Homologation of Pentanes and Hexanes on Ni Catalysts

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Summary Homologation of pentanes and isohexanes results in the formation of benzene and toluene on Ni black and on supported Ni catalysts.

The catalytic properties of Ni catalysts in the hydrogenolysis of saturated hydrocarbons (HC) have been extensively investigated. At high H_2 to HC ratios a selective C–C bond rupture takes place at the terminal position (α-splitting) but under hydrogen-deficient conditions 'deep' fragmentation prevails[1] resulting in the formation of methane and in poisoning of the surface by carbonaceous deposits. Until now little attention has been paid to the formation of hydrocarbons with larger carbon number than the parent, although formation of toluene[2] from n-hexane has already been observed on Ni black. In this communication we present data on the homologation activity of Ni catalysts.

The experiments were performed in a circulating system;[1] the preparation and physical characteristics of the catalysts† have been described elsewhere.[3] The formation of products in a typical experiment are shown in Figure 1. On Ni catalysts homologation of pentanes and isohexanes yields benzene and toluene. The reaction conditions and results are summarized in Tables 1 and 2. The product distribution

Table 1. Experimental conditions.[a]

Expt.	Catalyst	Hydrocarbon	T/K
1	16-Ni-Imp	n-Pentane	603
2	16-Ni-Imp	n-Pentane	523
3	16-Ni-Imp	2-Methylbutane	603
4	16-Ni-Imp	2,3-Dimethylbutane	603
5	16-Ni-Imp	Cyclopentane	603
6	16-Ni-Imp	2-Methylpentane	573
7	16-Ni-Imp	3-Methylpentane	573
8	0·9-Ni-B	n-Pentane	603
9	0·9-Ni-B	Cyclopentane	603
10	46-Ni-Dep	n-Pentane	603
11	46-Ni-Dep	Cyclopentane	603
12	0·6-Co-B	n-Pentane	603
13	0·6-Co-B	Cyclopentane	573
14	0·9-Pt-B	n-Pentane	610

[a] All measurements with mixtures of 4·65 kNm^{-2} of hydrocarbon and 6·85 kN m^{-2} of H_2.

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† The crystallite size (d_v) determined by *X*-ray diffraction is 25, 6·7, and 1·8 nm for samples 0·9-Ni-B, 16-Ni-Imp, and 46-Ni-Dep, respectively, where the initial number is the dispersion (%) measured by hydrogen chemisorption and B, Imp, and Dep, respectively, indicate metal black, impregnation using the method of incipient wetness, and precipitation of $Ni(NO_3)_2$ by urea on to the surface of SiO_2 aerogel (ref. 9). The high dispersity of sample 46-Ni-Dep was ensured by the low extent of reduction (25—31 %) as measured by thermogravimetric and magnetic measurements.

TABLE 2. Product distribution[a] (%)

Expt.	C_1	C_2	C_3	C_4	iC_5	nC_5	2MP[b]	2MH[b]	B[b]	T[b]	R_H[c]
1	69·5	17·6	4·5	1·5	0·8		—	—	6·1	tr[d]	$5{\cdot}7 \times 10^{-9}$
2	59·9	24·3	8·9	2·3	0·1		—	—	4·4	—	$8{\cdot}8 \times 10^{-10}$
3	78·3	16·6	3·7	1·1		—	0·1	—	0·15	—	$8{\cdot}8 \times 10^{-10}$
4	83·3	13·1	3·3	tr	—	—	0·3	—	0·1	—	$1{\cdot}1 \times 10^{-10}$
5	71·3	14·2	4·4	0·4	tr	tr	0·9	tr	8·3	0·5	$8{\cdot}2 \times 10^{-9}$
6	68·1	8·5	4·2	2·2	1·9	1·3		0·3	7·3	6·2	$6{\cdot}3 \times 10^{-9}$
7	73·2	9·3	2·5	0·2	0·3	—	—	—	5·7	8·8	$7{\cdot}5 \times 10^{-9}$
8	92·1	5·5	1·1	tr	—		0·1	—	1·1	—	$5{\cdot}1 \times 10^{-10}$
9	88·3	5·8	1·0	tr	—	—	0·2		4·7	—	$2{\cdot}3 \times 10^{-9}$
10	77·2	7·2	1·8	0·6	—		0·3	0·1	12·8	tr	$1{\cdot}8 \times 10^{-8}$
11	65·4	10·3	2·1	0·5	—	—	1·5	0·2	18·1	2·4	$4{\cdot}2 \times 10^{-8}$
12	75·9	14·7	4·3	0·58	—		—	—	4·4	—	$6{\cdot}3 \times 10^{-9}$
13	79·4	10·5	3·3	0·47	—	—	—	—	6·3		$8{\cdot}8 \times 10^{-9}$
14[e]	28·6	6·4	8·1	5·3	5·5		—	—	—	—	—

