2. 2,2,6,6-Tetramethyl-4-hydroxy-4-alkylpiperidines and the corresponding nitroxyl radicals were dehydrated by the action of sulfuric acid or $POCl_3 + C_5H_5N$.

3. IR spectroscopy indicated that 2,2,6,6-tetramethyl-4-hydroxy-4-alkylpiperidines have a boat conformation, while the corresponding nitroxyl radicals have a chain conformation.

4. ESR spectroscopy in the 2-mm range gave the magnetic resonance parameters for the 2,2,6,6-tetramethyl-4-hydroxy-4-alkylpiperidin-1-oxyls prepared. A similarity in the basic configurations of the nitroxyl groups of these radicals and of 2,2,6,6-tetramethyl-4-hydroxy-4-methylpiperidin-1-oxyl was noted.

LITERATURE CITED

- 1. E. G. Rozantsev and V. I. Suskina, Izv. Akad. Nauk SSSR, Ser. Khim., 1191 (1969).
- 2. B. Annaev, V. K. Kol'tover, L. M. Raikhman, and V. I. Suskina, Dokl. Akad. Nauk SSSR, 196, 969 (1971).
- 3. M. G. Goldfild, V. K. Kol'tover (Koltover), and E. G. Rozantsev (E. G. Rozantzev), Kolloid Z. Z. Polymere, 243, 62 (1971).
- 4. K. Watanabe, J. Yamauchi, H. Takaki, H. Nishiguchi, and Y. Deguchi, Bull. Inst. Chem. Res., Kyoto Univ., 48, 88 (1970); Chem. Abstr., 74, 87770a (1971).
- É. G. Rozantsev, A. B. Shapiro, N. N. Gorodetskii, V. V. Amerik, N. A. Tupikina, G. N. Antipina, L. N. Smirnov, D. V. Ivanyukov, and E. N. Matveeva, Inventor's Certificate No. 444,781 (1973); Byull. Izobr., <u>36</u>, 61 (1974).
- 6. A. Morrison and A. P. Davies, Org. Mass Spectrom., 3, 353 (1970).
- 7. R. E. Lyle, J. Org. Chem., 22, 128 (1957).
- 8. R. Briere, H. Lemaire, A. Rassat, and J. Dunand, Bull. Soc. Chim. France, 4220 (1970).
- 9. O. Ya. Grinberg, A. A. Dubinskii, V. F. Shuvalov, L. G. Oranskii, V. I. Kurochkin, and Ya. S. Lebedev, Dokl. Akad. Nauk SSSR, 230, 884 (1976).
- 10. A. A. Galkin, O. Ya. Grinberg, A. A. Dubinskii, N. I. Kabdin, V. A. Krymov, V. I. Kurochkin, Ya. S. Lebedev, L. G. Oranskii, and V. F. Shuvalov, Prib. Tekh. Eksp., 283 (1977).
- 11. S. A. Goldman, G. V. Bruno, S. F. Polnasrek, and J. H. Freed, J. Phys. Chem., 79, 489 (1975).

HYDROGENATION OF BENZENE OVER NAX

AND Na-MORDENITE ZEOLITES

Kh. M. Minachev, E. A. Udal'tsova, and I. I. Levitskii UDC 942.941.7:547.532:661.183.6

In [1] it was established that H_2 has a dual action on the activity of NaY zeolite in the hydrogenation of benzene. At 225-300°C H_2 activates the catalyst, whereas at 350-400°C it suppresses its activity. In the present investigation we have studied the effect of H_2 on the activity of NaX and Na mordenite (NaM) zeolites in the same reaction and the stability of the catalyst's activity on long-term operation.

EXPERIMENTAL

The principal conditions for conducting the experiments have been described in [1]. The amount of catalyst was 15 g. The molar ratio $H_2: C_6H_6 = 8$ at a total pressure of 30 atm. The feedrate of C_6H_6 was 0.01 mole/h per 1 g of catalyst [space velocity (s.v.) =0.6-0.7 h⁻¹], and in only the first series with NaX were the experiments conducted with a rate of 0.02 mole/h per 1 g of catalyst. Between the experiments the catalyst was treated with air for 5 h at 520°C so that it had a constant activity in each experiment. When studying the effect of H_2 after treatment of the catalyst with air it was treated with hydrogen, the treatment condition being varied from experiment to experiment. The catalyst was analyzed on a chromatograph having a flame-ionization detector and a column containing 15% Tween 85 on Chromosorb P.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimiya, No. 2, pp. 333-337, February, 1982. Original article submitted May 12, 1981.



Fig. 1. Effect of hydrogen treatment temperature on the activity of NaX zeolite in the hydrogenation of C_6H_6 . 225°C, 30 atm, $H_2: C_6H_6 = 8$, s.v. = 1.2 h⁻¹.

