JOURNAL OF CATALYSIS 89, 14–19 (1984)

CH_x Addition–Abstraction Mechanism of Aromatization of Methylpentanes on Nickel and Cobalt Catalysts

A. SÁRKÁNY

Institute of Isotopes of the Hungarian Academy of Sciences, P.O. Box 77, H-1525 Budapest, Hungary

Received October 14, 1983; revised March 13, 1984

The mechanism of dehydrocyclization has been investigated with a group of branched C_6 and C_7 isomeric hydrocarbons containing only four or five carbon atoms in the main chain on Ni and Co catalysts of small and medium dispersion in the temperature range 573–650 K. At low H_2/HC ratios transformation of 2-methylpentane, 3-methylpentane, and 3-ethylpentane yields toluene and ethylbenzene, respectively, besides benzene. Evidence is presented that the formation of benzene takes place via CH_x-addition to a vinylic group, 1,6-ring closure, and CH_x-abstraction in the adsorbed phase. In the proposed reaction sequence the rate of CH_x insertion is regarded as the rate-limiting step of aromatization. Participation of the bond-shift or the C_5-cyclization route of aromatization is not significant over Ni and Co.

INTRODUCTION

It is generally accepted in the literature that metal catalyzed aromatization of methylpentanes and dimethylbutanes requires C_5-cyclization and/or bond-shift activity (*1*) as well as stepwise dehydrogenation. Aromatization of geminal pentanes over Pt has been interpreted by 1,5-ring closure followed by ring expansion facilitated by the presence of geminal methyl groups (*2–4*). With nongeminal methylpentanes aromatization is proposed to involve three consecutive steps in the adsorbed phase: 1,5-ring closure, ring opening, and 1,6-ring closure (*3, 5*). Dimethyl- and trimethylbutanes can be forced to aromatize only at elevated temperatures (*6, 7*); the reaction must be initiated by carbon skeletal rearrangement (*6, 7*) producing thereby suitable species for 1,5- or 1,6-ring closure. Dehydroisomerization as opposed to isomerization producing saturated isomers is favored under hydrogen-deficient conditions which in turn points to the formation of dehydrogenated reaction intermediates (*6*). Mechanistic considerations are also treated in other papers (*8, 9*).

The proposed reaction steps or their combination account satisfactorily for aromatization over Pt, Pd, Ir, and Rh catalysts, since the above group of metals possess both bond-shift and C_5-cyclization activity (*10, 11*). As far as Ni and Co are concerned their isomerization activity has not been convincingly demonstrated, although the transformation of paraffins (the selectivity to various products) has been thoroughly investigated. Thus, alongside C–C bond rupture no isomerization has been detected in the transformation of *n*-pentane (*12*), *n*-hexane (*13*), 2,2-dimethylpropane (*14*), 2,3-dimethylbutane (*13, 15*), 2,2-dimethylbutane (*13, 15*), and 2- and 3-methylpentane (*11, 13*) over various forms of Ni and Co catalysts. In contrast to these results, isomerization of 2-methylpropane (*16*) and *n*-hexane (*17, 18*) over Ni and the aromatization of 2-methylpentane and 3-methylpentane over Ni and Co catalysts have been observed (*19, 20*).

The discrepancies in these results and the recognition that the partial pressure of hydrogen strongly influences the selectivity of individual reaction routes (*21*) prompted us to investigate the mechanism of dehydrocyclization with Ni and Co catalysts. We have reported recently that aromatization of 2-

0021-9517/84 $3.00

methylpentane and 3-methylpentane is accompanied by chain lengthening over Ni and Co, resulting in the formation of toluene (*19, 20*). Because of this observation, we are inclined to believe that benzene formation from 2-methylpentane and 3-methylpentane takes place via a CH_x-addition, 1,6-ring closure, CH_x-abstraction mechanism. To justify this proposal we have undertaken a systematic study of the dehydroisomerization activity of Co and Ni with a group of branched C_6 and C_7 isomeric alkanes containing only four or five carbon atoms in the main chain.

