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Hydrogenolysis of Propane on Supported Catalysts of Nickel, Cobalt, Iron, and Ruthenium

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The hydrogenolysis of propane was studied in a differential reactor system over supported catalysts of ruthenium, nickel, cobalt, and iron, some containing magnesia as a structural promoter. The kinetic data were fitted to a power rate equation. The results are in general agreement with those of similar experiments with ethane. Magnesia increased the activity of the nickel and cobalt catalysts, and stabilized the iron catalyst. Selectivities for ethane were fitted to a selectivity equation. The amount of ethane in the products decreased in the sequence: ruthenium, cobalt, nickel, iron.

INTRODUCTION

The hydrogenolysis of hydrocarbons over metal catalysts has been studied extensively; however, most of the studies have been with ethane. The earliest kinetic experiments of ethane hydrogenolysis were done on iron, cobalt, and nickel catalysts (*1*). Later the reaction was studied on other group VIII metals (*2*) and on alloys (*3*). Good reviews have been published by Sinfelt (*4, 5*). For most metals the hydrogenolysis of ethane was about first order in the hydrocarbon, but the hydrogen order varied with the catalyst: from small positive for iron, to small negative for cobalt, to large negative for most other metals, notably nickel and ruthenium. Apparent activation energies varied over a wide range, from 84 to 244 kJ/mol. Most of the kinetic data could be explained in terms of a reaction scheme proposed by Cimino *et al.* (*1*), and later modified by Sinfelt (*6*). The scheme involves reversible dissociative adsorption of ethane to form an unsaturated surface species, and the rate-limiting step is the irreversible rupture of the carbon–carbon bond. The monocarbon fragments then hydrogenate and desorb as methane. According to this scheme, the adsorbed ethane loses most of its hydrogen on many metals; this explains the large negative hydrogen exponents. In an alternate scheme, proposed by Boudart (*7*), the reaction is considered to be a two-step irreversible sequence on a nonuniform surface. For nickel, platinum, and copper–nickel catalysts, both models predict the same composition for the surface intermediates (*8*). Propane reacts more rapidly than ethane on supported nickel (*9*) and ruthenium (*10*). The amount of methane in the products increases with increasing temperature and decreasing pressure. A mechanism similar to that for ethane appears to be operative, the surface split-

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TABLE 1

Properties of the Catalyst Supports

Support	Composition (%)	Surface area (m^2/g)	Average pore radius (μm)
Silica gel (grace)	—	265	0.0075
Silicon carbide (carborundum)	77.0 SiC 5.6 Al_2O_3 15.5 SiO_2 0.4 Fe_2O_3 0.5 Na_2O	0.27	25.0
Alumina (carborundum)	96.0 Al_2O_3 2.4 SiO_2 0.6 Fe_2O_3 0.5 MgO	0.74	0.4
Silica (carborundum)	93.1 SiO_2 5.8 Al_2O_3 0.1 Fe_2O_3 0.3 MgO	0.45	5.0

ting reaction again is the rate-determining step.

In the present paper the hydrogenolysis of propane was studied in a differential reactor on a series of iron, cobalt, and nickel catalysts supported on silica gel and on several low-area–high-porosity carriers. Low-area supports have several advantages over high-area supports in kinetic studies. Because of their much larger pores, diffusion limitations are less likely and larger particles can be used so that there is a smaller pressure drop over the catalyst bed. These supports also have higher thermal conductivity and are more inert. Two commercial catalysts were also studied: Ru on alumina and an iron ammonia synthesis catalyst.

EXPERIMENTAL

Catalyst supports used in this work are described in Table 1. "High-area support" refers to the silica gel and "low-area supports" to the other materials in Table 1. The supports were crushed and sieved to the particle size ranges used in the kinetic experiments, 28 to 48 mesh for the silica gel, and 10 to 12 mesh for the low-area materials, and these sieve fractions were used in preparing the catalysts.

