A kinetic and surface study of the oxidation of ethane by nitrous oxide and by oxygen over manganese(III) oxide

CRAIG FAIRBRIDGE[1]
Department of Chemistry, Lakehead University, Thunder Bay, Ont., Canada P7B 5E1
AND
ROBERT ANDERSON ROSS
Alcan International Limited, Kingston Laboratories, Box 8400, Kingston, Ont., Canada K7L 4Z4

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The kinetics of the nitrous oxide/ethane and oxygen/ethane reactions on manganese(III) oxide have been studied from 573 to 673 K and from 523 to 593 K, respectively. The apparent activation energy for carbon dioxide formation was 130 ± 4 kJ mol^{-1} in both reactions while that for nitrogen formation in the nitrous oxide/ethane reaction changed from 106 ± 4 kJ mol^{-1}, 573–613 K, to 133 ± 4 kJ mol^{-1}, 623–673 K. The kinetic results for both reactions fit the same rate equation:

$$r = \frac{kap_{\mathrm{C_2H_6}}bp_{\mathrm{x}}}{(1 + ap_{\mathrm{C_2H_6}} + bp_{\mathrm{x}})^2} \cdot (p_{\mathrm{C_2H_6}}p_{\mathrm{x}})$$

where p_{x} represents either $p_{\mathrm{N_2O}}$ or $p_{\mathrm{O_2}}$. The rate-controlling step has been associated with the interaction of adsorbed species on the catalyst surface while both ethane and the oxidising gas appear to be directly involved in further steps in the mechanism. Samples were analysed routinely by scanning electron microscopy, X-ray powder diffraction, and infrared spectroscopy. Electron spectroscopy results from samples treated in various ways with hydrocarbon/oxidant mixtures gave O(1*s*) values from 528.7 to 529.7 eV which are indicative of binding energies usually associated with chemisorbed oxygen. No N(1*s*) spectrum was obtained from catalysts exposed to hydrocarbon/nitrous oxide mixtures, in agreement with the absence of bands in the infrared which are usually associated with nitrates or nitrogen/oxygen complexes. A binding energy value of 406.5 eV was measured in the comparable N(1*s*) spectrum of a catalyst used at 623 K for the oxidation of ethane by nitric oxide — a result which confirms conclusions from previous surface studies on the same system using infrared spectroscopy.

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La cinétique des réactions entre le protoxyde d'azote et l'ethane et entre l'oxygène et l'éthane a été étudiée sur l'oxyde de manganèse (III) à 573 jusqu'à 593 K respectivement. La valeur de l'énergie apparente d'activation du dioxyde de carbone était 130 ± 4 kJ mol^{-1} dans les deux réactions, pendant que la valeur originelle de 106 ± 4 kJ mol^{-1}, 573–613 K, pour la formation de l'azote dans la réaction du protoxyde d'azote avec l'éthane augmentait à 133 ± 4 kJ mol^{-1}, 623–673 K. Les valeurs cinétiques pour les deux réactions s'accordent avec la même équation de vitesse:

$$r = \frac{kap_{\mathrm{C_2H_6}}bp_{\mathrm{x}}}{(1 + ap_{\mathrm{C_2H_6}} + bp_{\mathrm{x}})^2} \cdot (p_{\mathrm{C_2H_6}}p_{\mathrm{x}})$$

dans laquelle p_{x} représente $p_{\mathrm{N_2O}}$ ou $p_{\mathrm{O_2}}$. Le procédé du contrôle de vitesse semble être lié avec l'interaction des éléments adsorbés sur la surface catalytique; mais l'influence directe de l'éthane aussi que celle du gaz oxydant apparément ne se manifeste que pendant les étapes suivantes du mécanisme. Un microscope électronique explorant, la diffraction de rayons X des poudres et la spéctroscopie infrarouge ont été utilizés dans une analyse courante des échantillons. Les résultats d'une analyse par la spéctroscopie électronique obtenus pour des échantillons traîtés de diverses manières par des mélanges des carbures d'hydrogène et d'un agent oxydant représentent les valeurs O(1*s*) de 528.7 à 529.7 eV, caractéristiques pour les énergies de liaison normalement associées avec l'oxygène absorbé chimiquement. Des catalyseurs exposés aux mélanages de la carbure d'hydrogène et du protoxyde d'azote ne produisaient pas de spêctre N(1*s*) et cela s'accorde avec l'absence des bandes normalement associées avec les nitrates ou les complexes nitrogène–oxygène en analyse par la spéctroscopie infrarouge. La valeur de l'énergie de liaison de 406.5 eV était obtenue en mesurant un spectre N(1*s*) comparable d'un catalyseur utilisé pendant l'oxydation de l'éthane par l'oxyde nitrique à 623 K cette valeur est en accord avec les résultats des analyses infrarouge executées auparavant à l'étude des surfaces d'un système identique.

