2. The activating effect of Py and Py·HCl apparently consists in the formation from $[Rh(CO)_2Cl]_2$ of catalytically active monomeric rhodium complexes, which contain Py, Cl^-, and CO as ligands.

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EFFECT OF CATALYST COMPOSITION AND REACTION CONDITIONS ON SYNTHESIS OF PHENYL ISOCYANATE BY CARBONYLATION OF NITROBENZENE

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Previously we had established [1] that the carbonylation of aromatic mononitro compounds using $PdCl_2$−pyridine−MoO_3 as the catalyst gives isocyanates in high yield and a study was made of the effect of the nature of the metal oxide on the activity of the Pd catalyst.

In the present paper, on the example of carbonylating nitrobenzene (NB), we studied the effect of the catalyst composition, temperature, contact time, and initial concentration of the starting NB on the synthesis of phenyl isocyanate (I).

$$C_6H_5NO_2 + 3CO \rightarrow C_6H_5N{=}C{=}O(I) + 2CO_2$$

The catalyst $PdCl_2$−pyridine−MoO_3 represents a homogeneous-heterogeneous system. Under the reaction conditions, as was shown previously [2], from $PdCl_2$ and pyridine are formed catalytically active complexes of the type $Pd(pyridine)_2Cl_2$ that are soluble in chlorobenzene. Molybdenum oxide is insoluble in chlorobenzene, but it increases the activity of the $PdCl_2$−pyridine catalyst by a factor of 3 (Table 1), which is apparently due to the faster rate of carbonylating NB in the coordination sphere of the pyridine complex of Pd, adsorbed on the MoO_3 surface, when compared with that of the same complex in solution. Actually, when MoO_3 is deposited on γ-Al_2O_3, despite a fivefold decrease in the amount of MoO_3, the carbonylation rate does not decrease (Fig. 1). A fivefold decrease in the amount of $PdCl_2$ in the $PdCl_2$−pyridine−20% MoO_3/Al_2O_3 catalyst leads to a ninefold decrease in the reaction rate (see Table 1).

Compound (I) forms at an initial rate of 1.5 moles/liter·h when NB is carbonylated on the $PdCl_2$−pyridine−MoO_3 catalyst (1:4:2) at 185° and an initial CO pressure of 100 atm. With increase in the reaction time both the NB conversion and the (I) yield increase and after 60 min respectively reach 100 and 95% (see Fig. 1). We will mention that under the same conditions, without adding MoO_3 to the $PdCl_2$−pyridine complex, the NB conversion was a total of 46%, and the yield was 40%. With further increase in the reaction time the NB conversion remains constant, while the yield of (I) drops due to tarring.

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TABLE 1. Effect of Catalyst Composition and Reaction Conditions on Carbonylation Rate of Nitrobenzene (NB) and Efficiency (185°C, P_{CO} 100 atm, pyridine concentration in chlorobenzene 2%)

Catalyst (weight ratio of components)	Initial NB conc. (mole/liter)	Average formation rate of isocyanate, mole/liter· h	Catalyst efficiency, g isocyanate/g Pd in 1 h
$PdCl_2$ + pyridine (1 : 4)	0,46	0,25	19,8
$PdCl_2$ + pyridine (1 : 4)	1,63	0,55	40,2
$PdCl_2$ + pyridine (1 : 4) *	0,41	0,16	–
$PdCl_2$ + pyridine+MoO_3 (1 : 4 : 2)	1,63	1,53	110
$PdCl_2$ + pyridine +MoO_3/Al_2O_3 (1 : 4 : 2)	1,63	1,82	118
$PdCl_2$ + pyridine +MoO_3/Al_2O_3 (1 : 20 : 10)	1,63	0,2	67

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* Phenyl isocyanate (1.22 moles/liter) was added to the starting solution.

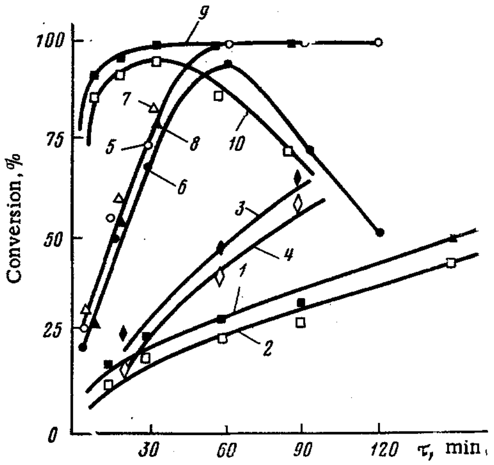

Fig. 1

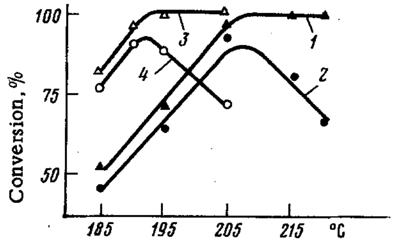

Fig. 2

Fig. 1. Effect of reaction time on NB conversion (1, 3, 5, 7, 9) and yield of (I) (2, 4, 6, 8, 10) at 185° and a CO pressure of 100 atm in the presence of the catalysts: $PdCl_2$–pyridine–20%MoO_3/Al_2O_3 (1:20:10) (1, 2); $PdCl_2$–pyridine (1:4) (3, 4); $PdCl_2$–pyridine–MoO_3 (1 : 4 : 2) (5, 6); $PdCl_2$–pyridine–20% MoO_3/Al_2O_3 (1 : 4 : 2) at 185° (7, 8) and at 205° (9, 10).

Fig. 2. Effect of reaction temperature on NB conversion (1, 3) and yield of (I) (2, 4) in the presence of $PdCl_2$–pyridine–20% MoO_3/Al_2O_3 catalyst (1:4:2) at a reaction time of 0.25 h (1, 2) and 1.5 h (3, 4).