Aqueous solutions of nitrates of iron, cobalt, or nickel were used in preparing the impregnated catalysts; the amount of solution was about 50% larger than the pore volume of the support. The excess solution was evaporated with stirring, the sample was dried at 105°C and subsequently calcined at 450°C to decompose the nitrates. The low-area supports were impregnated three times; the silica gel once. In some of the low-area preparations, magnesium nitrate was included in the impregnating solutions to incorporate MgO as a structural promoter in the final catalyst.

Two commercial catalysts were used: 0.5% ruthenium on γ-alumina from Engelhard Industries Inc., with a metal surface area of 0.8 m^2/g (*10*), and an ammonia synthesis catalyst (D3001). The composition of D3001 was: 67.4% total Fe, 4.6% MgO, 0.5% K_2O, 0.7% SiO_2, 0.6% Cr_2O_3; its surface area after reduction at 450°C was 14 m^2/g (*11*). This catalyst was also extracted with water in a soxhlet unit for 20 days to remove the alkali; this extraction also removed most of the magnesia, the MgO content decreasing to 0.9%.

Before characterization of the catalysts or use in kinetic experiments the catalysts were reduced in H_2 at a space velocity of about 1200 hr^{-1} for 16 hr at 350°C for ruthenium and for 24 to 40 hr at 450°C for other catalysts. Catalysts used in kinetic tests were reduced in the reactor. The chemical composition of the catalysts was determined by atomic absorption spectroscopy, the total surface area by nitrogen adsorption at 77°K, and the metal surface area by hydrogen chemisorption at room temperature (*12*). For the adsorption experiments a standard volumetric technique was used. Two hydrogen isotherms were measured, the second one after a 15-min evacuation period. The difference between the two isotherms was assumed to correspond to strongly chemisorbed hydrogen, and this amount was used to estimate the metal surface area. Dissociative adsorption was assumed and the area associated with a single nickel, cobalt, or iron atom was taken to be 0.065 nm^2/atom.

The reactor system was differential, and consisted of a stainless-steel reactor (i.d. 0.75 cm) and an external recycle pump (Metal Bellows Corporation, MB41). A bypass valve around the pump permitted control of the recycle flow. The reactor was surrounded by a 20-cm-long by 10-cm-diameter aluminum cylinder with six 15 cm, 250 W cartridge heaters equally spaced between the reactor tube and the outside of the cylinder. The catalyst (1 to 3 g) was placed at the center of the reactor on a retention device of 200-mesh stainless-steel gauze. A chromel-alumel thermocouple in the center of the bed was connected to a proportional controller (Electronic Control System, Inc.). The temperature could be held constant within ±0.2°C. The experiments were performed at total pressures between 1.1 and 2.1 atm, and the pressure drop across the catalyst bed did not exceed 0.2 atm for the high-area catalysts, and 0.05 atm for those on

TABLE 2

Properties of the Catalysts Prepared in this Research

Catalyst	Chemical composition[a] (wt%)	Total surface area[b] (m^2/g)	Metal surface area[c] (m^2/g)	Metal dispersion[d]
On high-area support				
Nickel on silica gel (28–48 mesh)	4.1 Ni	253	8.3	0.28
Cobalt on silica gel (14–28 mesh)	7.0 Co	248	3.2	0.06
Cobalt on silica gel (28–48 mesh)	6.3 Co	—	2.1	0.05
Iron on silica gel (28–48 mesh)	8.1 Fe	—	0.35	0.01
On low-area supports, all 10 to 12 mesh				
Nickel on silicon carbide	16.7 Ni	0.2	0.12	0.001
Nickel–magnesia on silicon carbide	14.9 Ni 1.0 Mg	2.6	2.0	0.02
Cobalt–magnesia on silicon carbide	17.3 Co 0.7 Mg	3.0	—	—
Iron–magnesia on silica	14.5 Fe 0.9 Mg	—	—	—

[a] By atomic absorption spectroscopy.
[b] By nitrogen adsorption at 77°K.
[c] By chemisorption of hydrogen at room temperature.
[d] The ratio of the number of hydrogen atoms adsorbed to the number of metal atoms present.