Introduction

In previous, related studies the kinetics of the nitrous oxide/carbon monoxide reaction were evaluated on several transition metal oxides (1–5) and the reaction mechanism held to involve the adsorption and reaction of carbon monoxide with surface oxygen followed by the formation of a surface carbonate. In a similar way, investigations of the water–gas shift reaction over manganese(II) oxide led to the proposal that the rate-controlling step was associated with the reducing action of adsorbed carbon monoxide on a surface oxygen species (6). Further, the decomposition of nitrous oxide on manganese oxides has been explained by a redox-

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[1] Present address: Energy Research Laboratories, Energy Mines and Resources Canada, 555 Booth Street, Ottawa, Ont., Canada K1A 0G1.

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type mechanism which would be enhanced by conditions which preserve the 3+ oxidation state of the metal (7).

Those features of the surface chemical properties of manganese oxides which appeared to contribute to catalysis were most recently investigated in a kinetic study of the reaction of nitric oxide with ethane over manganese(III) oxide (8). A contiguous investigation of the oxidation of ethane by both oxygen and nitrous oxide is reported here with the experimental rate data supplemented by structure analysis including the results of electron spectroscopic measurements on selected catalyst samples.

Experimental

Apparatus and procedure

A quartz reactor and Pyrex flow system (9) were used for the kinetic studies in conjunction with a Hewlett-Packard Research Chromatograph Model 5754B. Nitrogen, oxygen, carbon dioxide, nitrous oxide, ethane, and water were analysed by a thermal conductivity bridge using stainless steel columns 244 × 0.32 cm od packed with 61 cm Carbosieve B and 183 cm Poropak T. The column oven was temperature programmed with a 2 min post-injection interval at 353 K followed by a 60 K min^{-1} rise to 443 K where the temperature was maintained for 5 min prior to recycling.

Surface areas were determined by application of the BET theory to low-temperature krypton adsorption (77 K, $\sigma = 21.5$ Å^2).

The experimental conditions for which reaction rates were not influenced by internal or external diffusion were determined in the usual way by altering space velocity, catalyst mass, and particle size (10). Hence, kinetic measurements were conducted at a total flow rate of 350 $\text{dm}^3\ \text{min}^{-1}$ (NTP) on 1.0 g catalyst samples, <37 μm maximum diameter with surface area 15.5 $\text{m}^2\ \text{g}^{-1}$, and were recorded as the rate of nitrogen or carbon dioxide production after steady catalyst activity had been attained and at less than 15% total conversion to products. The temperature regions adopted for kinetic measurements were defined at the high end by the maximum of 15% conversion and at the low end by the reasonable limits of detection of nitrogen and carbon dioxide on the gas chromatograph, $>10^{-4}$ mol L^{-1}. The only products observed were nitrogen, carbon dioxide, and water in the nitrous oxide/ethane reaction, and carbon dioxide and water in the oxygen/ethane reaction. Because of the tailing involved in the water peak in the chromatogram, the area under the peak, and hence the water concentration, could not be estimated with acceptable accuracy.

Infrared spectra were obtained using KBr pellets (0.5% w/w) with a Beckman 1R-12 Spectrophotometer.

X-ray photoelectron spectra were obtained on a Vacuum Generator Limited ESCA-3 spectrometer using Al K_α radiation. A 50 eV electron analyzer pass energy was used. Samples were run as powders, mounted on double-sided tape and the spectra were corrected for charging by reference to the C(1*s*) line at 284.0 eV.

