Kinetics of the oxidation of ethane and 1-butene over manganese oxide supported on carbon fibres

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The oxygen/ethane and oxygen/1-butene reactions have been investigated in a continuous flow system at atmospheric pressure over a manganese oxide/carbon fibre catalyst. The products of reaction were carbon dioxide and water. Apparent activation energies were 108 ± 4 kJ mol^{-1} for the former reaction from 673 to 573 K, and 81 ± 4 kJ mol^{-1} for the latter from 573 to 473 K. Kinetic data for both reactions were best described by the rate equation:

$$r = \frac{kap_{\mathrm{O_2}}^{0.5}\, bp_{\mathrm{HC}}^{0.5}(p_{\mathrm{O_2}}\, p_{\mathrm{HC}})}{(1 + ap_{\mathrm{O_2}}^{0.5} + bp_{\mathrm{HC}}^{0.5})^2}$$

The surface mechanism may be complex and it is proposed that reactants interact as adsorbed species each of which is adsorbed on two surface sites. Both oxygen and the hydrocarbon gas appear to be directly involved in further steps. Scanning electron microscopy, X-ray photoelectron spectroscopy, and low temperature krypton adsorption were used to assess the catalyst structure.

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Les réactions oxygène/éthane et oxygène/1-butene sont étudiées à pression atmosphérique dans un systeme à débit continu sur un catalyseur oxyde de manganèse/fibre de carbone. Les produits de la réaction sont le dioxyde de carbone et l'eau. Les énergies d'activation apparentes sont 108 ± 4 kJ mol^{-1} pour la premiere réaction (673 à 573 K) et 81 ± 4 kJ mol^{-1} pour la deuxieme réaction (573 à 473 K). Les données cinétiques pour les deux réactions sont bien décrites par l'équation suivante:

$$r = \frac{kap_{\mathrm{O_2}}^{0.5}\, bp_{\mathrm{HC}}^{0.5}(p_{\mathrm{O_2}}\, p_{\mathrm{HC}})}{(1 + ap_{\mathrm{O_2}}^{0.5} + bp_{\mathrm{HC}}^{0.5})^2}$$

Les mécanismes des réactions de surface peuvent être assez complexes; il est proposé une accumulation des réactifs dans une couche adsorbée. Chaque réactif est probablement adsorbé en deux sites différents sur la surface. L'oxygene et l'hydrocarbure semblent être directement impliqués dans des réactions ultérieures. La microscopie à balayage électronique, la spectroscopie photoélectronique à rayons-X, et l'adsorption de krypton à faible température sont utilisées pour déterminer la structure du catalyseur.

Introduction

A number of key heterogeneous catalytic reactions have been examined over manganese oxides in recent years (1–4); including directly related work on the oxidation of ethane on manganese(III) oxide by nitric oxide (5), and by oxygen (6). These oxides were finely-divided, pure materials with no support or carrier, in contrast to the present investigation where high purity carbon fibres have been adapted for use as support media for manganese oxide in a study of the catalytic oxidation reactions of both ethane and 1-butene.

Catalysts consisting of metals on activated carbon supports have been used in many reactions including NO_x reduction (7, 8) and hydrocarbon oxidation (9) but the application of carbon fibres as catalyst supports has received relatively little attention. Carbon filaments alloyed with transition metals such as nickel, cobalt, chromium, and manganese have been used as catalysts for the dehydration of secondary alcohols (10), while a platinum/carbon fibre catalyst was described in connection with hydrocarbon conversion reactions (11). Because of their mechanical strength, thermal stability, flame and chemical resistance, carbon fibres could prove to be applicable as supports with long service life (12), particularly in the hydrocarbon conversion field (11).

Experimental

Apparatus and procedure

Helium was used as the carrier gas in the quartz reactor flow system (13) and in the Hewlett-Packard Research Chromatograph, Model 5754B. A thermal conductivity bridge and stainless steel analytical columns, 305 × 0.32 cm od packed with Poropak Q, were used to analyze for oxygen, carbon dioxide, ethane, 1-butene, and water. The column oven was temperature programmed with a 3 min post-injection interval at 333 K, followed by a 60 K min^{-1} increase to 408 K, whereupon the temperature was maintained for 8 min prior to recycling.

