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Metal Oxide Activities in the Oxidation of Ethylene

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The complete oxidation of ethylene over various supported metal oxides was studied as a means of assessing catalytic activities. The oxides of Co and Cr were most active. Comparison with other activity patterns shows that chromia is highly active whenever hydrogen in some form is present on the surface. When benzene is completely oxidized over chromia an inversion in activity is noted, suggesting a change in oxidation state.

The correlation of metal oxide activity with *d*-electron configuration advanced by Dowden, MacKenzie, and Trapnell (*1*) has suffered from criticisms of the experimental data upon which the theory is based. The two peaks of activity centering about the oxides of Co and Cr for H_2–D_2 exchange are not found for N_2O decomposition (*2–4*), CO oxidation (*5*), O atom recombination (*6, 7*), nor the hydrogen–oxygen reaction (*8*). In particular the relatively high activity for chromia is questioned and the work of De and Stone (*9*) demonstrates the importance of the reaction temperature in assessing activities. Furthermore, other criticisms have been levelled at the conclusions regarding CoO (*10*) and the data for NiO (*11*). However, a recent report by Dixon, Nicholls, and Steiner (*12*) concerning the disproportionation and dehydrogenation of cyclohexene confirms the twin peak activity pattern with maxima at Cr_2O_3 and Co_3O_4. The oxidation of methane also assigns high activity to chromia (*13*).

As an adjunct to our studies on the catalytic oxidation of benzene (*14*) we determined the activities of 13 supported metal oxide catalysts by their abilities to effect the oxidation of ethylene. This activity pattern, generated under uniform conditions, bears directly on the related problems of chromia activity and the twin peak pattern.

EXPERIMENTAL

Catalysts were prepared by impregnating 3-mesh silica or alumina-silica pellets (both gave equivalent results) obtained from Carborundum Co., Latrobe, Pennsylvania, with ammoniacal slurries of metal oxides or salts. For example, 10 g of ZnO in a porcelain casserole was treated with 25 ml of concentrated NH_4OH and attenuated with 100 ml of water. To this slurry there was added 100 g of pellets and the mixture was concentrated over steam for 2 hr with vibratory agitation. The catalyst was subsequently fired in air at 400°C for 45 min. The calcined pellets contained 6.75 wt % coating or 0.051 g Zn/g of finished catalyst. Uniform dispersal was shown by microscopic inspection of whole and sliced pellets. The same preparative procedure was followed for other catalysts except for adjusting weights to ensure the same number of metal atoms per gram of catalyst. The coated metal oxides were identified by X-ray examination using a Weissenberg camera of 57.3-mm diameter and Mo, $K\alpha$ radiation. The powder diffraction patterns were compared with standards (X-Ray Powder Data File, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania).

Experiments were conducted in the apparatus described previously (*14*) at constant feed composition, flow rate, and catalyst weight at several temperatures. A 48-g charge of catalyst was used for each run and was kept for 1 hr at 262°C under a stream of air prior to use. The feed stream contained 2.2% of ethylene in air and was conducted at 750 cc (STP)/min through the catalyst bed. The free volume of the packed 50-ml charge was measured by mercury displacement to be 25 ml. The effluent stream was analyzed for ethylene by gas chromatography on a 1-m column of hexamethylphosphoramide deposited on 30–60-mesh silica gel. The concentration of CO_2 was determined by infrared absorption and found to be twice the ethylene consumed. No other products were observed. Carbon recovery was at least 97%. Ultraviolet spectroscopy was used for the detection of benzene.

RESULTS AND DISCUSSION

The data are presented as per cent reaction at temperatures from 262° to 459°C. The Arrhenius parameters and the temperatures to which they are appropriate are recorded in Table 1. In all cases the plot of log per cent reaction versus the reciprocal of the absolute temperature was linear, indicating no change in the nature of the surface nor in the reaction. A representative example, Fe_2O_3, is shown in Fig. 1. No oxidation of ethylene was observed up to 426° using uncoated support. The compensation effect is shown in Fig. 2. Uncertainties in the apparent activation energies average less than 1 kcal/mole. Three oxides were studied only at 262°. Silver oxide, Cr_2O_3, and Co_3O_4 gave 62%, 88%, and 100% reaction, respectively. The activity sequence at 262° is given in terms of the metal in

