Hydrogenolysis of Cyclo-octane and Cyclo-octene on Supported Fischer–Tropsch Catalysts. Cyclic *vs.* Noncyclic Selectivity

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Hydrogenolysis of cyclo-octane or cyclo-octene over silica-supported ruthenium, nickel, and cobalt catalysts gives rise to n-alkanes and cycloalkanes (C_5—C_7); ruthenium strongly favours n-alkanes, cobalt strongly facilitates cycloalkane formation, and nickel is intermediate in selectivity.

The search for and understanding of selectivity in surface-catalysed reactions is of great current interest, and the hydrogenolysis of alkanes catalysed by supported and unsupported catalysts is an important subset of such reactions.[1,2] Cyclo-

Table 1. Product distributions derived from the hydrogenolysis of cyclo-octane at low conversions (<5%) over supported metal catalysts.[a,b]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	$\Sigma(C_5$—$C_7)$
Ru (80 °C)	48.1	6.4	6.3	1.9	9.4	6.8	21.0	37.2
(110 °C)	48.1	6.0	7.1	4.5	11.1	7.5	15.7	34.3
(130 °C)	50.1	8.1	8.1	5.7	10.4	6.7	10.8	27.9
Ni (190 °C)	70.4	1.3	1.2	0.8	3.9	5.4	17.0	26.3
(210 °C)	66.2	1.3	1.3	1.2	4.9	7.1	18.0	30.0
Co (190 °C)	74.3	1.4	0.5	0.2	10.2	9.5	3.9	23.6
(210 °C)	76.5	3.0	0.7	0.4	9.2	7.3	2.8	19.3

[a] Supported catalysts were prepared by the incipient wetness technique using aqueous solutions of ruthenium trichloride trihydrate, cobalt(II) nitrate hexahydrate, or nickel(II) nitrate hexahydrate and fumed silica (300 m^2/g) in ratios so as to obtain 5 wt% catalyst loadings with Ru and Ni, and 4 wt% with Co. The resulting mixture was heated at 100 °C under vacuum (12 h) and sieved (100 mesh). With the nickel catalyst only, the impregnated silica was then heated at 550 °C (4 h) in air. The catalyst was activated in the reactor in a stream of pure hydrogen at 450 °C for 12 h prior to reaction. The reactor was a 1 in. diameter glass tube with a sintered glass disk upon which the supported catalyst (75—250 mg) was placed. A tube furnace was used to achieve the desired temperature. The gas effluent after passing through the catalyst was sampled with a gas-tight syringe and analysed by g.l.c. (flame-ionisation detector) utilizing a 50 m OV-1 fused silica capillary column. Gas flow rates through the reactor were adjusted so as to effect 0.5—5% conversions of cyclo-octane. The cobalt and nickel catalysts were essentially inactive below 180 °C. [b] The values in the columns are percentage yields of products of a particular carbon number, irrespective of the structure. Typical product distributions for a particular carbon number fraction are given in footnotes b—d of Table 2.

(1)

(2)

alkane hydrogenolysis can, in principle, lead to α,ω-diadsorbed alkyl chains which might allow a study of cyclic *vs.* acyclic selectivities as a function of reaction conditions. The hydrogenolysis of cycloalkanes has been studied, but with few exceptions[3,4] the ring sizes utilized have been six or less.[4]

We now report our results concerning the hydrogenolytic reactions of cyclo-octane (**1**) and cyclo-octene (**2**) over silica-supported ruthenium, cobalt, and nickel catalysts. Passage of a (**1**)-saturated stream of hydrogen over 5% Ru/SiO_2 at 80 °C gave rise cleanly to n-alkane (C_7—C_1) hydrogenolysis products; no other products were observed. As the reaction temperature was raised however, cycloalkanes (C_5—C_7) began to be produced with the n-alkanes, so that at 130 °C the former were a reasonable fraction of the latter. Table 1 summarizes product distributions as a function of carbon number and Table 2, ratios of cycloalkanes to n-alkanes.

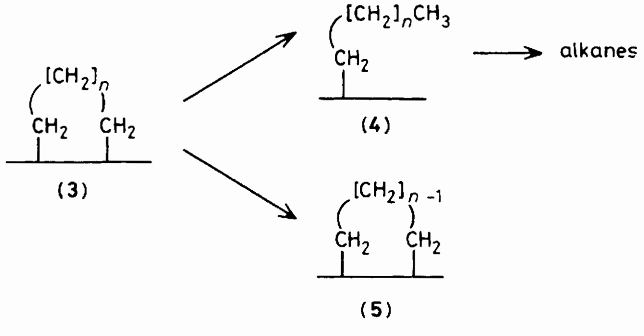
When (**1**)-saturated hydrogen was passed over a supported nickel catalyst at 180 °C, n-alkanes together with traces of C_5—C_7 cycloalkanes were produced. As the temperature was raised, cycloalkanes were produced, as with ruthenium (Table 2). In contrast, the same reaction over a supported cobalt catalyst at low temperatures (190 °C) strongly favoured the cycloalkanes (Table 2), and increasing temperatures led to increasing amounts of n-alkanes relative to cycloalkanes.