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Reaction rate measurements were conducted at a total flow rate of 350 mL min^{-1} (NTP) on 1 g catalyst samples, conditions which indicated that gas phase diffusion as well as heat and mass transfer effects were minimal (14). The experimental reaction rate, equated to the rate of carbon dioxide production, was recorded after steady catalyst activity had been achieved at <8% hydrocarbon conversion. The only products observed by gas chromatography were those expected from complete hydrocarbon oxidation, namely, carbon dioxide and water.

Catalyst surface areas measured by low temperature krypton adsorption (BET; 77 K; σ = 19.5 Å^2) were reproducible to ±0.2 m^2 g^{-1}. Surface structures were examined by a scanning electron microscope, Cambridge Stereoscan 600, and by an X-ray photoelectron spectroscope, Vacuum Generator ESCA-3.

Materials

"Modmor" high modulus reinforcing carbon fibre, Type III S, was supplied by Morganite Modmor Limited. Fibres, in 10 cm lengths, were sprayed with a 50% w/w aqueous solution of manganese(II) nitrate (BDH Chemicals Limited) and dried with a hot air gun at temperatures up to 573 K. The fibres were sprayed and dried in 10 cycles and chemical analysis (15) indicated 9.5% w/w manganese on the carbon after treatment in nitrogen at 773 K for 2 h. The fibre surface area increased from 1.8 to 3.8 m^2 g^{-1} as a result.

Ethane (99.0%), 1-butene (99.0%), and oxygen (99.99%) were supplied by Matheson of Canada Limited. Carbon dioxide (99.5%) and helium (99.995%) were obtained from Canadian Liquid Air Limited. Water used in the gas saturators was distilled, de-ionized, and degassed prior to use.

Results

Reaction rate order measurements

Rate orders were determined at 623 and 523 K, respectively, for the oxygen/ethane and the oxygen/1-butene catalytic reactions.

Oxygen/ethane

When the catalyst was exposed to 2.63 kPa oxygen and 2.62 kPa ethane at 673 K, the initial rate of carbon dioxide formation was very high, possibly due to partial oxidation of the carbon fibres. The rate of product formation decreased quickly to a steady level in 3 h and remained constant thereafter for at least 48 h. The surface area of catalysts treated in this way was 6.9 m^2 g^{-1}.

A reaction rate order of 0.3 with respect to oxygen partial pressure was determined at 623 K, Fig. 1, by altering the partial pressure from 0.31 to 14.15 kPa. The partial pressure of ethane was maintained at 2.57 kPa for these experiments.

With the partial pressure of oxygen held constant at 2.47 kPa, the partial pressure of ethane was adjusted from 0.69 to 10.05 kPa. The rate order with respect to ethane concentration was 0.4 as determined from the linear plot of ln (rate) versus ln (partial pressure), Fig. 1.

Variations in the carbon dioxide partial pressure from 0.67 to 6.44 kPa had no effect on the rate of reaction with oxygen and ethane partial pressures maintained at 2.68 and 2.74 kPa, respectively. Therefore, the rate order was zero with respect to carbon dioxide.

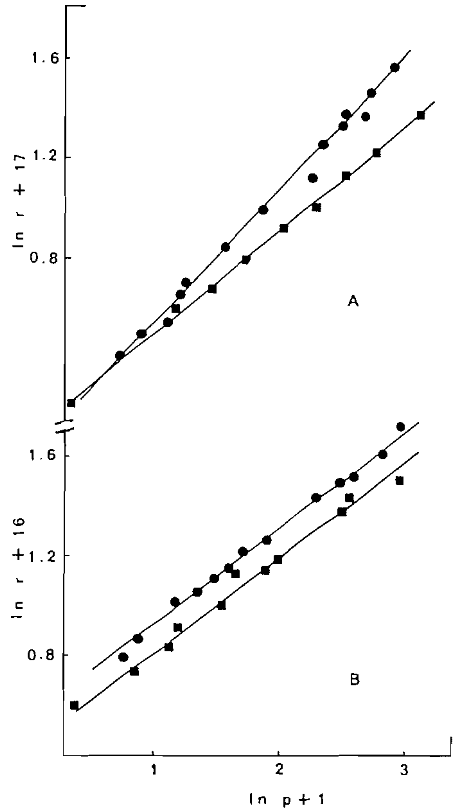

FIG. 1. The effects of component partial pressures (oxygen, ■; hydrocarbon, ●) on the reaction rate of the oxygen/ethane (*A*) and the oxygen/1-butene (*B*) reactions over manganese oxide/carbon fibre catalysts.