TABLE 1
ARRHENIUS PARAMETERS FOR ETHYLENE OXIDATION ON METAL OXIDES

Oxide	*E* (kcal/mole)	Log *A* (% reaction)	Temp. range (°C)
TiO_2	17.1	6.16	344–427°
V_2O_5	16.1	6.46	288–443°
CdO	16.9	6.77	320–443°
Mn_2O_3	13.5	6.75	262–344°
Fe_2O_3	15.9	6.28	320–459°
WO_3	11.7	4.50	344–427°
MoO_3	11.1	4.29	320–443°
ZnO	12.4	4.29	388–459°
NiO	14.3	5.84	320–443°
CuO	9.0	3.99	262–459°

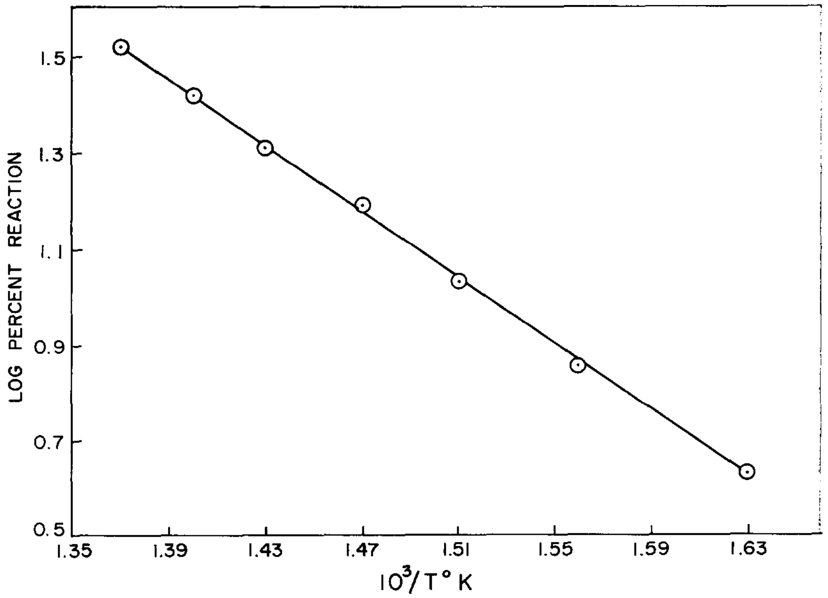

FIG. 1. Log per cent ethylene oxidation on Fe_2O_3 as a function of temperature.

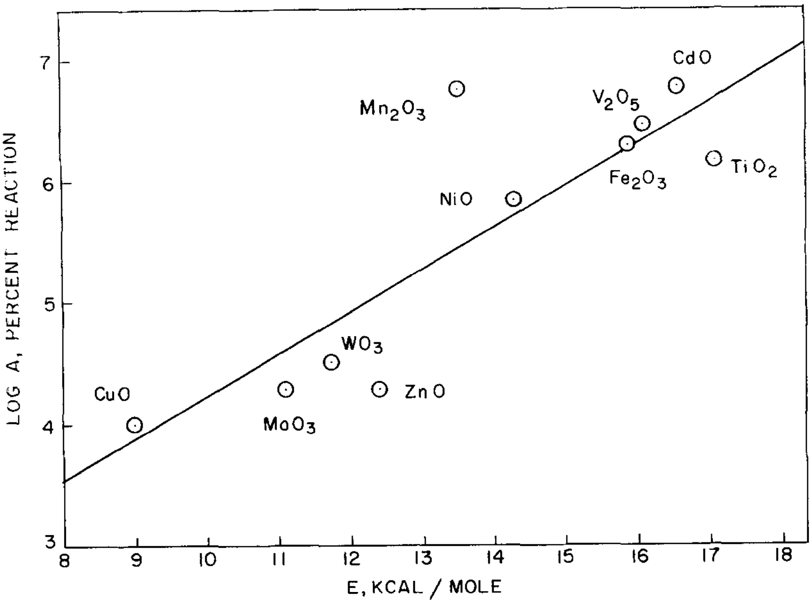

FIG. 2. Compensation effect for ethylene oxidation.

the oxide: Co > Cr > Ag > Mn > Cu > Ni > V Cd > Fe > Mo > W > Ti > Zn.