Control experiments established that under the conditions described above, the catalysts were not mediating the cyclodehydrogenation of the n-alkanes produced initially. Under these conditions neither oct-1-ene nor n-octane gave rise to any cycloalkanes, although hydrogenation of the former and hydrogenolysis of both substrates did occur.[2]

Table 2. Ratios of cycloalkanes/n-alkanes as a function of catalyst and temperature.[a]

	Cyclo-C_5/ n-C_5	Cyclo-C_6/ n-C_6	Cyclo-C_7/ n-C_7
Ru 110 °C (130 °C)[b]	0.024 (0.032)	0.20 (0.28)	0.086 (0.15)
Ni 190 °C (210 °C)[c]	0.49 (1.56)	0.83 (1.36)	1.43 (2.13)
Co 190 °C (210 °C)[d]	21.4 (9.36)	85.8 (41.3)	32.6 (23.1)

[a] Catalyst preparation, loading, and the reactor are described in footnote a, Table 1. The cyclic products for C_6 and C_7 may include methylcyclopentane (cyclo-C_5Me) and methylcyclohexane (cyclo-C_6Me), as well as C_6H_6 and PhMe, respectively. The linear species n-C_{5-7} may include the isoalkanes (i-C_{5-7}). Product distributions are given in footnotes b—d. [b] No aromatics were observed at these temperatures. At temperatures below 120 °C, the products were predominantly unsubstituted cycloalkanes and n-alkanes. At 130 °C typical product distributions were (given as a percentage of each carbon number fraction): C_5, n-C_5 (97), cyclo-C_5 (3), i-C_5 (0.3); C_6, n-C_6 (77), i-C_6 (1), cyclo-C_6 (22), cyclo-C_5Me (0.6); C_7, n-C_7 (87), i-C_7 (0.8), cyclo-C_7 (9), cyclo-C_6Me (4). [c] No aromatics observed at 190 °C. At 210 °C, typical product distributions were (% of each C-number): C_5, n-C_5 (33), i-C_5 (6), cyclo-C_5 (61); C_6, n-C_6 (40), i-C_6 (2), cyclo-C_6 (32), cyclo-C_5Me (23), C_6H_6 (2); C_7, n-C_7 (26), i-C_7 (6), cyclo-C_7 (4), cyclo-C_6Me (32), PhMe (32). [d] Aromatics at 190 °C were 10% of the C_6 and C_7 fractions. At 210 °C typical product distributions were (% of each C-number): C_5, n-C_5 (9), i-C_5 (1), cyclo-C_5 (90); C_6, n-C_6 (1), i-C_6 (0.8), cyclo-C_6 (35), cyclo-C_5Me (13), C_6H_6 (50); C_7, n-C_7 (4), cyclo-C_7 (45), cyclo-C_6Me (18), PhMe (33).



Scheme 1

Cyclo-octene (**2**) gave product ratios and temperature dependence of these ratios which were very similar to those from (**1**). Under conditions which gave only *ca.* 2% hydrogenolysis products, no (**2**) survived passage through the catalyst, having been transformed completely to (**1**). The hydrogenolytic reactions could be initiated about 20 °C lower using (**2**) rather than (**1**) as substrate. Preliminary work with other cycloalkanes (C_7 and C_{10}) indicates behaviour analogous to (**1**) and (**2**).

Examination of Table 1 reveals that the C_5—C_7 products of hydrogenolysis of (**1**) comprise a reasonable fraction of all those produced. The Ni and Co catalysts give only small amounts of C_2—C_4 species, whereas Ru fosters much higher yields of these species. The yields of C_7—C_4 exhibit an exponential decrease with Ni (190 °C, $r = 0.973$), but with Ru and Co no such pattern emerges under any conditions. If a simple assumption is made that each C_7 species generates one CH_4, and each C_6, two CH_4, *etc.*, then with Ni and Co, the methane produced is roughly accounted for (± 20%) in this way. In contrast, the Ru catalyst gives methane yields which are considerably lower than predicted on the basis of this assumption (*e.g.* 110 °C, predicted/found = 3.4). This may well be indicative of hydrogenolytic pathways which cleave more than a C_1 unit from the surface-bound species. Table 2 shows the remarkable selectivity that these three catalysts exhibit, *e.g.* (cyclo-C_5/n-C_5)Co(190 °C)/(cyclo-C_5/n-C_5)Ru(130 °C) = 645. These observations illustrate the diversity of behaviour caused by these three catalysts that can be monitored, using a medium-ring carbocycle as a probe.

Recognizing the complexity of the reactions described herein, it is still useful to focus on a potential intermediate which could be responsible for much of the observed behaviour. Species (3) (Scheme 1), a surface-bound α,ω-dialkyl ($n = 6$), could be generated from substrate (**1**) in several steps. Intermediate (**3**) could then partition either to (**4**), the precursor to the n-alkanes, or to (**5**) *via* loss of a CH_2 unit.[2] Species (**3**) and (**5**), as well as lower homologues could then generate cycloalkanes *via* any of several possible pathways.[1,2] The cycloalkane/n-alkane selectivities observed may well reflect the partitioning of species such as (**3**) to (**4**) and (**5**) as a function of the metal.

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