6. N. D. Zelinskii and M. B. Turova-Polyak, Collected Works of Academician N. D. Zelinskii [in Russian], Vol. 3, Izd. AN SSSR, Moscow (1955), pp. 271, 375.
7. P. Tetenyi, L. Guczi, and Z. Paal, Acta Chim. Acad. Scient. Hung., 83, 37 (1974).
8. Z. Paal, M. Dobrovolszky, and P. Tetenyi, J. Catal., 45, 189 (1976).
9. J. R. Anderson and N. R. Avery, J. Catal., 5, 446 (1966).
10. T. G. Olfer'eva, O. V. Bragin, and A. L. Liberman, Izv. Akad. Nauk SSSR, Ser. Khim., 1970, 1517.
11. O. V. Bragin, A. L. Liberman, A. V. Preobrazhenskii, and B. A. Kazanskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, 2260.
12. C. Corolleur, D. Tomanova, and F. G. Gault, J. Catal., 24, 401 (1972).
13. O. V. Bragin, A. V. Preobrazhenskii, A. L. Liberman, and B. A. Kazanskii, Kinet. Katal., 16, 472 (1975).
14. Z. Paal and P. Tetenyi, J. Catal., 30, 350 (1973).
15. A. L. Liberman, Kinet. Katal., 5, 128 (1964).
16. G. V. Isagulyants, O. V. Bragin, A. A. Greish, A. L. Liberman, and L. I. Kovalenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 1554.

EFFECT OF HYDROGEN REMOVAL THROUGH A MEMBRANE CATALYST ON DEHYDROCYCLIZATION OF n-HEXANE

V. I. Lebedeva and V. M. Gryaznov

UDC 542.97:542.941.8:66.095.252:547.216

The dehydrocyclization of n-hexane (NH) has been accomplished on unsupported Pd catalysts, and specifically on Pd ribbon [1] and foil made from Pd–Ni alloy [2]. The dehydrocyclization of NH on a membrane catalyst (MC), pervious only to H_2, was studied in the present paper.

EXPERIMENTAL

As the catalyst we used a spiral tube made from Pd alloy containing 5.89% of Ni, with an outside diameter of 2.5 mm, a length of 1 m, and a wall thickness of 0.1 mm. The prior treatment of the catalyst was described in [3]. The tube was contained in a steel cylinder and was washed on the outside with the vapors of a chromatographically pure NH–Ar mixture, which was fed from two thermostatted spargers. A part of the H_2, liberated during the dehydrocyclization of NH, diffused through the tube walls and was removed by the Ar fed inside the tube. After each experiment, which lasted 1 h, the catalyst was regenerated at 580°C, at first with air (1 h) and then with H_2 (1 h). While cooling to the experiment temperature and between experiments the catalyst was found in an Ar atmosphere.

The liquid reaction products were analyzed on a Tswett 1-64 chromatograph, equipped with a 2 m × 4 mm column packed with 5% Benton-34 and 12% dodecyl phthalate deposited on Chromosorb P. The gaseous products were analyzed on a 3 m × 3 mm column packed with Al_2O_3.

DISCUSSION OF RESULTS

The amount of benzene in the transformation products of NH on the given MC, at an Ar (carrier gas) flow rate of 13 ml/min and an NH partial pressure of 45 torr, increases up to 66 mole % when the temperature is raised to 515°. The dehydrocyclization is not accompanied by the formation of either methylcyclopentane or hexenes. Below 520° only H_2 was found in the gaseous products, and hundredths of a percent of ethane and ethylene at higher temperatures.

The H_2 partial pressure in the NH dehydrocyclization zone was decreased by increasing the rate of removing the formed H_2 through the MC. An increase in the Ar flow rate in the H_2 removal zone lowered the H_2 concentration in the dehydrocyclization zone.

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. P. Lumumba International Friendship University, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 611-613, March, 1981. Original article submitted April 23, 1980.

