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Ethane Hydrogenolysis Studies of TiO_2-Supported Group VIII Metal Catalysts

Evidence for strong metal-support interactions (SMSI) was recently reported for a new class of supported metal catalysts (*1, 2*). In particular, these catalysts, which were composed of Group VIII metals on Group IVB or VB metal oxides, were incapable of chemisorbing hydrogen and carbon monoxide at room temperature subsequent to reduction in dihydrogen at 500°C or above. In an effort to investigate the effect of these unusual metal-support interactions on catalytic properties, a study was made of the ethane hydrogenolysis reaction over all Group VIII metals on TiO_2. As presented below, it was found that the TiO_2-supported catalysts exhibited chemical behavior markedly different from that of Group VIII metals on a conventional support such as SiO_2.

The procedures and experimental apparatus employed in this study have been described previously (*1, 3*). Briefly, the catalysts were prepared by impregnating TiO_2 with an aqueous metal salt solution, then drying in air overnight at 110°C (*1*). All catalysts studied had a metal loading of 2 wt%. In a typical kinetic run, 0.2 g of catalyst (40/60 mesh) was mixed with 0.5 g of Corning glass diluent and reduced *in situ* with hydrogen at 500°C for 16 hr. Chemisorption experiments on selected samples confirmed that the reduction temperature was sufficiently high to induce the SMSI state as previously reported (*1*). The feed gases, consisting of hydrogen, ethane, and a helium diluent, were passed downflow through the reactor at a total gas flow rate of 1 liter/min for a period of 3 min, at which time a sample of the product was taken for chromatographic analysis. The ethane was then cut off and hydrogen flow was continued for 10 min before another measurement was made. A set of ethane and hydrogen partial pressures, 0.03 and 0.2 atm, respectively, were chosen as the standard conditions to study the partial pressure dependencies of the reaction rate. Any rate measurements at pressure conditions different from the standard were bracketed by rate determinations at the standard conditions. This bracketing technique served as an indication of the stability of the catalyst. In general, not much variation in catalyst activity was noted with the exception of the Ir/TiO_2 sample. The degree of conversion for all runs was kept low (of the order of 1%) so the reactor was essentially operated in a differential mode.

The kinetic parameters thus obtained for ethane hydrogenolysis on TiO_2-supported Group VIII metals are summarized in Table 1. No methane product was detected for Fe and Pt up to a reaction temperature of 500°C. This indicated that the activity for these two metals was at most comparable to, and more likely lower than, that of Pd. As pointed out earlier, the Ir/TiO_2 sample deactivated rapidly during the experiment preventing an accurate measure of the pressure effects. The values of n and m in Table 1 are exponents on ethane and hydrogen partial pressures, respectively, in the experimental power rate law of the form

$$r = kp_E{}^n p_H{}^m. \qquad (1)$$

It should be noted that the inability to obtain chemisorption data for these catalysts (*1, 2*) necessitated the assumption of a 100% fraction exposed in calculating the specific activities. X-Ray diffraction studies on the reduced samples showed no detect-

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TABLE 1

Kinetic Parameters for Ethane Hydrogenolysis on TiO_2-Supported Metals

Metal (2 wt%/TiO_2)	Temperature range (°C)	E_A[a] (kcal/mole)	r_0'[b] (molecules/sec-cm^2)	n[c]	m[d]	$T(n, m)$[e] (°C)
Fe	<500	—	Inactive	—	—	—
Co	456–512	35	1.7×10^{23}	0.6	+0.1	460
Ni	310–356	31	2.0×10^{24}	0.7	−0.9	309
Ru	187–231	32	1.0×10^{28}	0.9	−1.9	187
Rh	234–264	36	1.4×10^{28}	0.7	−2.1	244
Pd	437–497	59	4.2×10^{30}	0.9	−1.9	436
Os	202–224	32	6.9×10^{27}	0.7	−1.0	202
Ir	283–311	52	3.0×10^{33}	—	—	—
Pt	<500	—	Inactive	—	—	—

[a] Determined from the temperature dependence of the rate, r_0, at ethane and hydrogen partial pressures of 0.03 and 0.2 atm, respectively.

[b] Preexponential factor in the equation $r_0 = r_0' \exp(-E_A/RT)$.

[c] Exponent on ethane partial pressure in experimental power rate law.

[d] Exponent on hydrogen partial pressure in experimental power rate law.

[e] Temperature at which the values of n and m were determined.

able metal peaks. Therefore, while the calculated rates only represent a lower limit, they are expected to be within an order of magnitude of the actual rates.

The extensive work of Sinfelt (*4*, *5*) on ethane hydrogenolysis over silica-supported metals provided a firm basis on which results in this study could be compared. To do this specific activities were calculated for all TiO_2-supported metals at 205°C using the experimentally determined rate parameters (Table 1). As shown in Table 2, Fe, Co, Ni, Pd, and Ir supported on TiO_2 exhibited a decrease in ethane hydrogenolysis activity up to several orders of magnitude relative to that of their SiO_2-supported counterparts. This diminution is much greater than the uncertainty in the specific activity resulting from the assumption of 100% fraction exposed. The overall activity pattern for all Group VIII metals was found to be

$$\mathrm{Ru} > \mathrm{Os} > \mathrm{Rh} > \mathrm{Ni} > \mathrm{Ir} > \mathrm{Co} > \mathrm{Pd} > \mathrm{Pt} \sim \mathrm{Fe}.$$

