JOURNAL OF CATALYSIS **100**, 503–506 (1986)

CO Hydrogenation over Niobia-Supported Iron Catalysts

In recent years many studies have shown the unusual adsorptive and catalytic properties of catalysts which exhibit the so-called strong metal–support interactions (SMSI) (*1*, *2*). The behavior of these catalysts in CO hydrogenation is particularly interesting. In general TiO_2 enhances the activity of Group VIII metals as has been found for Ni (*3–5*), Pd (*6*), and Pt (*7*). One notable exception is Fe/TiO_2, which was reported to be several orders of magnitude less active than Fe/Al_2O_3 (*8*). However, a later study of Barrault and Renard (*9*) showed that Fe/TiO_2 and Fe/Al_2O_3 have comparable activity but different selectivity. Tau and Bennett (*10*) showed by transient kinetic measurements that the surface species on these two systems are also different during CO hydrogenation. In view of the facts that niobia (Nb_2O_5) shows similar support behavior to TiO_2 for Ir (*11*) and Ni (*12*, *13*) and also enhances CO hydrogenation activity for Ni (*13*), it would be of interest to use Nb_2O_5 as a support for Fe. Here we report kinetic results for CO hydrogenation over Fe/Nb_2O_5 and compare them with those for Fe/SiO_2.

The silica (SiO_2) support used in this study was a commercial product (Davison grade 952) with a BET surface area of 300 m^2/g. Niobia was prepared by adding ammonium hydroxide to a methanolic solution of niobium chloride. The resulting precipitate was repeatedly washed and then calcined to obtain Nb_2O_5 with a BET surface area of about 10 m^2/g (*12*).

Iron catalysts were prepared by the incipient wetness impregnation of an aqueous solution of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Fisher). The loadings for Fe/SiO_2 and Fe/Nb_2O_5 are 9.6 and 8.4 wt%, respectively. These values were confirmed by atomic absorption following extraction of iron with concentrated nitric acid. In the case of niobia, repeated impregnations were necessary to achieve the desired loading due to the small wetting volume of the support.

The average iron crystallite size was determined by X-ray line broadening and CO chemisorption. X-Ray diffraction studies were performed using a Rigaku D-max system with either copper or molybdenum radiation. Static chemisorption measurements were made in a conventional glass volumetric apparatus capable of a dynamic vacuum of 10^{-6} Torr. The adsorption of CO was measured at 195 K (dry ice–acetone bath) following the procedure described by Boudart *et al.* (*14*). The uptake was corrected for adsorption on the blank support.

Kinetic experiments were done in a stainless-steel microreactor operated in a differential mode at atmospheric pressure. Details about the reactor system and data analysis are described elsewhere (*13*). Each catalyst was reduced *in situ* in flowing hydrogen prior to the kinetic study. Broadly, two types of kinetic experiments were run. In the first type, the feed gas composition was kept constant at a H_2/CO ratio of 3/1 to obtain activity, selectivity, and apparent activation energy. In the second type, the feed gas composition was varied by simultaneously varying the individual flowrates of H_2 and CO while maintaining a constant total flow rate. Typically eight different gas compositions (with H_2/CO ratios ranging from 1 : 1 to 9 : 1) were used in each run. Each composition was bracketed by a fixed composition (a premixed gas of H_2/CO = 3/1) so that any catalyst deactivation could be

0021-9517/86 $3.00

TABLE 1

Characterization of Supported Iron Catalysts

Sample[a]	CO uptake[b] μmole/g	Particle size (nm)	
		Chemisorption	X-ray[c]
9.6% Fe/SiO_2	33.1	11	13
8.4% Fe/Nb_2O_5	16.3	35	39

[a] Both samples were reduced in H_2 at 673 K for 16 h.

[b] CO uptake obtained at 195 K and corrected for adsorption on the support.

[c] From line broadening of the (110) peak using the Scherrer equation with correction for instrumental broadening.

accounted for. The effect of changing composition on activity was then analyzed by multiple regression, which calculated the exponents on the partial pressures of H_2 and CO in an experimental power rate law.