Materials

Manganese(III) oxide was prepared and analysed as described previously (11). No change in the nature of the catalyst was observed from XRD, scanning electron microscopy, chemical analysis, or surface area measurements after reaction.

Ethane (99.0%) and oxygen (99.99%) were supplied by Matheson of Canada Ltd. Carbon dioxide (99.5%), nitrogen (99.99%), and helium (99.995%) were obtained from Canadian Liquid Air Ltd. and nitrous oxide (99.9%) from Liquid Carbonic Ltd. The water in the gas saturators was distilled and de-ionized prior to use.

Results

Reaction rate orders

Rate order measurements based upon the rates of nitrogen, r_1, or carbon dioxide, r_2, formation were determined at 623 K for the N_2O/C_2H_6 reaction and at 573 K for the O_2/C_2H_6 reaction.

Nitrous oxide/ethane

With the partial pressure of ethane held constant at 2.66 kPa, the effects of the partial pressure of nitrous oxide on r_1 and r_2 were observed and the results plotted as ln (rate) against ln (partial pressure), Fig. 1. A reaction rate order of 0.8 was obtained with respect to nitrous oxide partial pressure from 0.665 to 5.32 kPa.

The effects of variations in ethane partial pressure were observed with the partial pressure of nitrous oxide held at 2.66 kPa. A reaction rate order of 0.7 was obtained from 0.665 to 3.325 kPa and, as indicated in Fig. 1, a rate order of 0.2 was determined from 3.325 to 5.32 kPa.

With both ethane and nitrous oxide partial pressures held constant at 2.66 kPa, the effects on the rates of the partial pressures of the products, nitrogen and carbon dioxide, were observed from 0.333 to 5.32 kPa. In both cases, the reaction rate order was zero. Similarly, the addition of from 0.04 to 1.5 kPa of water vapour had no effect upon the reaction rates.

The experimental rate of reaction was therefore represented by the expressions:

$$[1] \quad r = kp_{N_2O}^{0.8}\,p_{C_2H_6}^{0.7}$$

for $0.665 < p_{C_2H_6} < 3.325$ kPa and

$$[2] \quad r = kp_{N_2O}^{0.8}\,p_{C_2H_6}^{0.2}$$

for $3.325 < p_{C_2H_6} < 5.32$ kPa where r and k represent either r_1 and k_1 or r_2 and k_2.

Oxygen/ethane

The dependence of the reaction rate, r_2, on variations in the oxygen partial pressure from 0.665 to 5.32 kPa was examined with ethane partial pressure maintained at 2.66 kPa. At 573 K, a reaction rate order of 0.5 was obtained, Fig. 1. With the partial pressure of oxygen held at 2.66 kPa, the rate order with respect to ethane partial pressure was 0.6 from 0.665 to 2.66 kPa and 0.85 from 2.66 to 5.32 kPa. The experimental reaction rate was not affected by variations in the carbon dioxide or water vapour partial pressures as in the nitrous