The twin peak activity pattern found agrees with that for H_2–D_2 exchange (*1*) and the cyclohexene reaction (*12*). In addition, the high activity for chromia is in accord with its relative activity in the oxidation of methane (*13*). A comparison of activities of similar metal oxides is shown in Table 2 for several kinds of reactions. A lack of agreement is anticipated due to the diverse reactions studied; however, minor discrepancies are evident even for the two series on oxygen atom recombination. But the major difference among the series is the relative position assigned to Cr_2O_3. Chromia assumes importance for reactions in which hydrogen in some form at the surface plays a prominent role. Otherwise, it is fairly inert, possibly because of its oxidation to CrO_3 (*7*) or a change to some other oxidation state. This explanation is one of the simpler ways in which the apparently conflicting results can be reconciled. The fact that some regularity must obtain is attested to by Fig. 3, which is a plot of the activation energies for ethylene oxidation and O atom recombination (*7*). It may be that the activation energy is a more accurate reflection of intrinsic activity than the measurement of the amount of reaction.

TABLE 2
COMPARISON OF METAL OXIDE ACTIVITY PATTERNS[a]

C_2H_4[b] oxidation	CH_4[c] oxidation	O atom[d] recombination	O atom[e] recombination	N_2O[f] decomposition	CO[g] oxidation
CO_3O_4	Cr_2O_3	CuO	CuO	CoO	CoO
Cr_2O_3	Mn_2O_3	Fe_2O_3	Mn_2O_3	Mn_2O_3	NiO
Mn_2O_3	CuO	Co_3O_4	NiO	NiO	Mn_2O_3
CuO	Co_3O_4	Mn_2O_3	Fe_2O_3	CuO	CuO
NiO	Fe_2O_3	NiO	Co_3O_4	ZnO	Fe_2O_3
Fe_2O_3	ZnO	ZnO	ZnO	Cr_2O_3	ZnO
ZnO		Cr_2O_3	Cr_2O_3	Fe_2O_3	Cr_2O_3

[a] The most active oxide is listed first.
[b] This work.
[c] Reference (*13*).
[d] Reference (*7*).
[e] Reference (*6*).
[f] References (*2–4*).
[g] Reference (*5*).

Partial corroboration for the ethylene oxidation activity sequence is provided by the complete oxidation of benzene (3.3% in air) on NiO, Mn_2O_3, and Cr_2O_3. The activities increased in that order with apparent activation energies of 14.3, 13.6, and 10.8

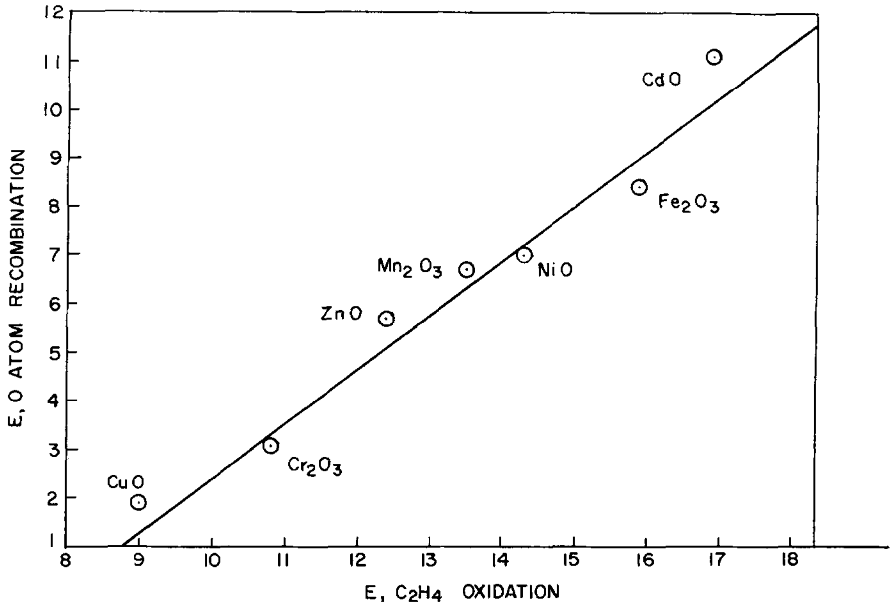

FIG. 3. Comparison of activation energies for ethylene oxidation and O atom recombination on similar catalysts.

kcal/mole, respectively. In the course of determining the temperature coefficient for Cr_2O_3 an abrupt inversion of activity was noted. The per cent of benzene reaction at 254°, 280°, and 302°C was 15.0, 24.5, and 6.4. The same figures were obtained with chromia catalysts calcined at 400°, 300°, and 200°. Obviously, some change in the catalyst to a less active state occurs under reaction conditions between 280° and 302°. The amount of water present cannot be a factor since the same results were obtained with catalysts calcined at different temperatures where the water content is expected to vary (*15*). Therefore, a change in the oxidation state of surface chromium is indicated.

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