Oxygen and ethane partial pressures were held at 2.63 and 2.71 kPa, respectively, while the partial pressure of water vapour was altered from 0.06 to 2.11 kPa. A zero rate order with respect to water vapour partial pressure was determined.

The experimental rate of the oxygen/ethane reaction at 623 K over the manganese oxide/carbon fibre catalyst was therefore expressed by:

$$[1] \quad r = kp_{O_2}^{0.3}p_{C_2H_6}^{0.4}$$

Oxygen/1-butene

Upon exposure of the catalyst to the reaction mixture, 2.69 kPa oxygen and 3.04 kPa 1-butene, a significant amount of carbon dioxide was initially liberated at 573 K. This was related to a measure of oxidation of the carbon fibres. The rate of production decreased over 24 h to a value which remained constant for at least 24 h. The catalyst surface area after this treatment was 11.1 m^2 g^{-1}.

The partial pressure of 1-butene was altered from

TABLE 1. The effect of temperature on reaction rate constants

Oxygen/ethane		Oxygen/1-butene	
Temperature (K)	$k \times 10^{-5}$ ($mol^{0.3}\ L^{-0.3}\ m^{-2}\ s^{-1}$)	Temperature (K)	$k \times 10^{-5}$ $mol^{0.2}\ L^{-0.2}\ m^{-2}\ s^{-1}$
673	26.0	573	95.3
663	20.5	563	66.2
653	13.4	553	48.8
643	9.55	543	36.1
633	7.07	533	27.3
623	5.16	523	18.7
613	3.61	513	13.4
603	2.48	503	9.34
593	1.91	493	5.71
583	1.31	483	4.08
573	0.922	473	2.46

0.82 to 7.15 kPa and a rate order of 0.4 was obtained while the oxygen partial pressure was held at 2.46 kPa, Fig. 1.

With 1-butene partial pressure maintained at 2.68 kPa, the oxygen pressure was adjusted from 0.32 to 7.36 kPa. The rate order derived from these results was 0.4 with respect to the partial pressure of oxygen.

The partial pressures of oxygen and 1-butene were maintained at 2.61 and 2.69 kPa, respectively, and the effects of a variation from 0.50 to 9.31 kPa in carbon dioxide partial pressure were observed. The results gave a rate order of zero with respect to carbon dioxide partial pressure.

Experiments were also carried out in which the partial pressure of water vapour was adjusted from 0.09 to 2.50 kPa in the reaction mixture of 2.57 kPa oxygen and 2.81 kPa 1-butene and a zero rate order dependence on water vapour partial pressure was determined.

The experimental rate of reaction was therefore given by:

$$[2] \quad r = kp_{O_2}{}^{0.4}p_{C_4H_8}{}^{0.4}$$

Temperature effects

Oxygen/ethane

After catalyst pretreatment with 2.63 kPa oxygen and 2.76 kPa ethane at 673 K for 4 h, rate constants were calculated from the integrated form of eq. [1] at 10 K intervals from 673 K to 573 K, Table 1. The data, when plotted in the Arrhenius fashion, Fig. 2, produced an apparent activation energy of 108 ± 4 kJ mol^{-1} and a pre-exponential factor of 5.42×10^4 $mol^{0.3}\ L^{-0.3}\ m^{-2}\ s^{-1}$.

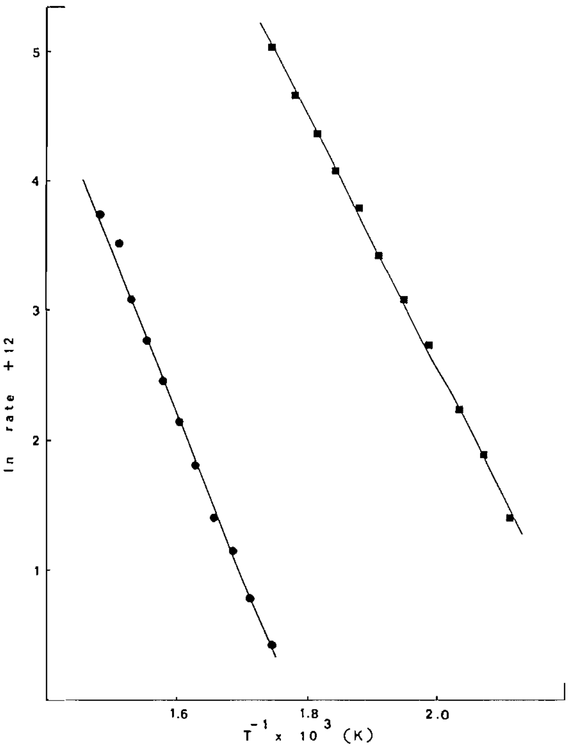

FIG. 2. Arrhenius plots for the oxygen/ethane (●) and oxygen/1-butene (■) reactions over manganese oxide/carbon fibre catalysts.