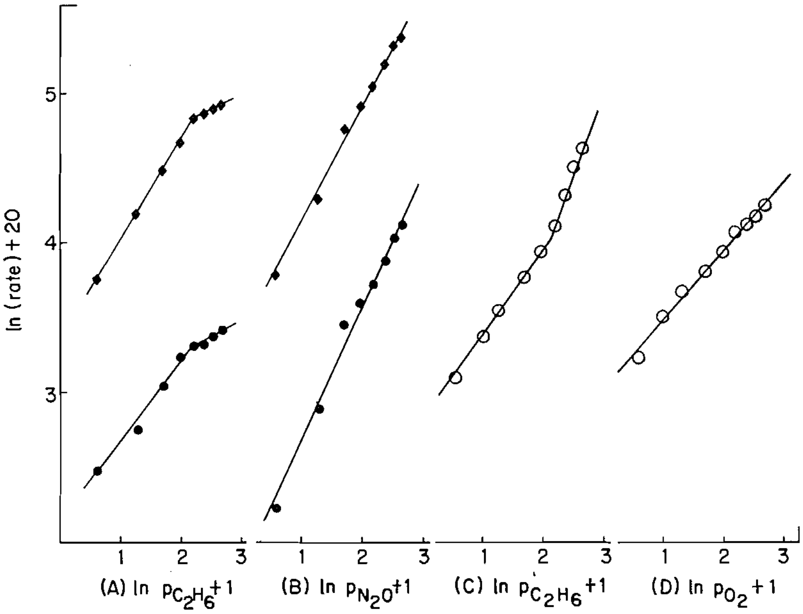

FIG. 1. Nitrogen (◆) and carbon dioxide (● in *A* and *B*, ○ in *C* and *D*) rate dependency on variations in the partial pressure of ethane (*A*) and nitrous oxide (*B*) in the N_2O/C_2H_6 catalytic reaction over Mn_2O_3 at 623 K; and ethane (*C*) and oxygen (*D*) in the O_2/C_2H_6 reaction at 573 K.

oxide/ethane reaction. The experimental reaction rate was therefore expressed as:

$$[3] \quad r_2' = k_2' p_{O_2}^{0.5} p_{C_2H_6}^{0.6}$$

where $0.665 < p_{C_2H_6} < 2.66$ kPa and

$$[4] \quad r_2' = k_2' p_{O_2}^{0.5} p_{C_2H_6}^{0.85}$$

where $2.66 < p_{C_2H_6} < 5.32$ kPa.

Temperature effects

Nitrous oxide/ethane

Steady catalytic activity was obtained after 2 h exposure to the standard mixture of 2.66 kPa each of nitrous oxide and ethane at 673 K. Reaction rate constants were calculated by integration of the rate equation [1] as a function of concentration from 673 to 573 K. Two apparent activation energies were obtained using r_1, namely 133 ± 4 kJ mol^{-1} from 673 to 623 K and 106 ± 4 kJ mol^{-1} from 613 to 573 K, Fig. 2. The pre-exponential factors were 6.35×10^8 and 3.27×10^6 mol L m^{-2} s^{-1}, respectively.

Oxygen/ethane

After catalyst pretreatment with 2.66 kPa oxygen and 2.13 kPa ethane at 593 K for 3 h, the rate of carbon dioxide formation was determined from 593 to 523 K at 10 K intervals. Rate constants were calculated from the integrated form of eq. [3] and plotted in the Arrhenius fashion, Fig. 2. The results lay on the same straight line as those for the rate of carbon dioxide formation in the nitrous oxide/ethane reaction. The apparent activation energy was 130 ± 4 kJ mol^{-1} and the pre-exponential factor, 9.72×10^7 mol L m^{-2} s^{-1}.

Infrared spectra

The infrared spectra of the catalysts after reaction with nitrous oxide/ethane or oxygen/ethane were similar to those observed previously for samples of manganese(III) oxide after catalysis in the nitric oxide/ethane reaction (8). However, a major difference was the absence of any nitrate bands in the spectra. Peaks were noted at 615(s), 490(s), 425(m), and 350(m) cm^{-1} which may possibly suggest the presence of some Mn_3O_4 phase as a surface trace since both chemical analysis and XRD indicated no apparent change from the original Mn_2O_3 composition.

X-ray photoelectron spectroscopy

O(1*s*) spectra on the fresh, unreacted manganese oxide gave a binding energy value of 528.7 eV. Samples exposed to 2.66 kPa each of ethane and nitrous oxide from 573 to 673 K in a kinetic temperature cycle gave an O(1*s*) value of 529.0 eV while 529.5 eV was obtained for the binding energy in a catalyst sample after exposure to the standard mixture of ethane and oxygen in a cycle from 523 to 593 K. All of these energy values are close to that expected for chemisorbed oxygen in metal oxides