The results for Fe/SiO_2 and Fe/Nb_2O_5 were obtained after an identical reduction treatment of 673 K for 16 h. Table 1 lists the characteristics of these two samples. Percentage reduction was determined by volumetric measurement of oxygen uptake to be 56% for Fe/SiO_2. With the known metal loading and percentage reduction an average particle size was calculated from the CO uptake by assuming an adsorption stoichiometry of $CO/Fe_s = 1/2$ (*14*). The value obtained from CO adsorption agrees well with that determined from X-ray diffraction line broadening. The Fe/Nb_2O_5 sample was assumed to be 100% reduced. It has been noted that metals on supports such as titania and niobia are more reducible than those on silica and alumina (*12, 15*). Tau and Bennett (*10*) and Santos *et al.* (*16*) both reported a near complete reduction of Fe/TiO_2 under similar conditions. Furthermore, the agreement between chemisorption and X-ray diffraction results confirms that little error is introduced by assuming complete reduction for Fe/Nb_2O_5.

Table 2 shows the steady-state kinetic parameters for Fe/SiO_2 and Fe/Nb_2O_5 in CO hydrogenation. Turnover frequency was based on the particle size determined from X-ray diffraction. The difference would be about 10% if particle size determined from chemisorption was used instead. The two samples have similar turnover frequency and activation energy. Both also show a very weak dependence on the partial pressure of CO (near zero order). The major difference lies in the dependence on the partial pressure of H_2, in that Fe/Nb_2O_5 has a higher reaction order.

Table 3 shows a comparison of product distribution at a conversion level of about 1.5%. The higher C_2^+/C_1 ratio for the Fe/Nb_2O_5-catalyzed reaction demonstrates a shift in product distribution toward higher hydrocarbons. Perhaps more dramatic is the difference in the olefin/paraffin ratio between the two catalysts. In addition to producing very little olefinic products, Fe/

TABLE 2

Steady-State Kinetic Data for CO Hydrogenation over Iron Catalysts[a]

Sample[b]	CO consumption				Methane formation			
	N ($\times 10^{-3}$, s^{-1})	E_A (kJ/mole)	x^c	y^c	N ($\times 10^{-3}$, s^{-1})	E_A (kJ/mole)	x^c	y^c
Fe/SiO_2	8.3	94	1.23	0.25	2.9	88	1.69	0.03
Fe/Nb_2O_5	6.7	94	1.98	0.23	1.9	92	2.51	0.12

[a] Experimental condition: $T = 523$ K, $H_2/CO = 3/1$, $P = 101$ kPa.

[b] Catalysts were reduced at 673 K for 16 h (see Table 1).

[c] x and y are exponents on the experimental power rate law, $r = kp_{H_2}^x p_{CO}^y$.

TABLE 3

Product Distribution of CO Hydrogenation over Iron Catalysts[a]

Sample[b]	CO conversion (%)	Selectivity[c]	Hydrocarbon distribution (mole %)					Olefin/paraffin ratio		C_2^+/C_1[d]
			C_1	C_2	C_3	C_4	C_5	C_2	C_3	
Fe/SiO_2	1.44	0.914	72.3	13.5	7.6	5.2	1.4	0.54	5.30	1.07
Fe/Nb_2O_5	1.51	0.965	58.4	17.1	13.4	6.8	4.3	0	0.18	2.11

[a] Reaction condition: $T = 523$ K, $H_2/CO = 3/1$, $P = 101$ kPa.

[b] Catalysts were reduced at 673 K for 16 h (see Table 1).

[c] Selectivity is defined as the fraction of CO converted to hydrocarbons.

[d] Ratio of moles of CO converted to higher hydrocarbons ($\geq C_2$) to moles of CO converted to methane.

Nb_2O_5 forms less CO_2 than Fe/SiO_2 (as shown by a higher selectivity).

The activity and product distribution of our Fe/SiO_2 catalyst are in good agreement with results reported in the literature (*17–19*). Furthermore, the particle sizes of Fe/SiO_2 and Fe/Nb_2O_5 catalysts are in a range over which a significant particle size effect is usually not expected (*20, 21*). The difference between the two samples could thus be attributed to a support effect. It is important to note that niobia affects iron and nickel differently. In comparison with a SiO_2-supported catalyst, there is an enhancement in activity for Ni but not for Fe. Furthermore, Ni/Nb_2O_5 produces more olefins than Ni/SiO_2 (*13*), whereas the reverse is true in the case of supported Fe. The reasons for these differences are not understood at present, but our results reinforce an earlier observation (*8*) that the interaction is metal-dependent.