0568-5230/81/3003-0452$07.50

TABLE 1. Effect of Increase in Ar Flow Rate in H_2 Removal Zone on H_2 Concentration in Dehydrocyclization Zone and Degree of Conversion of n-Hexane to Benzene (494°C; hexane partial pressure = 45 torr; Ar stream = 22 ml/min)

Ar flow rate in H_2 removal zone, ml/min	H_2 concentration, mole %		Degree of hexane conversion to benzene	Fraction of H_2 removed from DHC zone
	in H_2 removal zone	in DHC zone		
22	2,23	2,42	0,14	0,484
52	1,34	1,53	0,23	0,686
100	1,04	1,24	0,27	0,856
200	0,57	0,84	0,27	0,938
570	0,17	0,31	0,27	0,980

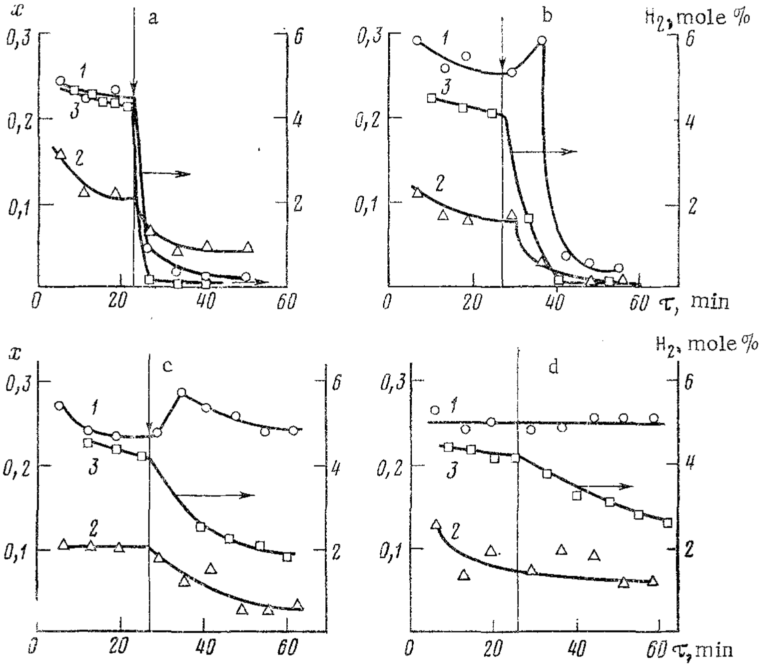


Fig. 1. Degree of n-hexane conversion to benzene (1), to condensation products on the catalyst (2), and H_2 concentration in dehydrocyclization zone (3) at 523° as functions of time at the moment, indicated by arrows, of replacing the Ar stream in the H_2 removal zone by a stream of either air (a) or an air–Ar mixture with a ratio of 1:3 (b), 1:8 (c), or 1:13 (d).

The amount of benzene in the products increases only when up to 86% of the formed H_2 is removed from the dehydrocyclization zone, and remains constant with further decrease in the H_2 concentration in the dehydrocyclization zone (Table 1).

At a constant dehydrocyclization activity of the catalyst, the addition of air to the H_2 removal zone lowered the H_2 concentration in the dehydrocyclization zone by ∿50 times (from 4.65 to 0.1 mole %). Here the degree of NH conversion to benzene in several minutes decreased from 23 to 1-2 mole %. The formation of condensation products on the catalyst also decreased in half (Fig. 1a).

When the air, fed into the H_2 removal zone, was diluted with argon in a 1:3 ratio, the degree of dehydrocyclization also dropped to several percent, but the degree of NH conversion to benzene showed little change in the first 10 min after admitting this mixture (Fig. 1b). The feeding of air, diluted with argon in a 1:8 ratio, increased somewhat the degree of dehydrocyclization (Fig. 1c), but when a mixture with an air:argon ratio of 1:13 was fed, the degree of NH conversion to benzene remained constant after replacing the Ar stream in the

H_2 removal zone by a stream of this mixture, while the formation of condensation products decreased somewhat (Fig. 1d). The H_2 concentration in the gas phase in the dehydrocyclization zone was 1.8-2 mole %.