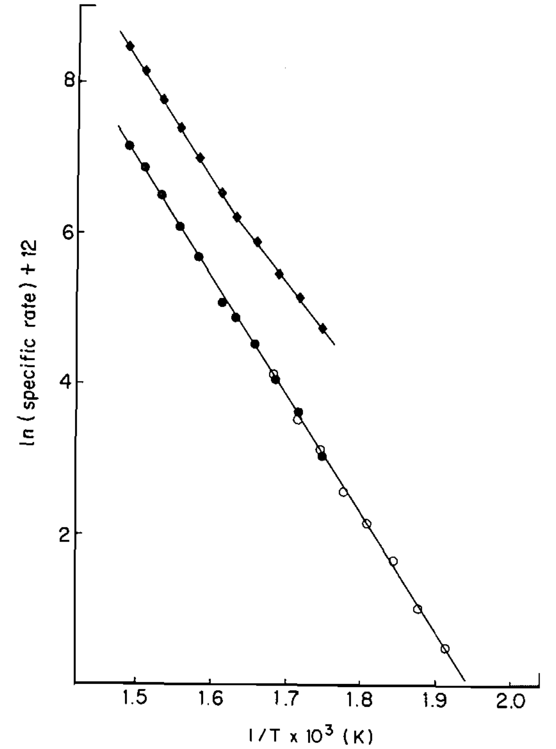

FIG. 2. Arrhenius plots for the N_2O/C_2H_6 (◆, r_1; ●, r_2) and O_2/C_2H_6 (○, r_2) catalytic reactions over Mn_2O_3.

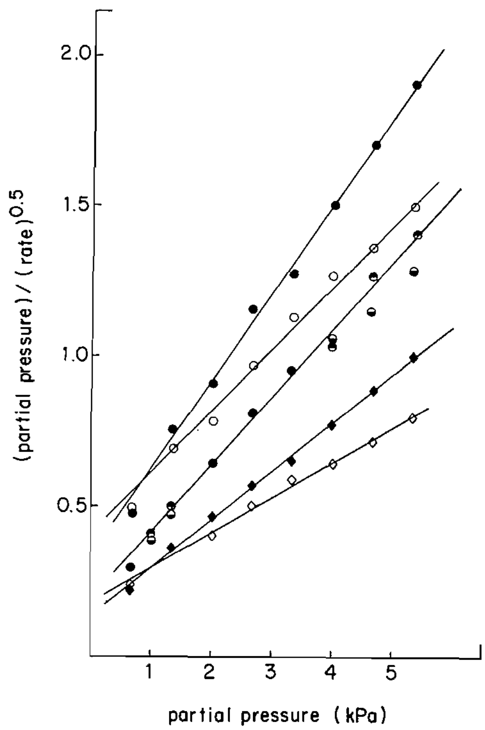

FIG. 3. Reduced plots corresponding to eq. [5] for the nitrous oxide (◇, r_1; ○, r_2) and ethane (◆, r_1; ●, r_2) rate orders in the N_2O/C_2H_6 reaction; and for the oxygen (◓, r_2) and ethane (◒, r_2) rate orders in the O_2/C_2H_6 reaction over Mn_2O_3.

and significantly less than an O(1*s*) value of 532–533 eV which usually characterises the presence of molecular oxygen (12).

Only two of the catalyst samples tested gave N(1*s*) spectra. Catalyst exposed to 2.66 kPa each of ethane and nitric oxide at 623 K, steady state, gave a binding energy of 406.5 eV and a sample used in a cycle from 573 to 673 K with the same gases before cooling to room temperature gave an N(1*s*) value of 406.4 eV.

Manganese(IV) oxide was not detected in any sample and it is difficult to distinguish between manganese(II) and manganese(III) oxides using this technique solely because the Mn/O intensities are similar in the two oxides (13). X-ray diffraction and chemical analysis confirmed that the metal was present as Mn_2O_3 in all bulk samples.

Discussion

Several plausible mechanistic schemes were evaluated by computer tests of the rate order results in many kinetic expressions related mainly to the Langmuir–Hinshelwood model (14, 15). The significance of such statistical criteria in the evaluation of the step-by-step nature of the catalytic process has been frequently analysed (16–18) and recently reviewed (19). The approach has been adopted here to obtain a broad guide to the interpretation of the kinetic results.

