J. CHEM. SOC., CHEM. COMMUN., 1983

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

Evan P. Kyba,* Huh-Sun Chiou, and Mary E. Cornell

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

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 surfacecatalysed 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	C7	$\Sigma(C_5 - C_7)$
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

* 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 $(300 \text{ m}^2/\text{g})$ 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 $^{\circ}$ 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 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.



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 silicasupported ruthenium, cobalt, and nickel catalysts. Passage of a (1)-saturated stream of hydrogen over 5% Ru/SiO₂ 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 1221

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)°	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 C₆ and C₇ may include methylcyclopentane (cyclo-C₆Me) and methylcyclohexane (cyclo-C₆Me), as well as C₆H₆ and PhMe, respectively. The linear species n-C₅₋₇ may include the isoalkanes (i-C₅₋₇). 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): C₅, n-C₅ (97), cyclo-C₅ (3), i-C₅ (0.3); C₆, n-C₆ (77), i-C₆ (1), cyclo-C₆ (22), cyclo-C₅Me (0.6); C₇, n-C₇ (87), i-C₇ (0.8), cyclo-C₇ (9), cyclo-C₆Me (4). ° No aromatics observed at 190 °C. At 210 °C, typical product distributions were (% of each Cnumber): C₅, n-C₅ (33), i-C₅ (6), cyclo-C₆ (61); C₆, n-C₆ (40), i-C₇ (6), cyclo-C₇ (4), cyclo-C₅Me (23), C₆H₆ (2); C₇, n-C₇ (26), at 190 °C were 10% of the C₆ and C₇ fractions. At 210 °C typical product distributions were (% of each C-number): C₅, n-C₅ (9), i-C₅ (1), cyclo-C₅ (90); C₆, n-C₆ (1), i-C₆ (0.8), cyclo-C₆ (35), cyclo-C₅Me (13), C₆H₆ (5); C₇, n-C₇ (4), cyclo-C₆ (40), c₆Me (18), PhMe (33).



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 (C₇ and C₁₀) 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 CH₄, and each C_6 , two CH₄, *etc.*, then with Ni and Co, the methane produced is roughly accounted for ($\pm 20\%$) 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. $(\text{cyclo-C}_5/\text{n-C}_5)\text{Co}(190 \,^\circ\text{C})/(\text{cyclo-C}_5/\text{n-C}_5)\text{Ru}(130 \,^\circ\text{C}) = 645$. 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 CH₂ 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.

We thank the National Science Foundation, the Robert A. Welch Foundation, and the Exxon Education Foundation for financial support, and referees for helpful comments.

Received, 23rd May 1983; Com. 656

References

- 1 J. A. Clarke, O. E. Finlayson, and J. J. Rooney, J. Chem. Soc., Chem. Commun., 1982, 1277 and references cited therein.
- 2 W. T. Osterloh, M. E. Cornell, and R. Pettit, J. Am. Chem. Soc., 1982, 104, 3759 and references cited therein.
- 3 K. Kochloefl and V. Bazant, J. Catal., 1968, 10, 140.
- 4 F. G. Gault, Adv. Catal., 1981, 30, 1.