JOURNAL OF CATALYSIS 7, 359-364 (1967)

Activity Pattern in the Hydrogenation of Ethylene over the Oxides of the First Series of Transition Elements

D. L. HARRISON, D. NICHOLLS,* AND H. STEINER

From the Development of Chemistry, Faculty of Technology, The University, Manchester, England

Received October 3, 1966; revised December 5, 1966

The activities of TiO_2, V_2O_3, Cr_2O_3, MnO, Fe_2O_3, Co_3O_4, NiO, and ZnO towards the hydrogenation of ethylene were studied. The catalysts were identified by X-ray powder crystallography, and as a criterion of the absence of metal the magnetic susceptibility of each sample was determined. An activity pattern was found which closely resembled that found previously in the hydrogen–deuterium exchange reaction, and the disproportionation and dehydrogenation of cyclohexene, catalyzed by the same oxides.

INTRODUCTION

Of the two electronic theories which attempt to account for the catalytic activity of transition metal oxides, the one which relates activity to semiconducting properties appears to be successful only for those reactions which involve complete electron transfer between catalyst and substrate (*1*). The second theory stresses the importance of the *d*-electron configuration of the metal ion. In the work of Dowden *et al.* (*2*), the catalytic activity of oxides from the first transition series in the hydrogen–deuterium exchange reaction was investigated below 20°C. Two peaks of activity were found, the first represented by Cr_2O_3 ($Cr^{3+} = 3d^3$) and the second by Co_3O_4 ($Co^{3+} = 3d^6$, $Co^{2+} = 3d^7$). These two peaks of activity were separated by those oxides whose cations possess the stable $3d^5$ configuration (MnO, Fe_2O_3). This activity pattern was correlated with crystal-field effects on the electronic levels of the metal ion (*3*). Later a similar activity pattern was obtained for the dehydrogenation of cyclohexene to benzene and the disproportionation of cyclohexene to benzene and cyclohexane, the oxides being tested in the temperature range 150–450°C depending on the temperature at which they first supported a measurable rate (*4*). Thus this pattern appears to be more general and applies to the activity of these oxides for breaking C–H as well as H–H bonds.

In the present investigation this approach has been continued using the hydrogenation of ethylene as a further model reaction. As in the previous investigation great care was taken to detect in the oxides traces of the parent metals, which powerfully catalyze the hydrogenation reaction and which can be formed from the easily reducible oxides either by nucleation on evacuation or by reduction by hydrogen or hydrocarbons.

In addition to the results on the hydrogenation of ethylene, some further data on the dehydrogenation and disproportionation of cyclohexene to benzene and benzene and cyclohexane, respectively, on Fe_2O_3 and ZnO are reported. These two oxides had not been included in the first investigation (*4*).

---

* Present address: Department of Chemistry, School of Forestry, Syracuse University, Syracuse, New York.

EXPERIMENTAL

Catalyst Preparations

The preparation of the following oxides was carried out as described previously (*4*): V_2O_3, Cr_2O_3, MnO, Co_3O_4, CoO, NiO. The preparations of the oxides given below either differs from the one described, or concerns oxides not previously used.

TiO_2. TiO_2 (rutile) was obtained from British Titan Products, Ltd., and was used without further treatment.

TiO_2 (anatase) was prepared from the gel according to Sprague *et al.* (*5*).

Fe_2O_3. α-Fe_2O_3 was prepared by precipitation with ammonia from an aqueous solution of $Fe(NO_3)_3$. The carefully washed hydroxide was left overnight in a stream of oxygen at various temperatures.

Two samples (A, B) were used in the ethylene hydrogenation experiments and another (C) in cyclohexene disproportionation. The pretreatment composition, specific surface area, and paramagnetic susceptibility of these samples are given in Table 1.

TABLE 1
CHARACTERISTICS OF α-Fe_2O_3 SAMPLES

Sample	Pretreatment T (°C)	Pretreatment Time (hr)	Fe content[a] (% Fe)	Surface area (m^2g^{-1})	χ[b] (c.g.s. units $g^{-1} \times 10^6$)
A	260°	12	63.1	490	29.1
B	400°	12	68.6	145	15.6
C	400°	24	69.2	28	16.1

[a] Theory Fe_2O_3 = 69.7% Fe; $Fe_2O_3 \cdot H_2O$ = 62.8% Fe.