EXPERIMENTAL

Experiments have been performed in a static circulation system (0.185 dm^3) connected via sampling valve to a Packard 427 gas chromatograph. The rates and selectivity parameters are defined in conformity with earlier papers (*19, 20*). Ni and Co black were reduced from the hydroxides, 5.3 wt% Co/SiO_2 and 8.7 wt% Ni/SiO_2 were prepared by impregnation of SiO_2 (SAS Scientific Chemicals) with Ni $(NO_3)_2$ and Co $(NO_3)_2$, respectively, utilizing the method of incipient wetness. Crystallite size (d_v) determined by X-ray diffraction is 15, 20, 5.7, 6.7 nm for samples 1.3-Co-B, 0.9-Ni-B, 23-Co-Imp, and 16-Ni-Imp, respectively, where the initial number is the dispersion (%) measured by hydrogen chemisorption (*19*) and B, Imp, respectively, indicate metal black and impregnation.

RESULTS AND DISCUSSION

Selectivities of product formation with 2 : 1 hydrogen/hydrocarbon mixtures (2.66 kPa hydrocarbon) on Co-B, 23-Co-Imp, Ni-B, 16-Ni-Imp, and the rate of product formation as a function of hydrogen pressure on 16-Ni-Imp are presented in Tables 1 and 2 and in Fig. 1, respectively.

As shown by the data in Tables 1 and 2, 2-methylpentane, 3-methylpentane, and 3-ethylpentane underwent aromatization. The selectivity of benzene formation, S_B, is about 5–10%. In contrast to this group of hydrocarbons, the yield of aromatics is negligible from 2,2-dimethylbutane, 2,3-dimethylbutane, 2,3-dimethylpentane, and 2,4-dimethylpentane; S_B is in the range of 0.4–0.01%. The main reaction route is a "zipfastener" fragmentation resulting mainly in the formation of methane. With 2-methylpentane, 3-methylpentane, and 3-ethylpentane, the rate of benzene formation passes through a maximum as a function of hydrogen pressure. No such definite maximum was observed with 2,2-dimethylbutane and 2,4-dimethylpentane.

TABLE 1

Product Selectivity (%) over Ni-B and 16-Ni-Imp Catalysts[a]

Starting HC[b]	Ni-B						16-Ni-Imp					
	Temp. (K)	α(%)	$\Sigma(C_1–C_5)$	B	T	Others	Temp. (K)	α(%)	$\Sigma(C_1–C_5)$	B	T	Others
n-H	633	6.6	39.2	43.5	15.5	1.8 (EB)	623	10.2	29.4	47.5	21.4	1.7 (EB)
CP	584	4.7	93.4	5.9	0.1	0.6 (2MP)	615	7.6	91.8	6.7	0.3	1.2 (2MP)
2-MP	623	5.6	87.5	8.9	3.6	—	623	5.8	84.9	8.8	6.3	—
3-MP	623	5.3	90.7	6.8	2.5	—	623	9.2	88.5	5.7	5.8	—
3-EP	633	6.2	81.8	15.5	0.6	2.1 (EB)	633	6.8	81.9	9.6	6.3	2.2 (EB)
2,2-DMB	623	7.6	99.99	0.01	—	—	623	5.9	99.99	0.01	—	—
2,3-DMB	635	6.8	99.97	0.03	—	—	635	10.7	99.93	0.07	—	—
2,4-DMP	635	5.8	99.98	0.01	0.01	—	633	6.3	99.86	0.13	0.01	—
2,3-DMP	635	10.2	99.82	0.17	0.01	—	603	5.3	99.59	0.34	0.07	—

[a] Conditions: 0.083–0.12 g catalyst; p_{HC} = 2.66 kPa, H_2/HC = 2.

[b] *n*-H, *n*-hexane; CP, cyclopentane; 2-MP, 2-methylpentane; 3-MP, 3-methylpentane, 3-EP, 3-ethylpentane; 2,2-DMP, 2,2-dimethylbutane; 2,3-DMB, 2,3-dimethylbutane; 2,4-DMP, 2,4-dimethylpentane; 2,3-DMP, 2,3-dimethylpentane; B, benzene; T, toluene; EB, ethylbenzene.

TABLE 2

Product Selectivity (%) over Co-B and 23-Co-Imp Catalysts[a]

Starting HC	Co-B						23-Co-Imp					
	Temp. (K)	α(%)	$\Sigma(C_1–C_5)$	B	T	Others	Temp. (K)	α(%)	$\Sigma(C_1–C_5)$	B	T	Others
n-H	615	6.2	46.2	41.5	11.7	0.6 (EB)						
c-P	623	7.7	89.9	8.7	1.3	0.12 (2MP)	635	5.2	85.1	10.2	3.6	1.1 (2MP)
2-MP	615	10.2	87.7	9.6	2.7	0.01 (EB)	627	7.1	80.7	13.2	5.3	0.8 (EB)
3-MP	618	12.3	87.4	10.3	2.2	0.09 (EB)	623	6.3	78.4	14.1	6.7	0.8 (EB)
3-EP	623	15.5	83.39	14.21	0.73	1.67	623	9.9	83.1	15.5	0.1	1.33 (EB)
2,2-DMB	637	10.2	100.0	—	—	—	650	3.7	100	—	—	—
2,3-DMB	623	7.1	99.99	0.01	—	—	637	5.2	99.97	0.03	—	—
2,4-DMB	623	10.3	99.83	0.17	—	—	635	6.3	99.93	0.07	—	—

[a] Conditions and abbreviations as in Table 1.