Fig. 2. Effect of hydrogen treatment period on the activity of NaX zeolite in the hydrogenation of C_6H_6 . Temperature of experiments and treatment: 1) 160°C; 2) 180°C; 3) 200°C; 4) 250°C.

TABLE 1. Hydrogenation of Benzene over NaX Zeolite $(225^{\circ}C, 30 \text{ atm}, H_2: C_6H_6 = 8, s.v. = 0.6 h^{-1})$

Catalyst treatment condi- tions prior to experiment	$ C_6H_6 \text{ con-} $ version to C_6H_{12}
Air, 1 atm, 5 h, 520°C Air, 1 atm, 5 h, 520°C No treatment Air, 1 atm, 5 h 5, 525°C No treatment No treatment	$\begin{array}{c} 38,9\\ 41,7\\ 10,1\\ 38,8\\ 15,7\\ 7,6\end{array}$

DISCUSSION OF RESULTS

Figure 1 shows the effect of H_2 on the activity of NaX zeolite. All the experiments in this series were conducted at 225°C, whereas the preliminary hydrogen treatment temperature was varied with a constant period for each treatment with hydrogen (2 h). With an increase in treatment temperature from 160 to 400°C the depth of the reaction was lowered from 13 to 6%. We may note that in the experiment with NaY at 225°C and for the same temperature of treating it with hydrogen the conversion of C_6H_6 was ~50% [1] against 11% in the present study. In order to study the effect of H_2 on the activity of NaX more fully a second series of experiments was conducted in which the hydrogen treatment was conducted at the temperature of the experiments and with a different period (Fig. 2). Whereas H_2 does not affect the activity of NaX at 160°C, an increase in the temperature of the experiments and hydrogen treatment from 180°C to 225°C led to an increase in the deactivation of the catalyst, both with an increase in temperature and an increase in the period of hydrogen treatment. Thus, in contrast to NaY, H_2 is not capable of activating NaX zeolite and only causes its deactivation at 180-400°C.

We then studied the stability of the hydrogenating activity of NaX zeolite at 225°C (Table 1). Even in the first experiments, conducted without preliminary treatment, the activity of the catalyst was greatly reduced and the conversion of C_6H_6 to cyclohexane C_6H_{12} was lowered from 39-42 to 10-16%. Regeneration of the catalyst with air restored its activity. All the experiments with NaX were conducted with a single sample of catalyst. The sorption capacity of the sample for N_2 before and after the experiments was the same and, consequently, its structure was unchanged.

In [2] the activation of NaM by hydrogen was established under conditions where experiments on the hy-



Fig. 3. Effect of hydrogen treatment temperature on the activity of Na mordenite zeolite in the hydrogenation of C_6H_6 . 200°C, 30 atm, s.v. = 0.7 h⁻¹, H₂: $C_6H_6 = 8$.

Fig. 4. The hydrogenation of C_6H_6 on Na mordenite zeolite under conditions of prolonged operation of the catalyst. 225°C, 30 atm, s.v. = 0.7 h⁻¹, H₂: C_6H_6 = 8: a) first experiment; b) second experiment.

drogenation of C_6H_6 at 190°C was alternated with hydrogen treatment of the catalyst (5 h) at the same temperature. An increase in the number of hydrogen treatments to ten led to a stepwise increase in C_6H_{12} yields from 10 to 86%. The investigation in [2] had to be continued and a study made of how H_2 affects the hydrogenating activity of NaM at other temperatures. Furthermore, it still remained unclear how long NaM may operate without a substantial decrease in hydrogenating activity.

The study of NaM zeolite commenced with an examination of the effect of H_2 on its activity. The experiments were conducted at 200°C while the hydrogen treatment temperature was varied from 160 to 400°C for a treatment period equal to 2 h (Fig. 3). The conversion of C_6H_6 in experiments conducted immediately after treatment with air was 37–39%, while additional treatment with hydrogen at 160, 200, and 250°C activated the catalyst and the depth of the reaction reached 44%, 42%, and 58%, respectively. However, a further increase in the hydrogen treatment temperature led to the deactivation of the catalyst and the conversion of C_6H_6 after treatment with H_2 at 400°C was lowered to 12%. Thus, H_2 has a dual effect on the hydrogenating activity of NaM, activating it at 160-250°C and deactivating it at 300-400°C. We may recall that H_2 also has such a double action on NaY zeolite.