[b] Literature, 16.6×10^6 c.g.s. unit g^{-1} (*11*).

ZnO. This was prepared by precipitation of $Zn(OH)_2$ with ammonia. After washing and drying the precipitate was treated in three cyclic treatments with hydrogen and oxygen at 400°C. Before testing the activity in ethylene hydrogenation sample A was evacuated at 260°C and sample B at 400°C. In the case of the cyclohexene reaction the sample C was pretreated with hydrogen at the reaction temperature of 300°C.

Other Materials

Ethylene. Ethylene was of 99.9% purity (Philips Petroleum Co.). After introduction into the vacuum apparatus the liquefied ethylene was outgassed and further purified by refluxing. On re-evaporation for storage the first and last portion of each sample was discarded. Before an experiment ethylene was once more liquefied and distilled from a cold trap.

Hydrogen. Cylinder hydrogen was purified by passing through a Deoxo unit (Engelhard Industries, Ltd.) and was dried by calcium chloride and molecular sieves (Type 4A).

Oxygen and nitrogen. B.O.C. White Spot gases were dried over magnesium perchlorate and silica gel.

Cyclohexene. This was purified as described previously.

Characterization of Catalysts

The catalysts were characterized by magnetic susceptibility measurements, by X-ray powder crystallography, and by surface area determinations. The magnetic susceptibilities were measured on a Gouy balance using fields from 0 to 5700 gauss. Reduction of the oxides to the corresponding metals could be detected not only by the large susceptibility increase, but also by the variation of susceptibility with field strength.

Copper and cobalt targets were used for the X-ray measurements and the surface areas were determined by the BET method, in general using argon at −183°C as adsorbate and in the case of the Fe_2O_3 samples, nitrogen at −196°C.

Apparatus

A simple vacuum apparatus which could be evacuated to 10^{-6} torr was used. The rate of the ethylene hydrogenation was followed by the pressure change in constant volume reaction vessels of about 150 cc. Using a cathetometer the pressure change was measured on a mercury manometer to 0.05 torr. The catalyst was protected from mercury and tap grease vapors by greaseless taps and by traps cooled to −78°C.

The reaction vessel could be heated in a furnace to temperatures up to 500°C, which were controlled to ±0.5°C.

RESULTS

All catalysts were crystalline as shown by their X-ray diffraction patterns. Cr_2O_3 and Fe_2O_3 were in the α modification.

Susceptibility Measurements

Susceptibility measurements of the oxide were carried out before and after the catalytic tests.

The relevant data are included in Table 2 and are discussed below.

TiO_2. Small increases in susceptibility were noted after reaction. This is probably due to reduction of small amounts of Ti^{4+} to Ti^{3+}. In any case Ti^{3+} is likely to be the catalytically active species, one *d* electron being available ($3d^1$ configuration) against none in Ti^{4+}.

V_2O_3. The susceptibility in this case showed a slight field dependence, the value given in Table 2 being obtained by extrapolation to infinite field. The small antiferromagnetic component must be associated with the oxide since reduction to metal is most unlikely at the temperatures used.

Co_3O_4. The susceptibility before and after reaction was identical and no field dependence could be detected. Reduction to metal or to the lower oxide is therefore excluded. This result may be due to the low temperature (20°C) at which the activity of the ethylene hydrogenation could be measured. In the case of the cyclohexene disproportionation, reported previously (*4*), the activity had to be tested at 150°C when some reduction to CoO took place.

NiO. A sample of the mainly paramagnetic green oxide (*6*) showed some field dependence, indicating a small ferromagnetic component. After reaction the susceptibility had decreased a little, showing about the same field dependence as before reaction. Reduction to metal is excluded by the decrease in susceptibility after reaction.

α-Fe_2O_3. All three samples (A, B, C; see Experimental section) showed a slight field dependence of the susceptibility before reaction which increased after reaction (formation of ferromagnetic Fe_3O_4). Titration of the Fe^{2+} formed (*7*) could adequately explain the increase in susceptibility and experiments with synthetic mixtures of pure Fe_3O_4 and diamagnetic ZnO showed that a 0.01–0.02% reduction of Fe_2O_3 to Fe_3O_4 would explain the increase in field dependence of the susceptibility found after reaction. There is therefore no reason to suspect reduction to Fe metal which is further made unlikely by the stability of the catalytic activity.

