluene	78	2-Methylphenyl isocyanate	75	—

*Excess free ligand, 4 moles/g-atom Pd.

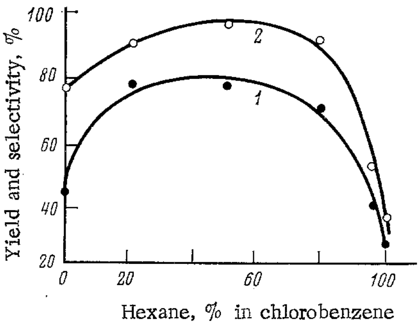

Fig. 2. Effect of hexane concentration in chlorobenzene on (1) yield and (2) selectivity of phenyl isocyanate formation, at 473°K, 10 MPa CO pressure, 1 h contact time, and 1 : 2 (by weight) $PdPy_2Cl_2$: pyridine.

In contrast to the patent data, we show that in the nitriles (CH_3CN and C_6H_5CN) no PI is formed and only 10-20% of the NB reacts at all. In benzene and toluene PI is formed in yields of 26 and 17%, respectively. In toluene, 16% of aniline and resins are also formed. The C_6-C_{10} normal paraffin hydrocarbons are good solvents; in their presence the PI yield is 30-50% and the NB conversion is 41-79%. The synergism between hexane and chlorobenzene is unusual and so far unexplained. As Fig. 2 shows, when 20-80% chlorobenzene is added to hexane, the PI yield and the selectivity increase sharply, reaching 72-81 and 91-97%, respectively.

We studied the effect of certain factors on NB carbonylation in heptane in the presence of $PdPy_2Cl_2$ supported on 20% MoO_3/Al_2O_3 (Table 4). At 473°K, 10 MPa CO pressure, and 5-10% NB in heptane, it is 70-74% converted to PI with a selectivity of 95-96%. Reduction of the catalyst : NB weight ratio to 0.05 reduces the PI yield to 20.2%, and at a ratio of 0.025 PI is no longer formed. Raising the pressure to 17 MP, and in particular, raising the temperature by even 10° decreases the PI yield sharply.

EXPERIMENTAL

IR spectra were recorded on a UR-20 apparatus. In a rotating steel autoclave of 0.15-liter volume were heated 0.5-3 g of nitro compound (Table 1, 3 g; Tables 2 and 3, 1 g; Table 4, 0.5 to 2 g), 8-10 g of solvent (Table 1, 10 g chlorobenzene; Table 2, 8 g chlorobenzene; Table 3, 4-8 g solvent), 0.2 g of pyridine, catalyst (Table 1, 50 mg; Tables 2 and 3, 100 mg; Table 4, 50-100 mg), and additive. The system was purged with CO, the CO pressure was raised to 8-17 MPa, and the mixture was heated at 413-473°K for 0.1-1 h.

$[Pd(CO)Cl]_n$ was synthesized at 433-453°K from $PdCl_2$ and CO at 5-15 MPa pressure, analogously to [5]. Pyridine complexes of $PdCl_2$ were obtained by the procedure of [3]. Before the test the starting materials were dried and distilled. $PdPy_2Cl_2$ was supported on 20% MoO_3/Al_2O_3 by impregnation from $CHCl_3$ solution and drying in a nitrogen current for 4 h at 473°K. Catalyst output was found from the average carbonylation rate over the 5-50% conversion range.

TABLE 3. Phenyl Isocyanate Synthesis in Various Solvents with 1 : 2 $PdPy_2Cl_2$: Pyridine (473°K, 10 MPa CO, 1 h reaction time)

Solvent	Nitrobenzene conversion, %	Phenyl isocyanate yield, %	Solvent	Nitrobenzene conversion, %	Phenyl isocyanate yield, %
Acetonitrile	10	0	Chloroform – chlorobenzene, 1:4	64	0
Benzonitrile	19	0	CCl_4 – chlorobenzene, 1:4	9	0
Benzene	33	26	Hexane	79	30
Toluene	44	17 *	Heptane	59	56
Chlorobenzene	57	44	Octane	41	34
Chloroform	90	0	Decane	49	38

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*16% Aniline formed.

TABLE 4. Phenyl Isocyanate Synthesis by Nitrobenzene Carbonylation in Heptane, in Presence of Pyridine, with 20% $PdPy_2Cl_2$ + 20% MoO_3/Al_2O_3 (1 h reaction time)

Catalyst : nitrobenzene (by wt.)	CO pressure, MP	Temp., °K	Nitrobenzene concn., %	Nitrobenzene conversion, %	Phenyl isocyanate yield, %
0,2	10	473	5	74	71
0,1	10	473	10	70	63
0,1	17	473	10	97	11,6
0,05	10	473	10	21	20,2
0,05	10	483	10	59	0
0,025	10	473	20	67	0

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CONCLUSIONS

1. In the synthesis of phenyl isocyanate by nitrobenzene carbonylation, when transition-metal oxides are replaced by their chlorides, inhibition by the Co compound is reduced, activation by the Mo and V compounds is retained, and the Fe, Cr, and Cu compounds become activators.

2. Carbonylation of nitrobenzene to phenyl isocyanate can be carried out in an aliphatic hydrocarbon medium or in a hexane–chlorobenzene mixture. Nitriles and aliphatic halohydrocarbons inhibit the process.

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