Oxygen/1-butene

The catalyst was treated at 573 K with 2.47 kPa oxygen and 2.71 kPa 1-butene for 24 h prior to kinetic studies. Rate constants, Table 1, were calculated from eq. [2] from 573 to 473 K. An apparent activation energy of 81 ± 4 kJ mol^{-1} and a pre-exponential factor of 2.16×10^4 $mol^{0.2}\ L^{-0.2}\ m^{-2}\ s^{-1}$ resulted from the Arrhenius plot, Fig. 2.

Scanning electron microscopy

The scanning electron micrographs, Fig. 3, show the effects of the oxygen/1-butene reaction at 573 K on the "Modmor" fibre supported catalyst. It

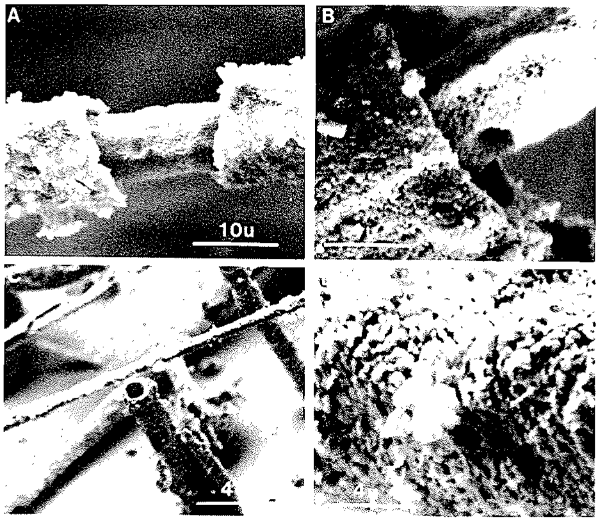

FIG. 3. Scanning electron micrographs of manganese oxide/carbon fibre catalyst after the oxygen/1-butene reaction at 573 K.

appears that the outer sheath and central core of the carbon fibre remain intact, while the radial continuum (16) has been oxidized, Fig. 3*A* and *B*. In many cases, the ends of the fibres seem hollow, Fig. 3*C*, and the fibre surface rough and pitted, Fig. 3*D*. The outer sheath of some fibres may have peeled away.

The manganese oxide particles appeared to be well dispersed on the fibre surface. Their texture resembled that observed for manganese(III) oxide catalysts in similar studies (5). The structure of the manganese oxide/carbon fibre catalyst after the oxygen/ethane reaction at 623 K was very similar to that shown in Fig. 3.

X-ray photoelectron spectroscopy

X-ray photoelectron spectra were obtained using Al K_α radiation and a 50 eV electron analyzer pass energy. Spectra were corrected for charging by reference to the C(1*s*) line at 285.0 eV. CHN analysis of pure "Modmor" gave weight percentages of 92.7 carbon, 1.5 hydrogen, 5.8 nitrogen, and 1.5 oxygen (by difference), while XPS indicated surface atomic percentages of 78 carbon, 3 nitrogen, 14 oxygen, 1 sodium, 3 sulphur, and 1 calcium. The presence of the surface impurities sodium, sulphur, and calcium indicated by XPS are difficult to rationalize and it should be noted that neither sulphur nor calcium was detected on the manganese oxide/carbon fibre catalyst after reaction.

Atomic percentages determined after the oxygen/ethane reaction at 623 K were 53 carbon, 33 oxygen, 10 manganese, and 4 sodium. After catalysis of the oxygen/1-butene reaction at 523 K, the catalyst surface contained 48% carbon, 36% oxygen, 11% manganese, and 5% sodium. The O(1*s*) spectra gave a binding energy of 529.0 eV on all samples; the Mn($2p_{3/2}$), a binding energy of 641.0 eV; the Na(1*s*), 1071 eV; and the N(1*s*) spectra on pure "Modmor" gave 400.5 eV.