The low selectivity of benzene formation from 2,2-dimethylbutane and 2,3-dimethylbutane permits us to suggest that bond shift isomerization activity of Co and Ni catalyst of low and medium dispersion is negligible over the entire hydrogen pressure range investigated. Rejecting the contribution of the bond shift-type rearrangement to aromatization, one might argue that benzene from 2-methylpentane and 3-methylpentane, and toluene from 3-ethylpentane, are formed via the C_5-cyclization route. The low value of S_B and S_T observed with 2,4-dimethylpentane and 2,3-dimethylpentane, however, allows one to reject this assumption.

Aromatization of 2-methylpentane, 3-methylpentane, and 3-ethylpentane, as shown by the results in Tables 1 and 2 and Fig. 1, accompanies the formation of toluene and ethylbenzene, respectively. The formation of toluene and ethylbenzene can be interpreted by carbene insertion into a terminal olefin via a metallocyclobutane intermediate as proposed by O'Donohoe *et al.* (*22, 23*), followed by 1,6-dehydrocyclization (*19, 20*). Previous results (*19, 20, 22, 23*) and the present results in Table 1 and Fig. 1. have proved that the probability of chain lengthening strongly depends on the structure of the starting hydrocarbon. Owing to steric and/or electrical effects, the presence of a methyl group adjacent to an end methyl group (2,3-dimethylbutane, 2,4-dimethylpentane) or of a quaternary carbon atom in the β position to the end methyl group (2,2-dimethylbutane) inhibit CH_x in-

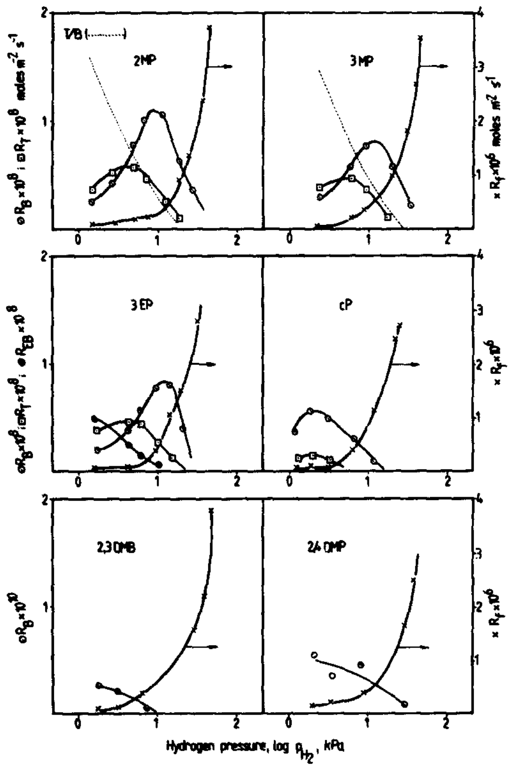

FIG. 1. Rate of formation of benzene (O), toluene (□), ethylbenzene (◑), and rate of fragmentation (×) as a function of hydrogen pressure on 16-Ni-Imp at 603 K. Benzene/toluene ratio (B/T) is given by dotted line. Conditions: 0.04 g catalyst, p_{HC} = 3.99 kPa.

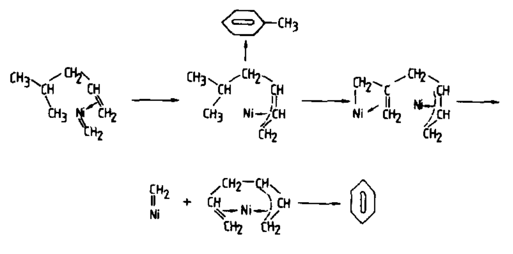

FIG. 2. CH_x addition–abstraction mechanism of aromatization of 2-methylpentane.

sertion. CH_x insertion is not inhibited into 2-methylpentane, 3-methylpentane, and 3-ethylpentane and therefore the formation of surface species containing six carbon atoms in the main chain is ensured and in this way 1,6 dehydrocyclization may occur. Benzene is then formed, as shown in Fig. 2 with 2-methylpentane, from a C_7 species via CH_x abstraction.