The stability of the hydrogenating activity of NaM was studied at 225° C in two experiments lasting many hours. Samples of the catalysts for analysis were taken each 1-1.5 h. In the first experiment the conversion of C_6H_6 over the course of 20 h was 90%, it then decreased and reached 80% at the 40th hour (Fig. 4a). Air treatment of NaM restored its activity and after such treatment the catalyst operated in the second experiment for 20 h with a C_6H_6 -to- C_6H_{12} conversion equal to 90% (see Fig. 4b).

The data in Fig. 4 show that after treatment with air the catalyst is "developed" under the reaction conditions. In order to examine whether "development" exists investigations should be carried out, commencing with a relatively low C_6H_6 conversion. Therefore, the following experiment was conducted at 200°C (Fig. 5). Over the course of the first 10 h the conversion of C_6H_6 increased from 45% to 90% and then remained at this level for more than 10 h. Thus, the activation of NaM may also be achieved by the reaction mixture. It remains unclear whether such a substantial activation occurs as a result of the chemisorption of H_2 , C_6H_6 , or C_6H_{12} .

We may note that methylcyclohexane (MCH) suppresses the hydrogenating activity of NaM virtually completely. Twelve grams of MCH was fed for 2 h over the catalyst at 200°C, 30 atm, and H_2 : MCH = 11. The result was that the conversion of C_6H_6 to C_6H_{12} was lowered from 44% to 2%. Treatment with air restored the activity of NaM. Such a great deactivation of NaM on chemisorption of MCH would seem to be due to the presence of the tertiary C atom with a reduced electron density in its molecule, which makes MCH a fairly strong electron acceptor. The role of the electron-acceptor and electron-donor properties of the reactants and the reaction products in oxidation—reduction reactions over zeolites without transition metals has not been investigated, although it is probably of great importance.

In [1] the stability of the hydrogenating activity of NaY under conditions of prolonged operation was not studied. In order to fill this gap we studied NaY at 225°C at 30 atm (Fig. 6). Like NaM, NaY zeolite is capable of being "developed," the conversion of $C_{\rm g}H_{\rm g}$ being increased from 45% to 60-70%, then lowered to the initial



Fig. 5. Development of Na mordenite zeolite under conditions of prolonged operation of the catalyst. 200°C, 30 atm, s.v. = $0.7 h^{-1}$, H₂: C₆H₆ = 8.

Fig. 6. Hydrogenation of C_6H_6 on NaY zeolite under conditions of prolonged operation of the catalyst. 225°C, 30 atm, s.v. = 0.6 h⁻¹, H₂: C_6H_6 = 8.

conversion, and remaining constant for 10 h.

Thus, H_2 exerts a dual action on the hydrogenating activity of NaM and NaY zeolites, activating them at comparatively low temperatures (200-250°C) and suppressing their activity at 300-400°C. On the other hand, the activity of NaX is suppressed by hydrogen over almost the whole temperature range (180-400°C). In [1] it is postulated that two forms of chemisorbed hydrogen exist. One of them is formed preferentially at a comparatively low temperature and increases the hydrogenating activity of the zeolite, while the other deactivates the catalyst, the optical conditions for its formation being a relatively high temperature and pressure. From this point of view the dual action of H_2 on the hydrogenating activity of NaM and NaY is due to the formation of two forms of chemisorbed H_2 . On the other hand, only the second of these forms is formed on NaX, which leads to the deactivation of NaX.

The sharp difference in the catalytic properties of the two faujasites, NaY and NaX, and, conversely, the similarity in the catalytic properties of NaY and NaM also indicates a stability in their hydrogenating activity. From the data presented it can be concluded that NaM and NaY zeolites are "developed" during the course of the reaction and are capable of operating for a relatively long time without a substantial loss in activity. NaX, however, is deactivated even in the first experiment. Thus, NaY, which belongs to the faujasite group, is very similar to NaM in hydrogenating properties and differs greatly from NaX.

CONCLUSIONS

1. A dual action of hydrogen on the activity of Na mordenite in the hydrogenation of benzene has been established. Thus, hydrogen activates the catalyst at 160-250°C and deactivates it at 350-400°C. However, NaX zeolite is only deactivated by hydrogen in this reaction at 180-400°C.

2. A high stability has been shown for the catalytic activity of Na mordenite, which catalyzes the hydrogenation of benzene at a conversion of 80-90% for more than 40 h without regeneration. NaY zeolite also possesses a good stability of the hydrogenating activity, whereas the hydrogenating activity of another faujasite, NaX, is lowered greatly, even after the first hour of operation of the catalyst.

LITERATURE CITED

- 1. Kh. M. Minachev, V. I. Garanin, T. A. Isakova, E. A. Udal'tsova, and I. I. Levitskii, Izv. Akad. Nauk SSSR, Ser. Khim., 770 (1980).
- 2. T. A. Isakova, Dissertation, Moscow (1976), p. 117.