Only one kinetic expression clearly accommodated the rate order data. It was the same for both reactions:

$$[5] \quad r = \frac{kap_{C_2H_6}bp_x}{(1 + ap_{C_2H_6} + bp_x)^2}(p_{C_2H_6}p_x)$$

where p_x represents the partial pressure of nitrous oxide or oxygen and a and b are adsorption coefficients. As shown in Fig. 3, plots of $p/r^{0.5}$ versus p were linear for both nitrogen and carbon dioxide rate order results in the nitrous oxide/ethane reaction and for the carbon dioxide results in the oxygen/ethane reaction. A similar kinetic expression was evaluated previously for the nitric oxide/ethane reaction (8). It may be interpreted to represent an irreversible bimolecular reaction between reactive species adsorbed on the same type of site (20). The reaction rate is proportional to the probability that the reactants are adsorbed on neighbouring sites, and thus also proportional to the product of the fraction of surface covered by each reactant, $\theta_{C_2H_6}$ and θ_{N_2O} or θ_{O_2}. The $(p_{C_2H_6}p_x)$ multiplier term in eq. [5] suggests that additional interactions involve nitrous oxide and ethane or oxygen and ethane in the appropriate reaction.

On a test/reject basis (6), surface mechanisms consistent with eq. [5] were formulated:

Nitrous oxide/ethane

[6] $N_2O_{(g)} = N_2O_{(ads)}$

[7] $C_2H_{6(g)} = C_2H_{6(ads)}$

[8] $C_2H_{6(ads)} + N_2O_{(ads)} + [O] \rightarrow C_2H_{5(ads)} + [OOH] + N_2$

[9] $C_2H_6 + [OOH] \rightarrow H_2O + C_2H_{5(ads)} + [O]$

[10] $2C_2H_{5(ads)} + 13N_2O \rightarrow 4CO_2 + 5H_2O + 13N_2$

with an overall stoichiometry:

[11] $C_2H_6 + 7N_2O \rightarrow 2CO_2 + 3H_2O + 7N_2$

Oxygen/ethane

[12] $O_{2(g)} = O_{2(ads)}$

[13] $C_2H_{6(g)} = C_2H_{6(ads)}$

[14] $C_2H_{6(ads)} + O_{2(ads)} + [\ \ ] \rightarrow C_2H_{5(ads)} + [OOH]$

[15] $C_2H_6 + [OOH] \rightarrow H_2O + C_2H_{5(ads)} + [O]$

[16] $2C_2H_{5(ads)} + [O] + 6O_2 \rightarrow 4CO_2 + 5H_2O + [\ \ ]$

with an overall stoichiometry:

[17] $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Previous studies of ethane oxidation over nickel(II) oxide have indicated that the hydrocarbon was adsorbed prior to surface reaction with preadsorbed oxygen while chemisorption of ethane on iron(III) and nickel(II) oxides was shown to involve C—H bond rupture to give a $C_2H_{5(ads)}$ species (21). The rate-determining step in the oxidation of ethane over nickel(II) oxide was thought to be either the adsorption of ethane as a C_2H_5 radical or the interaction of adsorbed oxygen with gas phase or adsorbed ethane through attack at the C—H bond (22). In the homogeneous oxidation of ethane by oxygen the formation of C_2H_5 and HO_2 radicals was postulated as the initial step (23); indeed, peroxide species are often formed in gas phase hydrocarbon oxidation reactions.

It seems likely then that the rate-limiting step in the oxidation of ethane over manganese(III) oxide involves the formation of an adsorbed C_2H_5 species, which may occur through the interaction of adsorbed ethane with adsorbed nitrous oxide or oxygen, eqs. [8] or [14]; or through the action of a surface peroxide radical on gas phase or weakly adsorbed ethane, eqs. [9] or [15].

The apparent activation energies are in good agreement with those determined for the nitrous oxide/carbon monoxide reaction, 493 to 573 K (3), the decomposition of isopropyl alcohol, 483 to 638 K (11), and the dehydration of formic acid, 523 to 573 K (24), all over similar manganese oxide catalysts. These reactions, together with the water–gas shift reaction (6), all appear to involve both Mn^{2+} and Mn^{3+} reactive surface species in the catalytic cycle. The same species may also occur in the present reactions, as well as in the oxidation of ethane by nitric oxide (8).

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