1,6-Dehydrocyclization in contrast to 1,5-cyclization is favored by hydrogen-deficient conditions. The occurrence of thermally induced 1,6-cyclization of 1,3,5-hexatriene (*24, 25*) provides also some additional evidence as to why 1,6-dehydrocyclization as opposed to 1,5-cyclization (*11*) is not subjected to strict geometrical requirements such as the interatomic distances in the metals. The ease of 1,6 cyclization over Ni and Co is indicated by the selectivity of aromatization with *n*-hexane in Table 1. Although the transformation of *n*-hexane is accompanied by fragmentation, S_{B+T} is 0.53, 0.59, and 0.69 with Co-B, Ni-B, and 16-Ni-Imp, respectively. In an earlier study (*26*) S_{B+T} was found to be 0.65 at 570 K over Ni-black prepared similarly to our present Ni-B.

The last step of the proposed mechanism, CH_x abstraction, requires some discussion. Hydrodealkylation of toluene takes place readily at 573 K over Ni resulting in the formation of benzene with selectivity 0.94 (*27*).

With increasing hydrogen pressure the toluene/benzene ratio drops drastically, as shown by the dotted line in Fig. 1, with 2-methylpentane and 3-methylpentane. A systematic change of the benzene/toluene ratio as a function of hydrogen pressure has also been observed in aromatization of heptane isomers over Pt-black (*7*). The change of the toluene/benzene ratio could be interpreted as due to an increasing participation of the C_5-cyclization route, but the absence of benzene, toluene and of C_6 and C_7 isomers with 2,3-dimethylbutane and 2,4-dimethylpentane, respectively, makes this tentative proposal highly questionable. Investigations with 2-methylpentane and [^{14}C]toluene labeled in the ring have revealed further details of demethylation. If benzene were entirely formed from toluene according to the reaction sequence 2-methylpentane → toluene → benzene, then the specific activity of benzene should be close to that of toluene. Data in Table 3 prove that in most cases the specific activity of benzene is significantly less than that of toluene. The low specific activity of benzene in comparison to that of toluene can be explained in the following ways: (i) Benzene is formed from toluene but the adsorbed toluene intermediate is not equilibrated with the vapor phase, because the rate of demethylation exceeds the rate of adsorption of toluene. Hindrance of in-

TABLE 3

Specific Radioactivity of Benzene and Toluene Formed in the Transformation of [^{14}C]Toluene + 2-Methylpentane Mixtures[a]

Catalyst	Temp. (K)	$\alpha(\%)$[b]	ρ_B/ρ_T0[c]	ρ_T/ρ_T0[c]
0.9-Ni-B	603	6.3	0.12	0.71
0.9-Ni-B	573	15.5	0.35	0.83
16-Ni-Dep	563	10.5	0.23	0.55
23-Co-Imp	563	17.7	0.33	0.76
1.3-Co-B	593	26.3	0.18	0.84

[a] Experimental conditions: 2MP = 3.99 kPa, H_2 = 7.8 kPa, ^{14}C-T = 23 Pa (^{14}C-T labeled in the ring exclusively).

[b] Conversion.

[c] ρ_T0, initial specific activity of toluene; ρ_T and ρ_B are the actual specific activities of toluene and benzene, respectively.

TABLE 4

Specific Radioactivity of Benzene and Toluene Formed from a Mixture of [^{14}C]Benzene and 2-Methylpentane[a]

Catalyst	Temp. (K)	α(%)	ρ_T/ρ_B0[b]	ρ_B/ρ_B0[b]	I_B/I_B0[b]
0.9-Ni-B	573	6.7	0.01	0.90	0.85
0.9-Ni-B	573	25.5	0.07	0.49	0.87
0.9-Ni-B	623	30.5	0.22	0.36	0.38
46-Ni-Dep	563	17.8	0.03	0.63	0.82
16-Ni-Imp	573	16.6	0.05	0.43	0.91
23-Co-Imp	593	10.2	0.03	0.83	0.92
1.3-Co-B	573	17.2	0.08	0.64	0.63

[a] Experimental conditions: 2-MP = 3.99 kPa; ^{14}C-B = 13.3 Pa; p_{H_2} = 7.8 kPa.