TABLE 3

Summary of Kinetic Parameters for Propane Hydrogenolysis[a]

Catalyst	Temperature range (°C)	E_a (kJ/mol)	log A[b]	n	m	T_r[c] (°C)	Selectivity for ethane[d] at		
							$X = 0.0$	$X = 0.4$	$X = 0.8$
Ru/alumina	150–180	155	19.15	0.80	−1.98	167	0.99	0.97	0.88
Ni/silica gel	254–303	175	18.00	0.73	−1.57	255	0.53	0.46	0.29
Ni/SiC	277–305	217	20.82	0.86	−2.41	297	0.56	0.46	0.25
NiMg/SiC	250–281	193	19.46	0.67	−2.29	268	0.50	0.42	0.23
Co/silica gel (28–48 mesh)	228–268	93	9.96	0.79	−0.72	244	0.20	0.16	0.07
Co/silica gel (14–28 mesh)	233–268	140	15.95	0.70	−0.95	252	0.19	0.14	0.06
CoMg/SiC	245–266	204	20.99	1.03	−0.78	252	0.19	0.14	0.06
FeMg/SiO$_2$ (low area)	314–353	149	12.59	0.65	0.67	360	0.05	0.02	0.01
D3001	288–330	129	11.07	1.17	2.00	353	0.06	0.01	0.00
D3001 (extracted)	270–338	124	11.01	0.80	−0.06	341	0.07	0.04	0.02

[a] $r = A \exp(-E_a/RT)P_{C_3H_8}{}^{n}P_{H_2}{}^{m}$.

[b] Units of A are based on r in [μmol sec^{-1} (g cat)$^{-1}$], with partial pressures in atm.

[c] Temperature at which the rate of reaction is 1.0 [μmol sec^{-1} (g cat)$^{-1}$] with hydrogen and propane partial pressures of 1.5 and 0.25 atm, respectively.

[d] At different fractional conversion X of propane, and in the center of the temperature interval for the catalyst.

low-area supports. The temperature range was 150 to 330°C and depended on the activity of the catalyst. The recycle to feed ratio was kept high (>20), and there was always an excess of hydrogen; hydrogen to propane ratios in the feed varied from 100:1 to 4:1. Conversions of propane varied from 2 to 90%. The reactants used in the experiments were hydrogen (UHP) and propane (CP), both from Matheson.

The analysis of the products was performed with two Varian 90-P gas chromatographs with isothermal columns. A charcoal column at 79°C with argon as carrier gas was used to measure hydrogen, and a Porapak Q column at 166°C with hydrogen as carrier gas in the second system, separated the hydrocarbons. A Hewlett–Packard Integrator (3380A) recorded the chromatograms and printed the composition of each sample.

The reaction rates, fractional conversions of propane, and selectivities were determined from the flow rate and composition of the effluent stream. The selectivities for ethane and methane were defined as the moles of ethane or methane formed per mole of propane reacted, and can have maximum values of 1.0 and 3.0, respectively. The activity of the catalysts was checked periodically at standard conditions using a premixed 10% propane in hydrogen mixture (Matheson). Carbonaceous deposits were never observed on the catalyst samples, and satisfactory carbon balances were obtained in tests in which both the feed and the effluent were analyzed.