The oxygen binding energy is close to that expected in metal oxides and significantly less than that usually characteristic of molecular oxygen. Although it is difficult to distinguish between manganese(II) and manganese(III) oxide by XPS alone, the spectra resemble those obtained with manganese(III) oxide catalysts (6) when both XRD and chemical analysis confirmed that the oxide was present as manganese(III) oxide in all bulk samples. If it is assumed that all manganese is associated as Mn_2O_3 then this accounts for approximately 15% oxygen and leaves remaining the amount of oxygen found on the original fibre surface. In terms of weight percentages, there is 30% manganese on the surface of the fibres, compared with 9.5% based on chemical analysis. This implies that the manganese is concentrated near the surface as was observed by scanning electron microscopy.

Discussion

The interpretation of kinetic data by the application of the extended Langmuir–Hinshelwood theory to describe possible surface mechanisms has been discussed (17–19) and the limitations inherent in methods of deriving mechanistic schemes from the correlation of statistical relationships with surface reaction models have been well analyzed (20–23). The approach is applied to the present results as a useful guide to the possible nature of the surface interactions especially when considered in conjunction with the surface analysis data.

Computer analysis of the oxygen and hydrocarbon rate order results gave only one kinetic expression of a Langmuir–Hinshelwood type which could accommodate the data. It was the same for both oxygen/ethane and oxygen/1-butene reactions:

$$[3] \quad r = \frac{ka{p_{O_2}}^{0.5} b{p_{HC}}^{0.5}(p_{O_2}p_{HC})}{(1 + a{p_{O_2}}^{0.5} + b{p_{HC}}^{0.5})^2}$$

where p_{HC} represents appropriately the partial pressure of ethane or 1-butene, while *a* and *b* are adsorption coefficients. Plots of $p^{0.5}$ against $(p^{1.5}/r)^{0.5}$ were linear, Fig. 4.

The form of eq. [3] suggests that oxygen and hydrocarbon interact initially as two adsorbed species, each adsorbed possibly on two surface sites as indicated by the square root relationships of partial pressure (24). The $(p_{O_2}p_{HC})$ term indicates

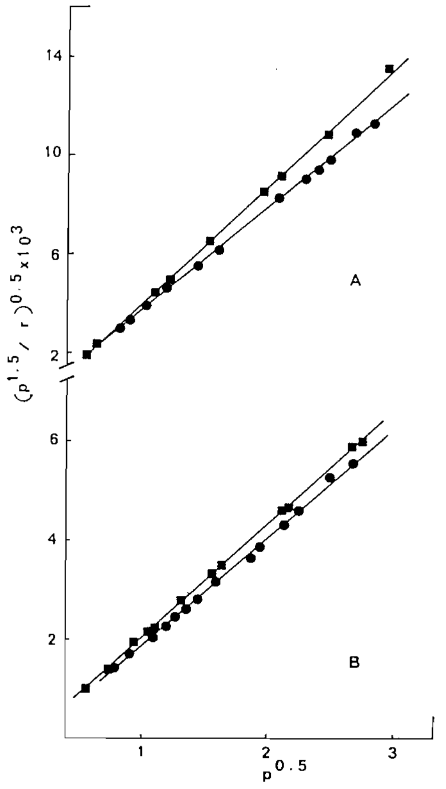

FIG. 4. Reduced plots corresponding to the Langmuir–Hinshelwood expression [3] for oxygen, ■, and hydrocarbon, ●, rate orders in the oxygen/ethane (*A*) and oxygen/1-butene (*B*) reactions over manganese oxide/carbon fibre catalysts.

that both oxygen and hydrocarbon interact in further steps within the complex overall reaction.

Evidence presented by Thomas (25) concerning ethane oxidation over nickel(II) oxide suggests that ethane was adsorbed prior to surface reaction with preadsorbed oxygen. Chemisorption of ethane was thought to involve C—H bond rupture. Yu Yao and Kummer (26) described the rate-determining step in the oxidation of ethane on nickel(II) oxide as involving the formation of a $C_2H_{5(ads)}$ species. This was believed to arise through the adsorption of ethane as C_2H_5 or by the interaction of adsorbed oxygen with gas phase or adsorbed ethane with attack at the C—H bond. In the absence of specific evidence regarding the adsorbed intermediates and based upon a Langmuir–Hinshelwood kinetic interpretation, a plausible surface reaction scheme for the oxygen/ethane reaction may be formulated:

[4] $C_2H_6 + 2S = C_2H_{6(ads)}$

[5] $O_2 + [\ \ ] + C_2H_{6(ads)} \rightarrow C_2H_{5(ads)} + [OOH]$

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

with additional reactions summarized by:

[7] $2C_2H_{5(ads)} + [O] + 6O_2 \rightarrow 4CO_2 + 5H_2O + [\ \ ] + 4S$

where S represents a surface site and [ ], a surface anion vacancy.