[b] ρ_B0, initial specific activity of benzene; ρ_T and ρ_B are the actual specific activities of toluene and benzene, respectively; I_0 and I, initial and actual activity of benzene, respectively.

termediate product desorption has already been observed in hydrogenolysis reactions with Ni catalysts (*28*, *29*). (ii) An alternative possibility that benzene is not formed exclusively from adsorbed toluene but from other C_7 species and the CH_x is removed from the C_7 intermediate before or in the course of 1,6-cyclization. Most probably, both (i) and (ii) are responsible for the low specific activity of benzene formed in a small excess of hydrogen.

In principle the observed alkylaromatics might also be formed via direct alkylation of the benzene ring. The reaction is known to be favored on strongly acidic sites or in the presence of Lewis acids (*30*). The possibility of benzene alkylation over Ni and Co catalysts has been checked using a mixture of 2-methylpentane and radioactive benzene. The lack of radioactivity in the toluene, assuming that benzene is not fragmented, would confirm the CH_x addition mechanism to 2-methylpentane whereas the opposite case, i.e., that benzene is not fragmented but toluene shows radioactivity, would provide evidence for the benzene alkylation route. The results of the radiotracer experiments are presented in Table 4. With Ni-B and 16-Ni-Imp below 593 K and with Co-B below 573 K only a small fraction of benzene is fragmented as shown by the last column in Table 4. The low specific activity of toluene in comparison with benzene eliminates the direct alkylation of benzene and hence the transformation of 2-methylpentane to benzene by bond-shift or the C_5-cyclization route as well. At elevated temperatures, typically above 610 K, toluene becomes more and more radioactive, most probably due to participation of fragments formed from [^{14}C]benzene in chain lengthening. Benzene fragmentation exceeds its formation at 625 K over Ni-B, as shown in an earlier study (*31*).

The evidence presented in Tables 1–4 and in Fig. 1 shows that the dehydroisomerization of 2-methylpentane, 3-methylpentane, and 3-ethylpentane over Co and Ni can convincingly be interpreted by a CH_x-addition, 1,6-dehydrocyclization, CH_x-abstraction mechanism. In the proposed reaction sequence the rate of CH_x insertion can be regarded as the rate limiting step of aromatization. Participation of the bond-shift or the C_5-cyclization route in aromatization does not seem to be significant over Ni and Co catalysts of low and medium dispersion, in contrast to Pt-based catalysts. Rearrangement of molecules by a combined action of metallic sites and the acidic function of the support can also be ruled out. The presence of surface carbon plays an important role both in chain lengthening and in aromatization, since its presence suppresses the destructive sites which lead to fragmentation. As shown by Fig. 1, a change of the hydrogen partial pressure from 75 to 2.6 kPa brings about a 70-fold decrease of the hydrogenolysis rate with 2-methylpentane. It is important to note at this point that although the carbon coverage at a 1 : 1 hydrogen/hydrocarbon ratio is significant (*20*) the Ni catalysts still do not resemble Ni–Cu alloys as regards isomerization activity (*18*). Apparently the high reactivity of surface carbon atoms toward hydrogen (*20*) and the mechanism of carbon deposit formation (*32*) render formation of small, isolated Ni ensembles impossible.

Finally, we should like to emphasize that the stereoselectivity of CH_x addition shows close similarity with homologation chain lengthening and with Fischer–Tropsch synthesis. One of the basic features of the Fischer–Tropsch reaction is the selectivity of isomer formation: unbranched $\gg$ branched. As far as branched hydrocarbons are concerned the hierarchy is monomethyl $\gg$ dimethyl $\sim$ trimethyl, and hydrocarbons containing quaternary carbon atoms are not formed (*33–35*). As shown by the data in Tables 1 and 2, once branched hydrocarbons are formed the chance of chain lengthening becomes limited if there is no possibility for the formation of a vinyl group. The occurrence of chain lengthening in a metal–hydrocarbon system also provides additional evidence that chain growth in the Fischer–Tropsch synthesis takes place via an oxygen-free CH_x intermediate (*36*).