Of the samples (A, B) used in ethylene hydrogenation, A had a much larger surface and susceptibility than B (see Table 1). Model calculations show that approximately half of all Fe ions in A were in the surface and the iron content indicates a large amount of surface hydroxylation. These properties would explain the increase in susceptibility of sample A when compared with B and C and also the literature value (*11*). The comparatively low susceptibility of the antiferromagnetic Fe_2O_3 (Neél point 960°K) is ascribed to strong Fe–O–Fe interactions. The combined effect of a large surface and of surface hydroxylation is likely to lead to a break up of these interactions with an increase in susceptibility, as observed.

Activity Tests

The activities of the oxides for the ethylene hydrogenation were tested at temperatures of from −120° to 400°C. In nearly all cases standard initial pressures of hydrogen of 30 ± 1 torr and of ethylene of 15 ± 1 torr were used. For Fe_2O_3 the pressures were 50 and 25 torr for hydrogen and ethylene, respectively.

The measured pressure decrease for the reaction $C_2H_4 + H_2 = C_2H_6$ agreed quantitatively with mass spectral analysis with ethane as the only product. All results are given in Table 2, which also include susceptibility and surface area measurements. This table gives for comparison the results obtained for cyclohexene (*4*) and includes

TABLE 2

RATES OF ETHYLENE HYDROGENATION AND CYCLOHEXENE DISPROPORTIONATION AND DEHYDROGENATION[a]

	Ethylene					*Cyclohexene*				
	Paramagnetic susceptibility[b,c] (c.g.s. χ units g^{-1} $\times 10^6$)					Paramagnetic susceptibility[b] (c.g.s. χ units g^{-1} $\times 10^6$)				
Oxide	Before activity test	After activity test	Surface area (m^2g^{-1})	Temp. of test (°C)	Rate (mole sec^{-1} m^{-2} $\times 10^{11}$)	Before activity test	After activity test	Surface area (m^2g^{-1})	Temp. of test (°C)	Rate (mole sec^{-1} m^{-2} $\times 10^{11}$)
TiO_2, rutile	0.24	0.40	38.9	100°	0.0	—	—	—	—	—
				400°	1.39	—	—	1.95	400	2470
TiO_2, anatase	0.036	0.14	41.6	100°	0.0	—	—	—	—	—
				400°	0.311	—	—	—	—	—
V_2O_3	—	13.1	11.4	100°	125	—	—	8.40	350	698
Cr_2O_3	—	23.7	21.0	−120°	6360	—	—	24.6	218	860
MnO	—	72.4	2.6	100°	0.0	—	—	—	—	—
				400°	0.0	—	—	5.2	465	1020
Fe_2O_3(A)	29.1	35.1	490	140°	0.77	(C)16.1	16.9	28.0	140	0.0813
Fe_2O_3(B)	15.6	22.0	145	140°	3.11	—	—	—	—	—
Co_3O_4	31.4	31.5	13.2	20°	1520	29.0	31.1	20.2	156	1.98
NiO	68.9	60.3	15.7	100°	198	Reduction to metal				
ZnO(A)	Diamagnetic[d]		9.6	100°	910	(C)Diamagnetic		9.6	350	420
ZnO(B)	Diamagnetic[e]		—	100°	2620	—		—	—	—

[a] All cyclohexene data from ref. (*4*) except for Fe_2O_3(C) and ZnO(C).

[b] All χ values at 20° ± 2°C.

[c] Literature values for $\chi \times 10^6$: V_2O_3, 13.9 (*12*); Cr_2O_3, 25.0 (*13*); MnO, 71.1 (*14*); Fe_2O_3, 16.6 (*11*); Co_3O_4, 30.7 (*15*).

[d] Treated by evacuation at 260° after activation in O_2 at 400°C.

[e] Activated in O_2 at 400°C followed by evacuation at 400°C.

those not previously reported using ZnO and Fe_2O_3 as catalysts.*

Small traces of carbon, of the order of 0.1–0.3% by weight of the catalyst, were detected on most but not all catalyst samples. This corresponds to 0.02–0.04% of ethylene decomposed, if all the ethylene which has been in contact with a particular sample of catalyst is taken into account. These quantities seem too small to affect the results of either rate or susceptibility measurement.