Replacing the air stream in the H_2 removal zone by an Ar stream leads to a gradual increase in both the H_2 concentration in the dehydrocyclization zone and the yield of benzene, which in ∿1 h approaches that observed before replacing the Ar by air in the H_2 removal zone.

As a result, removing a definite portion of the H_2, formed during the dehydrocyclization of hexane, through an MC increases the yield of benzene. If a greater portion of the liberated H_2 is removed from the dehydrocyclization zone, then the yield of benzene either remains constant or even decreases. A further depletion of the surface layer of the catalyst in hydrogen, for example, by feeding air or air-rich mixtures with Ar into the H_2 removal zone, suppresses the dehydrocyclization reaction, while a decrease in the intensity of H_2 removal through the MC leads to a gradual increase in the rate of this reaction. Consequently, a certain concentration of H_2 is necessary for the progress of dehydrocyclization. A similar effect was observed during the dehydrogenation of isoamylenes on an MC made from Pd–Ni alloy [4]: when H_2 was added the dehydrogenation rate passed through a maximum and it decreased only when the H_2 partial pressures exceeded the initial partial pressure of the isoamylenes. The removal of H_2 from the hexane dehydrocyclization zone through an MC suppresses, as the 3 curves in Fig. 1 show, side reactions that lead to the formation of condensation products on the catalyst surface. Together with an increase in the yield of benzene, this fact makes it quite practical to remove a part of the H_2 that is formed during dehydrocyclization through an MC.

The observed differences in the effect of the method for removing the H_2 that diffuses through the MC from the dehydrocyclization zone on the degree of progress of this reaction also seem of interest. The passage of Ar into the H_2 removal zone, even at such a high rate that 98% of the formed H_2 is extracted from the zone, does not lower the yield of benzene (see Table 1). The transition from Ar to Ar–air mixtures does not change this result until the O_2 partial pressure in the mixture reaches a value where the rate of oxidizing the H_2 that diffuses through the MC now exceeds the rate of forming H_2 on another surface of the catalyst. Under such conditions the MC is depleted in hydrogen and the yield of benzene drops. When air, not diluted with argon, is fed the yield of benzene immediately decreases sharply (see Fig. 1a), while when the air is diluted with argon (1:3) it proves that the MC contains a sufficient amount of H_2 to maintain the dehydrocyclization rate at a level, corresponding to the admittance of Ar into the H_2 removal zone, for another 10 min (see Fig. 1b).

The presence of a certain O_2 partial pressure at the exit surface of a Pd membrane, through which H_2 diffuses, facilitates, according to the data in [5], the transition of hydrogen atoms from the lattice of the metal to the surface and excludes the step of recombining the H atoms prior to desorption from the surface of the membrane, since they react with the O_2 and are desorbed as a molecule of water. If an inert gas is found on the H_2-exit surface of the membrane, then the removal of H_2 is limited by the step of recombining its atoms. For all of these reasons the rate of extracting H_2 from an MC, on one surface of which dehydrocyclization occurs, differs sharply when the H_2 removal zone is blown with argon and when the H_2 that diffuses through the catalyst is oxidized by oxygen. In the latter case the MC is depleted in hydrogen to such an extent that its accumulation up to a concentration, needed for the dehydrocyclization of hexane, requires a longer time span after replacing the air stream by an Ar stream.

CONCLUSIONS

When the effect of the rate of removing hydrogen from the n-hexane dehydrocyclization zone by diffusion through a membrane catalyst was studied, it was established that the removal of up to 86% of the formed hydrogen increases the yield of benzene, while a more complete removal of hydrogen from the membrane catalyst by feeding either air or air-rich mixtures with argon along another surface of the catalyst lowers the yield of benzene.

LITERATURE CITED

1. V. M. Gryaznov, K. Maldonado, E. Khajjar, and D.-K. Oluoch Okeio, Kinet. Katal., 9, 435 (1968).
2. V. M. Gryaznov and V. S. Smirnov, Usp. Khim., 43, 1717 (1974).