With increase in the reaction temperature the yield of (I) passes through a maximum, while the NB conversion increases and reaches 100% (Fig. 2). Selection of the optimum temperature is determined by the reaction time: A maximum yield of (I) of 92%, with a NB conversion of 96-98%, was obtained either at 190° and τ = 1.5 h, or at 205° and τ = 0.25 h. Consequently, the catalyst efficiency can be varied, maintaining the yield of (I) and the selectivity of its formation constant, by a coordinated change in the temperature and reaction time.

As was seen from Fig. 3, the yield of (I) and the efficiency of the catalysts, of both $PdCl_2$–pyridine and $PdCl_2$–pyridine–20% MoO_3/Al_2O_3, pass through a maximum with increase in the initial NB concentration. Here the optimum NB concentration is higher in the case of the more active catalyst, containing MoO_3 (3 moles/liter as compared to 0.4 mole/liter for the $PdCl_2$–pyridine catalyst). The observed character of the change in the yield of (I) as a function of the initial NB concentration is apparently due to inhibition by the reaction product, namely the isocyanate.

Actually, from the data given in Table 1 and Fig. 4, it can be seen that the carbonylation of NB is inhibited by the formed isocyanate. Thus, when (I) is added to the starting solution of NB in chlorobenzene the reaction rate decreases by ~1.6 times, with a simultaneous increase in the decomposition of (I). Evidently, with increase in the amount of (I) in the reaction mixture it displaces by adsorption the NB from the coordination sphere of the Pd complexes, which, on the one hand, lowers the carbonylation rate of NB, and on the other hand, leads to further transformations of (I), especially if the contact time is increased.

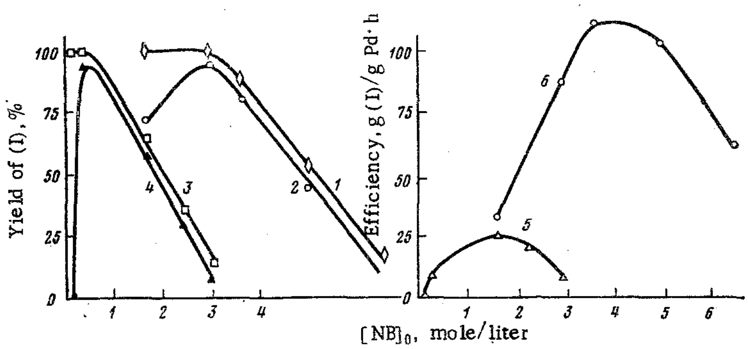

Fig. 3

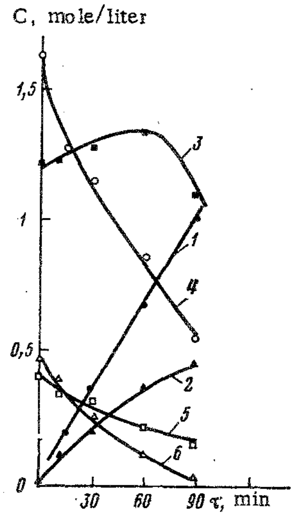

Fig. 4

Fig. 3. Effect of initial NB concentration on NB conversion (1, 3), yield of (I) (2, 4), and efficiency (5, 6) in presence of catalyst Pd–pyridine (1 :4, 185°) (3,4,5) and $PdCl_2$–pyridine–20% MoO_3/Al_2O_3 (1 : 4 : 2, 205°) (1, 2, 6). Reaction time 1.5 h.

Fig. 4. Change in concentration of (I) (1, 2, 3) and NB (4, 5, 6) with time during carbonylation of NB in presence of $PdCl_2$–pyridine catalyst (1:4) at 185°, $[NB]_0 = 1.63$ (1, 4), 0.46 mole/liter (2, 6), and $[(I)]_0 = 1.22$ moles/liter (3, 5).

EXPERIMENTAL

Carbonylation of Nitrobenzene (NB). Into a rotated 0.15-liter steel autoclave were charged 0.01-0.05 g of $PdCl_2$, 8 g of chlorobenzene (solvent), 0.2 g of pyridine, 2 g of NB (or 0.2-16 g when studying the effect of its concentration), and 0.1 g of MoO_3 (or 20% of $MoO_3/\gamma\text{-}Al_2O_3$). The autoclave was purged with CO, the CO pressure was raised to 100 atm, and the autoclave was heated at the given temperature for a predetermined time. After separating the catalyst, the reaction products were analyzed on an LKhM-8MD chromatograph (phase 5% of XE-60 deposited on Chromaton N-AW-DMCS, 0.16-0.22 mm, and helium as the carrier gas at a flow rate of 40 ml/min), with a programmed elevation of the thermostat temperature from 80° at a rate of 20°C/min. The quantitative composition of the reaction products was determined relative to chlorobenzene as the internal standard. Molybdenum oxide was obtained by decomposing molybdic acid at 500° for 5 h, and the MoO_3 was deposited on $\gamma\text{-}Al_2O_3$ by impregnation with aqueous H_2MoO_4 solution and subsequent heating at 500° for 4 h.

CONCLUSIONS

1. The addition of MoO_3 or MoO_3/Al_2O_3 to the $PdCl_2$–pyridine catalyst increases the carbonylation rate of nitrobenzene by ~ 3 times.

2. The yield of phenyl isocyanate passes through a maximum with change in the temperature (in the range 185-220°), reaction time (0.25-1.5 h), and initial nitrobenzene concentration (0.5-5 moles/liter).

3. The carbonylation of nitrobenzene is accelerated with increase in its concentration and is retarded in the presence of phenyl isocyanate.

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