[a] Expressed in terms of carbon content. [b] 2MP = 2-methylpentane, 2MH = 2-methylhexane, B = benzene, T = toluene. [c] R_H = rate of formation of homologues (C_{n+1}) in mol m^{-2}(Ni) s^{-1}. [d] Traces. [e] 40·4% Pentenes, 3·4% cyclopentane, and 1·8% cyclopentene.

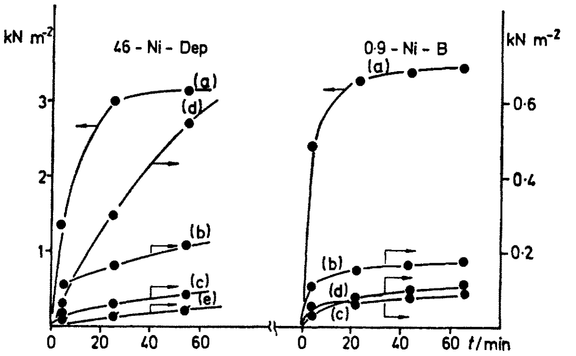


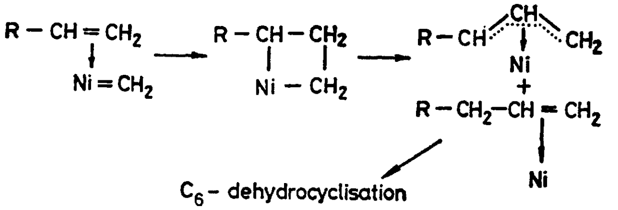
FIGURE 1. Formation of products from cyclopentane on 46-Ni-Dep and 0·9-Ni-B catalysts at 523 K: (a) C_1; (b), C_2; (c), C_3; (d), benzene; (e), toluene ($H_2/HC = 2$; $p_{HC} = 4{\cdot}65$ kN m^{-2}).

measured at 5—10% conversion and the maximum rate of formation of the first homologues (C_{n+1}) are presented in Table 2.

Branched hydrocarbons were found to be less efficient in this reaction than straight-chain ones as is the case for W films.[4] Thus, 2-methylbutane gave only trace amounts of 2-methylpentane and benzene and only trace amounts of benzene and 2-methylpentane were detected from 2,3-dimethylbutane. 2,2-Dimethylpropane gave only fragments and no 3-methylpentane and 3-methylhexane was formed from n-pentane and n-hexane, respectively. In contrast with results from W films, a considerable amount of benzene and, to a smaller extent, 2-methylpentane was formed from cyclopentane.

The reaction proceeds also on Co-B, but we failed to detect homologation on Pt-B.

The observed product distribution and the sensitivity of the reaction to the $CH_2/(CH + CH_3)$ ratio in the parent hydrocarbon supports the suggestion[4] that the C–C bond is formed by carbene insertion into an α-olefin *via* a metallocyclobutane intermediate. Examples of carbene insertion into Ni–alkyl bond of homogeneous mono- and di-alkyl-nickel(II) complexes[5] and evidence suggesting the formation of nickelacyclobutane[6] have recently been reported. C–C Bond formation is then followed by C_6-dehydrocyclization[7] resulting in the formation of aromatics. As shown by the product distribution, carbene addition to non-terminal carbon atoms or to internal π-bonds is hindered. For this reason we tentatively suggest that in the case of cyclopentane carbene insertion is preceded by ring opening.



The rate of benzene formation from n-pentane passes through a broad maximum as a function of hydrogen pressure between 2·6 and 10 kN m^{-2} [p(nP) = 5·5 kN m^{-2}] and drops at higher pressures on catalysts 0·9-Ni-B and 16-Ni-Imp at 570 K. In the same pressure range [$p(H_2)$: 2·6—36 kN m^{-2}] the subsequent rate of fragmentation increases with increasing hydrogen pressure giving a reaction order with respect to hydrogen of 0·6—1·3. The apparent activation energies are 17—32 and 104—125 kJ mol^{-1} for benzene formation and fragmentation, respectively, in the temperature range 550—600 K. At high hydrogen to n-pentane ratios, the C–C bond formation is inhibited probably by the low coverage of carbene and terminal olefin whereas at low hydrogen pressures the active sites resulting in the formation of carbene may be readily deactivated.