DISCUSSION

From the data of Table 2 it is clearly evident, particularly if the relative temperatures at which the catalytic activities were determined are taken into consideration, that on all oxides, with the exception of the low-activity oxides, TiO_2 and MnO, the ethylene hydrogenation is 10^4 to 10^6 times faster than the cyclohexene reactions. At the same time the rates follow a similar twin peak pattern, shown in Fig. 1, as in the case of the slower cyclohexene reactions (*4*) and the faster hydrogen–deuterium exchange (*2*). The twin peaks for Cr_2O_3 and Co_3O_4 would be further accentuated if it had been possible to measure these activities at 100°C, the standard temperature, instead of at the lower temperatures indicated.

The outstanding features are again the peak activities of Cr_2O_3 and Co_3O_4 separated by the inactive MnO and the very little active Fe_2O_3. The small activity of the latter is in agreement with the results of Dowden *et al.* (*2*) on the hydrogen–deuterium exchange.

---

*Due to a computational error the activity for Co_3O_4 reported in ref. (*4*) is too large by a factor of 10. While this does not alter the characteristic twin peak pattern of activities, it reduces the Co_3O_4 peak below that of Cr_2O_3, thus giving relative activities similar to those found in ethylene hydrogenation.

Both Mn^{2+} and Fe^{3+} are in the $3d^5$ configuration, the stability of which is demonstrated by the comparatively high ionization potentials and the low electron affinities of these ions (*8*).

Crystal-field effects have been invoked to explain this lack of catalytic activity but direct experimental evidence for this theory is lacking. Until this is forthcoming the difficulty, because of its stability, of exciting a $3d^5$ ion into a state where bonding to an adsorbed substrate can take place seems to be a less specific, but still sufficient, explanation for the low activities. In any case the crystal-field explanation of the effect also requires the stability of the $3d^5$ configuration as a basic condition.

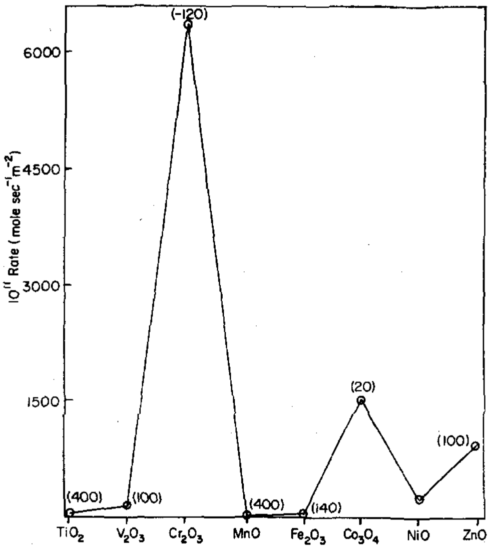

FIG. 1. Activity pattern in the hydrogenation of ethylene. Figures in parenthesis denote reaction temperature.

The high activities of Cr_2O_3 and Co_3O_4, on the other hand, must be attributed to easier promotion of the electrons in the $3d^3$ and $3d^7$ configurations coupled with the absence of strong electronic interactions of neighboring metal ions in these oxides. In Ti_2O_3 and V_2O_3, where these interactions are strong, the catalytic activity is much reduced (*9*).

In the previous investigations (*2, 4, 10*) some uncertainty had been attached to the existence of catalytic activity in NiO. In the deuterium exchange a reduction to nickel metal was suspected and in the cyclohexene reactions such a reduction, with a concomitant progressive increase in catalytic activity, was clearly demonstrated. In the present case absence of reduction has been established by the susceptibility measurements and a progressive decrease (poisoning) of catalytic activity instead of an increase, due to progressive reduction to metal, was noticed. Thus one must conclude that NiO is active in ethylene hydrogenation, though less so than the neighboring very active Co_3O_4.