The square root relationships with respect to ethane and oxygen are rationalized in steps [4] and [5] respectively. Reaction [5] represents the adsorption of oxygen and interaction with adsorbed ethane to produce a surface C_2H_5 species. An additional reaction involving ethane is described by step [6] which represents dissociative adsorption. The additional and complex reactions involving oxygen are summarized in [7].

Rate constants derived for the oxygen/ethane reaction over unsupported manganese(III) oxide (6) were approximately sixteen times greater than those found in the present study under similar conditions from 573 to 593 K. The apparent activation energy determined in the earlier work, 130 kJ mol^{-1}, was somewhat higher than that here, 108 kJ mol^{-1}. Similarly, the pre-exponential factor for the reaction over unsupported manganese(III) oxide was higher, 9.72×10^7, than that obtained with the supported oxide, 5.42×10^4. Reaction rate orders with respect to oxygen and ethane were 0.5 and 0.6, respectively, for the oxygen/ethane reaction over manganese(III) oxide at 573 K, and 0.3 and 0.4 for the reaction over the present supported catalyst at 623 K. Comparison of the values for apparent activation energies and pre-exponential factors obtained for ethane oxidation over the two preparations of manganese oxide catalysts shows an isokinetic effect similar in extent to that analyzed for a number of hydrocarbon oxidation reactions over metallic oxides (27). A simple explanation of this would be that the catalytic rate of the oxygen/ethane reaction over unsupported manganese(III) oxide is higher because there are more active sites per unit area for catalysis. It appears also that the adsorption of each reactant may require two surface sites on the supported catalyst, and one only on the unsupported manganese(III) oxide (6).

A similar reaction scheme may be applicable to the oxygen/1-butene reaction:

[8] $C_4H_8 + 2S = C_4H_{8(ads)}$

[9] $O_2 + [\ \ ] + C_4H_{8(ads)} \rightarrow C_4H_{7(ads)} + [OOH]$

[10] $C_4H_8 + S + [OOH] \rightarrow C_4H_{7(ads)} + [O] + H_2O$

[11] $2C_4H_{7(ads)} + 11O_2 + [O] \rightarrow 8CO_2 + 7H_2O + [\ \ ] + 4S$

The square root relationships in eq. [3] with respect to 1-butene and oxygen are rationalized in steps [8] and [9], while the influence of the $(p_{O_2}p_{C_4H_8})$ term is apparent from [11] which represents the total stoichiometry of a number of reactions that have not been identified separately. The overall stoichiometry for both the oxygen/ethane and oxygen/1-butene reactions corresponds to that expected for complete hydrocarbon oxidation.

The value obtained for the apparent activation energy in the oxygen/1-butene reaction in the present study was only slightly lower than that determined over unsupported manganese(III) oxide (28), 81 as opposed to 88 kJ mol^{-1}. The pre-exponential factor was 2.16×10^4 for catalysis on the supported oxide and 2.94×10^5 for unsupported manganese(III) oxide. The activation energy corresponds closely to that found for the complete oxidation of ethane on both palladium (29) and nickel(II) oxide (26), and to that for the oxidation of propane over manganese(IV) oxide (30). Other comparable results may be noted elsewhere including ethylene or benzene oxidation over supported manganese(III) oxide which gave activation energies of 57 kJ mol^{-1} (31) while ethylene oxidation on copper(II) oxide yielded values from 84 to 113 kJ mol^{-1} (32).

The rate-determining step in these reactions may involve C—H bond rupture as has been postulated previously for the oxygen/ethane reaction over various catalysts (6, 25, 26). The present investigation has indicated that carbon fibres may be used as catalyst supports in deep oxidation reactions. Further studies of various impregnation techniques should be carried out with the aim of producing a higher surface area fibre support which is able to maintain mechanical strength and physical properties.