Transient response experiments verified that the reactor system acted as a CSTR at the feed flowrates used in the experiments, and calculations showed that interparticle and intraparticle mass and heat transfer were more rapid than the reaction

TABLE 4

Kinetic Parameters at Constant Temperatures[a]

Catalyst	Temperature (°C)	m	n
Ni/silica gel	254	−2.37	1.00
	278	−2.04	0.76
	303	−1.43	0.73
Ni/SiC	277	−2.98	0.77
	291.5	−2.50	0.80
	305	−2.33	0.85
Co/silica gel (28–48 mesh)	228	−1.89	0.75
	248	−1.25	0.90
	268	−0.61	0.78
Fe–Mg/SiO$_2$ (low area)	314	−0.53	0.45
	334	0.23	0.63
	353	0.78	0.69

[a] $r = k\, P_{C_3H_8}{}^{n} P_{H_2}{}^{m}$.

rates and the generation of heat by factors of 10 to 100.

RESULTS AND DISCUSSION

The properties of the catalysts prepared in this research are shown in Table 2. Catalysts containing silica gel had large total areas; nickel was well dispersed, but cobalt and particularly iron were not. Catalysts on the low-area supports had low total areas, metal areas, and metal dispersions, unless the impregnating solutions contained magnesium nitrate. The resulting MgO served as a structural promoter and increased both the total and metal areas about 10-fold.

In the hydrogenolysis of propane unpromoted iron catalysts on silica gel and on the three low-area supports all deactivated very rapidly and these catalysts could not be reactivated by treatment with hydrogen. All the other catalysts, including the promoted iron catalyst, had a nearly constant activity for periods of several weeks.

The kinetic data for all catalysts were fitted to a power rate expression, using a nonlinear regression program to minimize the sum of squares of the differences between the experimental and calculated rates:

$$r = A P_{H_2}{}^{m} P_{C_3H_8}{}^{n} \exp(-E_a/RT). \quad (1)$$

First, Eq. (1) was applied to the data for each catalyst over the entire temperature range; these data are given in Table 3. The average deviations between the calculated and experimental rates were between 10 and 25%, except for the iron ammonia synthesis catalyst, for which the fit was worse. Experimental errors are estimated to be 10–12%. Thus, the power rate law was often not suitable for representing the data at different temperatures. Activation energies for a given metal varied with the support used, but the hydrogen exponents followed a pattern, being about −2 for Ru and Ni, −0.7 for Co, and positive for Fe. For Ni and Co the hydrogen and propane exponents were more or less independent of the support or the presence of MgO.

Second, Eq. (1) was applied to the data for a given catalyst at constant temperatures. For all of the catalysts of Table 3, the hydrogen exponent increased with increasing temperature, while the propane exponent remained essentially constant. Examples are shown in Table 4; similar observations have been made by other workers (*2*, *9*, *13*). At constant temperatures the average deviation between experimental and calculated rates were smaller, about 8 to 12%. The exponents in Table 3 are "average" values over the entire temperature range. The change in the H$_2$ exponent with temperature is a factor contributing to the poor representation of the data by the power rate law. Several mechanistic rate equations, all involving dissociative chemisorption of propane as the initial step and Langmuir–Hinshelwood-type equations for surface coverage, were tested with data at constant temperature, but none of them fit the data better than the power rate law and the parameters varied erratically with temperature.

In Table 3, the temperature T_r is a measure of the activity of the catalysts, and is defined as the temperature at which the rate of reaction is 1.0 μmol sec^{-1} (g cat)$^{-1}$ using hydrogen and propane partial pressures of 1.5 and 0.25 atm, respectively (*14*). The promoted low-area catalysts and the corresponding high-area catalysts have nearly the same activity, and the promoted catalysts were 10 times as active as the corresponding unpromoted samples. The activity of the catalysts of the same metal appears to be proportional to the metal area and independent of the support used. The sequence of activity of the metals is: Ru > Co > Ni > Fe, when the activity is expressed either per gram or per unit metal area of catalyst.