This pattern is significantly different from that previously observed for SiO_2 (*4*), namely,

$$\mathrm{Os} > \mathrm{Ru} > \mathrm{Ni} > \mathrm{Rh} > \mathrm{Ir} > \mathrm{Co} > \mathrm{Fe} > \mathrm{Pt} > \mathrm{Pd}.$$

Vannice and Garten (*6*) recently found that the activity of Ni/TiO_2 was greater than that of Ni/SiO_2 with respect to CO–H_2 reactions. Furthermore, Ni/TiO_2 exhibited a high selectivity to C_2^+ paraffins whereas Ni/SiO_2 was predominantly a methanation

TABLE 2

Specific Activities[a] for Ethane Hydrogenolysis at 205°C

Metal	SiO_2-supported[b]	TiO_2-supported[c]
Fe	1.2×10^{-5}	$<10^{-13}$
Co	3.4×10^{-5}	1.0×10^{-9}
Ni	8.0×10^{-4}	8.0×10^{-7}
Ru	1.8×10^{-3}	1.4×10^{-3}
Rh	2.2×10^{-4}	2.9×10^{-5}
Pd	6.7×10^{-10}	2.6×10^{-13}
Os	4.2×10^{-2}	9.6×10^{-4}
Ir	1.1×10^{-4}	3.0×10^{-7}
Pt	7.2×10^{-10}	$<10^{-13}$

[a] Expressed in units of moles of ethane converted/hr/m^2.

[b] Calculated from Ref. (*4*).

[c] Calculated from Table 1.

catalyst. In the present study the ethane hydrogenolysis activity of Ni/TiO_2 was drastically reduced compared to that of Ni/SiO_2. These results are indicative of the potential alteration of selectivity in catalytic reactions as a result of metal-support interactions.

The TiO_2-supported metals exhibited a large inverse dependence of the reaction rate on the hydrogen partial pressure as previously found for a SiO_2 support. The kinetic analysis developed by Sinfelt (*5*) was therefore applied to the TiO_2 samples. Sinfelt (*5*) has shown that a rate expression of the form

$$r = kp_E{}^n p_H^{-na} \tag{2}$$

is consistent with kinetic data for ethane hydrogenolysis on SiO_2 catalysts. The kinetic sequence involves the chemisorption of ethane with dissociation of a carbon–hydrogen bond as the initial step, followed by carbon–carbon bond scission of the resulting hydrogen-deficient species, C_2H_x, in the rate-determining step. In the derivation of Eq. (2) the assumption is made that competition between hydrogen and hydrocarbon for surface sites is negligible. This assumption is clearly justified for SMSI catalysts which do not chemisorb hydrogen. The parameter, a, in Eq. (2) is related to x by the relationship

$$a = (6 - x)/2. \tag{3}$$

The value of a provides a measure of the relative dehydrogenation to hydrogenolysis activities of a catalyst. The highest a values are associated with metals having a large ratio of dehydrogenation to hydrogenolysis activities (*5*).

Sinfelt's rate equation (2), was found to provide a satisfactory fit to the TiO_2-supported metals with the proper choice of a (Table 3). The successful application of the rate expression to both SiO_2- and TiO_2-supported metals then lends support to the validity of the formalism. The near-zero hydrogen partial pressure dependence observed for Co/TiO_2 was likely to have been due to a breakdown of the chemisorption equilibrium (*7*) as kinetic measurements were carried out at a very high temperature. In order to provide the best fit to the data lower values of a were necessary for Ni, Pd, and Os on TiO_2 than on SiO_2, indicative of a less hydrogen-deficient surface intermediate and lower dehydrogenation activity. Since these metals also suffer a pronounced decrease in ethane hydrogenolysis activities, as discussed earlier, these results signify a suppression in both hydrogenolysis and dehydrogenation activities, yet another manifestation of the SMSI effect on catalytic properties.

TABLE 3

Analysis of Power Rate Law Exponent on Hydrogen pressure, p_H

Metal	a	Calculated $-na$[a]	Observed m[b]	a'[c]
Ni	1	−0.7	−0.9	2
Ru	2	−1.8	−1.9	2
Rh	3	−2.1	−2.1	3
Pd	2	−1.8	−1.9	3
Os	1	−0.7	−1.0	2

[a] From Eq. (2).
[b] From Eq. (1).
[c] Corresponding value for SiO_2-supported metals (Ref. (5)).

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REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100**, 170 (1978).

2. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
3. Sinfelt, J. H., *Chem. Eng. Sci.* **23,** 1181 (1968).
4. Sinfelt, J. H., *Catal. Rev.* **3,** 175 (1969).
5. Sinfelt, J. H., *J. Catal.* **27,** 460 (1972); *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 23. Academic Press, New York/London, 1973; *Catal. Rev. Sci. Eng.* **9**(1), 147 (1974).
6. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979).
7. Taylor, W. F., and Sinfelt, J. H., *Trans. Faraday Soc.* **64,** 3086 (1968).

E. I. KO[1]
R. L. GARTEN[2]

Corporate Research Laboratories
Exxon Research and Engineering Company
Linden, New Jersey 07036

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[1] Present address: Department of Chemical Engineering, Carnegie–Mellon University, Pittsburgh, Pa. 15213.

[2] Present address: Catalytica Associates, Inc., 3255 Scott Blvd., Suite 7-E, Santa Clara, Calif. 95051.