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1. E. F. McCaffrey, D. G. Klissurski, and R. A. Ross. J. Catal. **26**, 380 (1972); Can. J. Chem. **49**, 3778 (1971).
2. B. W. Krupay and R. A. Ross. Can. J. Chem. **51**, 3520 (1973).
3. B. W. Krupay and R. A. Ross. J. Catal. **39**, 369 (1975).
4. B. W. Krupay and R. A. Ross. Can. J. Chem. **56**, 10 (1978).
5. R. A. Ross and C. Fairbridge. Can. J. Chem. **59**, 2232 (1981).
6. C. Fairbridge and R. A. Ross. Can. J. Chem. **60**, 893 (1982).
7. G. H. Meguerian, A. L. Hensley, Jr., and E. P. Steigelmans, Fr. 2,072,561 (cl. B01J, C01B, F01n), 29 Oct. 1971, US Appl. 800,850, 28 Nov. 1969.
8. N. Ninomiga, H. Nishino, T. Aibe, and K. Itoga. Ger. Offen. 2,433,076 (Cl. B01D), 06 Feb. 1975, Japan Appl. 73,78,980, 12 Jul. 1973.
9. K. Fujimoto and T. Kunugi. Proc. Int. Cong. Catal., 5th. *Edited by* J. W. Hightower. North-Holland, Amsterdam. Paper No. 28 (1973).
10. I. N. Ermolenko, A. M. Safonova, R. I. Bel'skaya, G. K. Berezovik, and Ya. M. Paushkin. Vesti. Akad. Nauk Belorus. SSSR, Ser. Khim. Nauk, **6**, 20 (1974).
11. T. G. Olfer'eva, O. V. Bragin, I. N. Ermolenko, and A. M. Safonova. Kinet. Katal. **18**, 933 (1977).
12. A. Kuroda, H. Aizawa, Y. Masubuchi, G. Ishihara, S. Matsuhisa, and S. Taira. Japan. Kokai. 75, 33, 187 (Cl. 13aG02, 13aG01), 31 Jul. 1973, Appl. 73, 83,608, 26 Jul. 1973.
13. D. V. Fikis, W. J. Murphy, and R. A. Ross. Can. J. Chem. **56**, 2530 (1978).
14. C. N. Satterfield. Mass transfer in heterogeneous catalysis. M.I.T. Press. 1970.
15. A. I. Vogel. A textbook of inorganic analysis. Longmans, Green and Co., London. 1962. p. 434.
16. F. R. Barnet and M. K. Norr. US NTIS AD Rep. 1974, No. 784415/2 GA.
17. O. A. Hougen and K. M. Watson. Ind. Eng. Chem. **35**, 529 (1943).
18. K. H. Yang and O. A. Hougen. Chem. Eng. Prog. **46**, 146 (1950).
19. O. A. Hougen and K. M. Watson. Chemical process principles. Part III. Wiley, New York and London. 1966.
20. M. Boudart. AICHE J. **18**, 465 (1972).
21. M. Zdrazil. J. Catal. **31**, 313 (1973).
22. S. W. Weller. Chemical reaction engineering reviews. *Edited by* H. M. Hulbert. Am. Chem. Soc., Washington, DC. 1975.
23. L. Beranek. Catal. Rev. Sci. Eng. **16**, 1 (1977).
24. P. H. Emmett (*Editor*). Catalysis. Vol. V. Reinhold, New York. 1954.
25. W. J. Thomas. Trans. Faraday Soc. **53**, 1124 (1957); Trans. Faraday Soc. **55**, 624 (1959).
26. Y-F. Yu Yao and J. T. Kummer. J. Catal. **28**, 124 (1973).
27. A. K. Galwey. Adv. Catal. **26**, 247 (1977).
28. C. Fairbridge. Ph.D. Thesis. The University of St. Andrews, St. Andrews, Scotland. 1981.
29. C. F. Cullis and T. G. Nevell. Proc. R. Soc. London A, **349**, 523 (1976).
30. O. S. Zanevskaya, V. Ya. Vol'fson, and O. T. Chugaeva, Kinet. Katal. **10**, 8 (1973).
31. B. Dmuchovsky, M. C. Freerks, and F. B. Zienty. J. Catal. **4**, 577 (1965).
32. E. P. Koutsoukas and K. Nobe. Ind. Eng. Chem., Prod. Res. Devel. **4**, 425 (1965).