3. V. M. Gryaznov, A. P. Mishchenko, V. P. Polyakova, E. M. Savitskii, V. S. Smirnov, and E. V. Khrapova, in: Noble Metals and Their Substitutes [in Russian], No. 28, Izd. AN SSSR, Sverdlovsk (1971), p. 218.
4. N. V. Orekhova, M. M. Ermilova, V. S. Smirnov, and V. M. Gryaznov, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 260.
5. E. Wicke and K. Meyer, Z. Physik. Chem. (BRD), 64, 225 (1969).

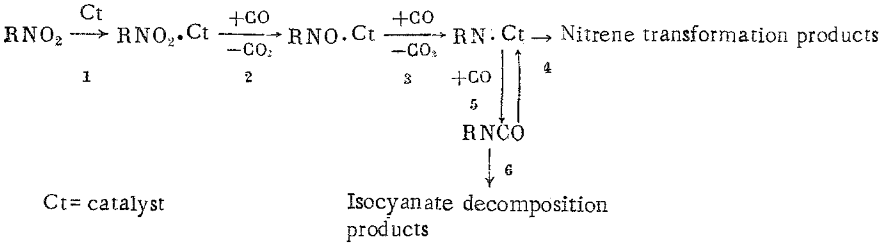
EFFECT OF CARBON MONOXIDE PRESSURE, PYRIDINE CONCENTRATION, AND TEMPERATURE ON SYNTHESIS OF 1-METHYLBENZENE 2,4-DIISOCYANATE BY CARBONYLATION OF 2,4-DINITROTOLUENE

V. I. Manov-Yuvenskii, B. A. Redoshkin,
G. P. Belyaeva, and B. K. Nefedov

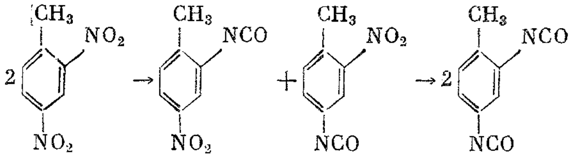
UDC 542.91:541.12.034:546.262.3-31:547.546

In the catalytic carbonylation of aromatic nitro compounds the yield of isocyanates as a function of the concentration of the promoters of the palladium catalyst, the CO pressure, and the temperature has a maximum [1-3]. In order to ascertain the reasons, causing the extremal character of these functions, we studied the effect of temperature, and of the pressure and concentration of pyridine, used as the promoter of the Pd catalyst, on the yield of 1-methylbenzene 2,4-diisocyanate (MBDIC).

In harmony with the nitrene hypothesis [4], the formation of isocyanates by the carbonylation of nitro compounds can be depicted by the scheme



The character of the changes in the yield of the mono- and diisocyanates during the carbonylation of 2,4-dinitrotoluene (DNT) makes it possible to assume that the MBDIC is formed in two steps (Fig. 1) via the intermediate mononitro isocyanates:



The overall selectivity of the reaction in mono- and diisocyanates is determined by the ratio of the rates of steps 4-6. The equilibrium constant of step 5 apparently depends on the nature of the catalyst; on Rh and Pd catalysts the equilibrium is shifted toward the formation of isocyanates [4], while on Fe catalysts the nitrene complex is stable and can be isolated from the reaction mixture [5]. Increasing the CO pressure should change the ratio of the rates of steps 4 and 5 toward the reaction of the nitrene complex with CO [4]. Actually, as can be seen from Fig. 2, the selectivity of synthesizing isocyanates increases with increase in the CO pressure in the range 25-200 tech. atm. Increasing the pressure from 25 to 200-300 tech. atm is accompanied by an increase in the conversion of DNT and the yield of MBDIC; the yield of the mononitro monoisocyanates passes through a maximum. Consequently, the overall selectivity of synthesizing the mono- and diisocyanates increases only up to $\sim$150 tech. atm, while in the range 150-300 tech. atm it shows little change.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, N. M. Lobachevskii Institute of Chemistry, Gorki State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 614-617, March, 1981. Original article submitted January 21, 1980.

0568-5230/81/3003-0455$07.50