The shape of curves of product concentration *vs.* time proves that the metal surface is covered by carbonaceous deposits in the first moments of reaction. This carbonaceous deposit may then serve as a source of carbene intermediates during the C–C bond formation unless the surface carbon undergoes deactivation. The low activity of 0·9-Ni-B is probably due to the rapid deactivation of surface carbon.

Temperature programmed hydro-desorption (TPHD) measurements presented in Figure 2 seem to support this assumption. On catalysts 0·9-Ni-B and 16-Ni-Imp the surface carbon formed from ethylene (three 0·2 ml aliquots at NTP heated to 583 K in He) transformed readily into

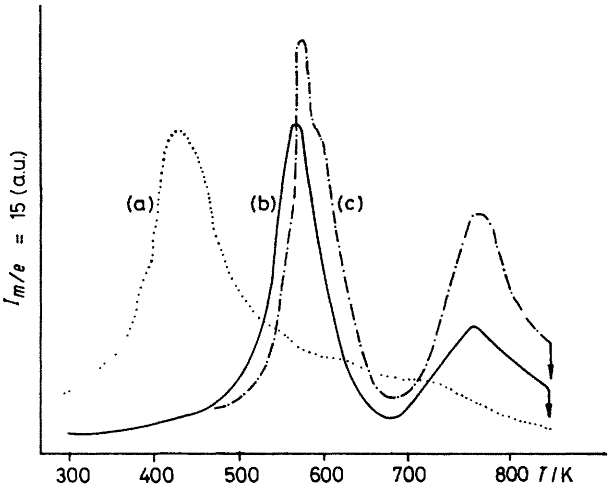


FIGURE 2. TPHD of carbon deposited by exposure to C_2H_4 at 583 K; heating rate 0·5 K s^{-1}; hydrogen flow rate 32 ml min^{-1}: (a), 46-Ni-Dep; (b), 16-Ni-Imp; (c), 0·9-Ni-B.

amorphous carbon that can be removed at elevated temperatures only (T = 785 K); a more reactive form of carbon was observed at peak temperatures of 565 and 555 K, respectively. On the more disperse sample formation of amorphous carbon is inhibited; the catalyst surface is covered mainly with isolated carbon atoms of high reactivity (*T* 427 K). The rapid deactivation of carbon on low-index facets of Ni crystallites (the dispersion of 0·9-Ni-B is 0·9%) may explain the higher activity of catalyst 46-Ni-Dep and its larger selectivity in C–C bond formation may point to the importance of sites of low co-ordination.

Finally, the homologation of hydrocarbons on a large group of metal catalysts (Ni, Co, W, Rh, and Pd) demonstrates the feasibility of chain propagation by carbene insertion in a metal–hydrogen–carbon heterogeneous system. Thus the presented results support the suggestion that incorporation of surface carbon into hydrocarbons during Fischer–Tropsch synthesis can take place *via* oxygen-free CH_x species.[8]

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[1] L. Guczi, A. Sárkány, and P. Tétényi, in Proc. 5th Int. Cong. Catal., Miami Beach, 1973, North Holland, Amsterdam, vol. 2, p. 1111.

[2] L. Guczi, J. Kálmán, and A. Sárkány in 'Mechanism of hydrocarbon reactions,' Symposium 5—7 June 1973 and 1975, Hung. Acad. Sci., p. 175.

[3] A. Sárkány and P. Tétényi, *React. Kinet. Catal. Lett.*, 1979, **12**, 297.

[4] C. O'Donohoe, J. K. A. Clarke, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1979, 648.

[5] T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1978, 1003.

[6] R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, 1978, **100**, 7418.

[7] Z. Paál and P. Tétényi, *Acta Chim. Acad. Sci. Hung.*, 1967, **54**, 175.

[8] P. Biloen, J. N. Helle, and W. M. H. Sachtler, *J. Catal*, 1979, **58**, 95.

[9] J. A. VanDillen, J. W. Geus, L. A. M. Hermans, and J. Van der Meijden, 6th Int. Cong. Catal., London, 1976, vol. 2, The Chemical Society, London, p. 677.