We also observed a more severe manifestation of metal–support interaction for this system under a higher reduction temperature. When Fe/Nb_2O_5 was reduced at 873 K for 16 h, the steady-state activity for CO hydrogenation dropped by more than a factor of 10 and the apparent activation energy (E_{CO}) increased from 94 to 137 kJ/mole. Figure 1 shows the X-ray diffraction patterns of the reduced catalysts. The diffractogram of the sample reduced at 673 K contains only Fe and Nb_2O_5 peaks. By contrast the diffractogram of the sample reduced at 873 K is more complex. When a better resolved pattern was obtained with Cu radiation, peaks corresponding to $FeNbO_4$ (*22*) and NbO_2 were identified in addition to Nb_2O_5 peaks. Apparently the oxidation of Fe into $FeNbO_4$ was accompanied by the reduction of Nb_2O_5 to NbO_2 under the more severe reduction conditions.

In summary, this study demonstrates that steady-state kinetics for CO hydrogenation are significantly different between Fe/Nb_2O_5 and Fe/SiO_2. At a reduction temperature of 673 K niobia does not enhance

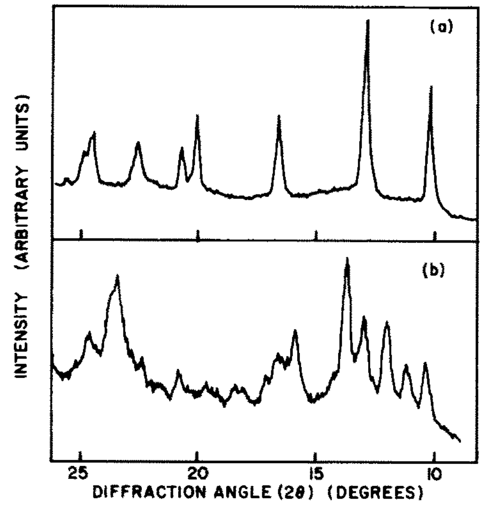

FIG. 1. X-Ray diffraction patterns for Fe/Nb_2O_5 catalysts. Sample reduced at (a) 673 K, 16 h; (b) 873 K, 16 h.

the activity for Fe as it does for Ni. The formation of $FeNbO_4$ following reduction at 873 K leads to a suppression in activity.

ACKNOWLEDGMENTS

The authors thank Sun Company, Inc., for an equipment grant and the Center for the Study of Materials at Carnegie-Mellon University for use of its Central Research Facilities.

REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
2. Tauster, S. J., Fung, S. C., Baker, R. T. K ., and Horsley, J. A., *Science* **211,** 1121 (1981).
3. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979).
4. Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65,** 335 (1980).
5. Burch, R., and Flambard, A. R., *J. Catal.* **78,** 389 (1982).
6. Vannice, M. A., Wang, S.-Y., and Moon, S. H., *J. Catal.* **71,** 152 (1981).
7. Vannice, M. A., Twu, C. C., and Moon, S. H., *J. Catal.* **79,** 70 (1983).
8. Vannice, M. A., *J. Catal.* **74,** 199 (1982).
9. Barrault, J., and Renard, C., *Nouv. J. Chim.* **7**(3), 149 (1983).
10. Tau, L. M., and Bennett, C. O., *J. Catal.* **89,** 285 (1984).
11. Tauster, S. J., and Fung, S. C., *J. Catal.* **54,** 29 (1978).
12. Ko, E. I., Hupp, J. M., Rogan, F. H., and Wagner, N. J., *J. Catal.* **84,** 85 (1983).
13. Ko, E. I., Hupp, J. M., and Wagner, N. J., *J. Catal.* **86,** 315 (1984).
14. Boudart, M., Delbouille, A., Dumesic, J. A., Khammouna, S., and Topsøe, H., *J. Catal.* **37,** 486 (1975).
15. Jiang, X.-Z., Stevenson, S. A., and Dumesic, J. A., *J. Catal.* **91,** 11 (1985).
16. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81,** 147 (1983).
17. Raupp, G. B., and Delgass, W. N., *J. Catal.* **58,** 361 (1979).
18. Vannice, M. A., *J. Catal.* **50,** 228 (1977).
19. Amelse, J. A., Butt, J. B., and Schwartz, L. H., *J. Phys. Chem.* **82,** 558 (1978).
20. Boudart, M., "Advances in Catalysis," Vol. 20, p. 153. Academic Press, New York, 1969.
21. Jung, H.-J., Walker, P. L., Jr., and Vannice, M. A., *J. Catal.* **75,** 416 (1982).
22. Roth, R. B., and Warring, J. L., *Amer. Mineral.* **49,** 242 (1964).

M. D. PHADKE[1]
E. I. KO[2]

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received August 29, 1985

---

[1] Present address: Rohm & Haas Company, Research Laboratories, 727 Norristown Road, Spring House, Pa. 19477.

[2] To whom correspondence should be addressed.