REFERENCES

1. Paál, Z., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 29, p. 273. Academic Press, New York, 1980.

2. Kazanskii, B. A., Liberman, A. L., Loza, G. V., and Vasina, T. V., *Dokl. Akad. Nauk SSSR* **128,** 1188 (1959).

3. Barron, Y., Maire, G., Muller, J. M., and Gault, F. G., *J. Catal.* **5,** 428 (1966).

4. Muller, J. M., Thèse d'Etat, Caen, 1969.

5. Amir-Ebrahimi, V., and Gault, F. G., *J.C.S. Faraday Trans. I* **77,** 1813 (1981).

6. Paál, Z., and Tétényi, P., *J. Catal.* **29,** 176 (1973).

7. Zimmer, H., Paál, Z., and Tétényi, P., *Acta Chim. Hung. Acad. Sci.* **111,** 513 (1982).

8. Callender, W. L., Brandenberger, S. G., and Meerbott, W. K., Proc. Int. Congr. Catalysis, 5th (Florida, 1972), p. 1265. North-Holland/American-Elsevier, Amsterdam/New York, 1973.

9. Gault, F. G., Amir-Ebrahimi, V., Garin, F., Parayre, F., and Weisang, F., *Bull. Soc. Chim. Belg.* **88,** 475 (1979).

10. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **20,** 223 (1971).

11. Paál, Z., and Tétényi, P., *Nature (London)* **267,** 234 (1977).

12. Kikuchi, E., Tsurumi, M., and Morita, Y., *J. Catal.* **22,** 182 (1971).

13. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **19,** 101 (1970).

14. Boudart, M., and Ptak, L. D., *J. Catal.* **16,** 90 (1970).

15. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58,** 260 (1979); Machiels, C. J., and Anderson, R. B., *J. Catal.* **58,** 268 (1979).

16. Taylor, J. F., and Clarke, J. K. A., *Z. Phys. Chem. N.F.* **103,** 216 (1976).

17. Anderson, J. R., and MacDonald, R. J., *J. Catal.,* **19,** 227 (1970); Anderson, J. R., MacDonald, R. J., and Shimoyama, Y., *J. Catal.* **20,** 147 (1971).

18. Ponec, V., and Sachtler, W. M. H., Proc. Int. Congr. Catalysis, 5th (Florida, 1972) p. 654. North-Holland/American Elsevier, Amsterdam/New York, 1973.

19. Sárkány, A., and Tétényi, P., *J.C.S. Chem. Commun.* 525 (1980).

20. Sárkány, A., Pálfi, S., and Tétényi, P., *Acta Chim. Hung. Acad. Sci.* **111,** 633 (1982).

21. Tétényi, P., Guczi, L., and Paál, Z., *Acta. Chim. Hung. Acad. Sci.* **83,** 37 (1974).

22. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J.C.S. Chem. Commun.* 648 (1979).

23. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J.C.S. Faraday I* **76,** 345 (1980).

24. Rozengart, M. I., Martinov, E. S., and Kazansky, B. A., *Dokl. Akad. Nauk SSSR* **166,** 619 (1966).

25. Paál, Z., and Tétényi, P., *J. Catal.* **30,** 350 (1973).

26. Guczi, L., Kálmán, J., and Sárkány, A., Proc. Symp. on the Mechanism of Hydrocarbon Reactions, Siófok 1973, p. 173. Akadémiai Kiadó, Budapest, 1975.

27. Grenoble, D. C., *J. Catal.* **56,** 32 (1979).

28. Guczi, L., Sárkány, A., and Tétényi, P., Proc. Int. Congr. Catalysis, 5th (Florida, 1972), p. 1111. North-Holland American Elsevier, Amsterdam/New York, 1973.

29. Sárkány, A., Guczi, L., and Tétényi, P., *Acta Chim. Hung. Acad. Sci.* **84,** 245 (1975).

30. Olah, G. A., "Friedel-Crafts and Related Reactions," Vols. I–IV. Interscience, New York, 1964.

31. Guczi, L., Matusek, K., and Tétényi, P., *React. Kinet. Catal. Lett.* **3,** 291 (1974).

32. Rostrup-Nielsen, J., Trimm, D. L., *J. Catal.* **48,** 155 (1977).

33. Storch, H. H., Golumbic, H., and Anderson, R. B., "Fischer-Tropsch and Related Synthesis." Wiley, Chichester, 1951.

34. Friedel, R. A., and Anderson, R. B., *J. Amer. Chem. Soc.* **72,** 1212 (1950).

35. Anderson, R. B., Friedel, R. A., and Storch, H. H., *J. Chem. Phys.* **19,** 313 (1951).

36. Ponec, V., *in* "Catalysis" (Specialist Periodical Reports), Vol. 5, p. 48. Royal Society of Chemistry, London, 1982.