Fe_2O_3, as already discussed, is expected to be inactive because of its stable $3d^5$ configuration. However, in relation to the active Co_3O_4 some activity is shown in the ethylene hydrogenation (rate Fe_2O_3/rate $Co_3O_4 = 1/10^7$ after approximate correction for the temperature difference of the tests) and a much greater relative activity in the cyclohexene disproportionation (rate Fe_3O_3/rate $Co_3O_4 = 1/9$). The low paramagnetic susceptibility of Fe_2O_3, due to Fe–O–Fe interactions has been discussed already. The measured susceptibility indicates that on the average one electron per ion remains unpaired. Because of the Fe–O–Fe interactions the energy levels of the $3d^5$ configuration will be perturbed and as a result the unpaired electron will be favorably placed energetically to interact with a substrate on chemisorption.

The condition may explain the four times higher activity in ethylene hydrogenation of the lower surface area sample B, when compared with that of the higher surface area sample A (Table 2). In the lower surface area and also low-susceptibility sample B the better annealed and less hydroxylated surface would contain more interacting Fe–O–Fe groupings, with Fe ions capable of chemisorbing substrates.

The effect may also be the reason for the very high activity of sample C relative to Co_3O_4 in the cyclohexene reaction. Sample C had been annealed for a prolonged time at 400°C (Table 1) and as a result had a much lower specific but probably much better annealed surface with still more Fe–O–Fe groupings capable of catalytic action than samples A and B.

An alternative explanation of the effect might be found in the small amounts of Fe^{2+} ions ($3d^6$ configuration) which were shown to be present in these catalysts. However, this explanation is unlikely because approximately equal amounts of Fe^{2+} ions were present in samples A and B, but their activities differed by a factor of our, and, secondly, because on a given catalyst sample the reduction of the Fe^{3+} to Fe^{2+} should progress from experiment to experiment and consequently the activity should increase, but no such increase was found.

The considerable activity of ZnO, which lies between that of Co_3O_4 and that of NiO, is very likely due to interstitial Zn^+ ions or interstitial Zn atoms and their associated electrons, since the normal Zn^{2+} ions have a closed-shell $3d^{10}$ configuration. The interstitial species are formed on evacuation of ZnO at elevated temperatures and in accordance with this the activity increases with the temperature of evacuation.

ACKNOWLEDGMENTS

The authors take the opportunity to thank the former Department of Scientific and Industrial Research for the award of a research studentship to D.N. and the Scientific Research Council for a similar award to D.L.H. They are also very grateful for financial support by Marchon Products, Ltd.

REFERENCES

1. STONE, F. S., *in* "Chemistry of the Solid State," p. 367. Butterworths, London, 1955.
2. DOWDEN, D. A., MCKENZIE, N., AND TRAPNELL, B. M. W., *Proc. Roy. Soc. (London)* **A237,** 245 (1956).
3. DOWDEN, D. A., AND WELLS, D., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2,** 1499 (1961).
4. DIXON, G. M., NICHOLLS, D., AND STEINER, H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1,** 815 (1965).
5. SPRAGUE, J. W., U.S. Patent, 3,092,457 (Cl 23–202), June 4th, 1963.
6. TEICHNER, S. J., AND MORRISON, J. A., *Trans. Faraday Soc.* **51,** 961 (1955).
7. SNELL, F. D., AND SNELL, C. T., "Colorimetric Methods of Analysis," Vol. 2, p. 316. Van Nostrand, Princeton, New Jersey 1949.
8. COTTON, F. A., AND WILKINSON, J., "Advanced Inorganic Chemistry," 2nd ed., p. 797, Table 21–1. Interscience, New York, 1966.
9. DE, K. S., ROSSITER, M. J., AND STONE, F. S., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1,** 520 (1965).
10. STONE, F. S., *Advan. Catalysis* **13,** 34 (1962).
11. JUILLARD, C., *J. Phys. Radium* **12,** 489 (1961).
12. WEDEKIND, E., AND HORST, C., *Chem. Ber.* **45,** 262 (1912).
13. SELWOOD, P. W., *Advan. Catalysis* **3,** 29 (1961).
14. "American Institute of Physics Handbook," 2nd ed. pp. 5–196. McGraw-Hill, New York, 1963.
15. Gmelins Handbuch der Anorg. Chemie, 8. Aufl. Part 58A (Supplement), p. 494. Verlag Chemie G.M.B.H. Weinheim/Bergstrasse, 1961.