Table 3 also includes values for the selectivities for ethane at three levels of propane conversion on all the catalysts. The ethane selectivity appears to be rather insensitive to the support and to whether or not the promoter is present, but it is very sensitive to the metal used. The amount of ethane produced decreases rapidly in the sequence—Ru, Ni, Co, Fe. A selectivity equation was derived (*10*) that relates the selectivity for ethane, S_2 and the conversion of propane, X:

$$S_2 = \frac{\dfrac{k'_2}{k'_2 + k^*_2}}{1 + \dfrac{k''_2}{k''_3}\dfrac{X}{1 - X}}.$$

In this equation k'_2 and k^*_2 are the rate constants of desorption and cracking of the adsorbed C_2 species; k''_2 and k''_3 can be regarded as overall first-order rate constants for the hydrogenolysis of ethane and propane. If the surface splitting reaction is rate controlling, the parameter $k'_2/(k'_2 + k^*_2)$ will approach unity. The experimental selectivities at constant temperatures were fitted to Eq. (2) using nonlinear least squares; values of the constants for tests at 2.0 to 2.2 atm are given in Table 5. At lower total pressures, k^*_2/k'_2 values are somewhat lower. Values of k''_2/k''_3 ratios behave erratically with temperature, but the k^*_2/k'_2 ratios increase with increasing temperature, suggesting that the cracking step has a higher activation energy than the desorption step. The values for k^*_2/k'_2 indicate that only for ruthenium is the rate of desorption of the adsorbed C_2 species fast compared to the rate of cracking. On nickel these rates are roughly equal, and for cobalt the cracking is faster than the desorption. The difference between the rates of hydrogenolysis of ethane and propane is largest on ruthenium. Ethane selectivities on iron were too small to allow these calculations, but values of k^*_2/k'_2 must be larger than 16.

TABLE 5

Ethane Selectivities at 2.0–2.2 atm

Catalyst	Temperature (°C)	$k^*_2/k'_2{}^a$	$k''_2/k''_3{}^a$
Ru/alumina	150	0.01	0.03
	180	0.02	0.01
Ni/silica gel	255	0.4	0.6
	278	0.9	0.2
	304	1.6	0.2
Ni/SiC	277	0.4	1.4
	292	0.8	0.3
	305	1.2	0.2
NiMg/SiC	251	0.3	0.1
	266	0.5	0.6
	281	1.0	0.3
Co/silica gel	228	0.9	3.6
	248	2.6	0.5
	268	4.2	0.5
CoMg/SiC	245	4.0	0.7
	255	4.2	0.3
	265	4.3	0.6

[a] $S_2 = [k'_2/(k'_2 + k^*_2)]/1 + (k''_2/k''_3)(X/1 - X)$.

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REFERENCES

1. Cimino, A., Boudart, M., and Taylor, H. S., *J. Phys. Chem.* **58**, 796 (1954).
2. Sinfelt, J. H., and Taylor, W. F., *Trans. Faraday Soc.* **64**, 3086 (1968).
3. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24**, 283 (1972).
4. Sinfelt, J. H., *Catal. Rev.* **3**, 175 (1969).
5. Sinfelt, J. H., *Advan. Catal.* **23**, 91 (1973).
6. Sinfelt, J. H., *J. Catal.* **27**, 468 (1972).
7. Boudart, M., *A.I.Ch.E. J.* **18**, 465 (1972).
8. Ollis, D. F., and Taheri, H. T., *A.I.Ch.E. J.* **22**, 1112 (1976).
9. Sheppard, F. E., *J. Catal.* **14**, 148 (1969).
10. Tsjeng, P. K., and Anderson, R. B., *Canad. J. Chem. Eng.* **54**, 101 (1976).
11. Anderson, R. B., and Hofer, L. J. E., *J. Amer. Chem. Soc.* **73**, 944 (1951).
12. C. J. Machiels, Ph.D. thesis, McMaster University, Hamilton, 1978.
13. Guczi, L., Sarkany, A., and Tetenyi, P., "Catalysis" (J. W. Hightower, Ed.), Vol. 2, p. 1111. Elsevier, Amsterdam, 1973.
14. Boudart, M., "Kinetics of Chemical Processes." Prentice Hall, Englewood Cliffs, 1968.