Kinetics of Reaction between Nitrogen Mono-oxide and Carbon Mono-oxide over Palladium–Alumina and Ruthenium–Alumina Catalysts

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The kinetics of reaction between CO and NO over alumina-supported palladium and ruthenium catalysts have been studied in a closed system by monitoring gas composition mass spectrometrically. Over the palladium catalyst the reaction may be represented by (i) in the range 300—450 °C (at total pressures up to *ca.* 10 kN m^{-2} and

$$\mathrm{d}p_{CO_2}/\mathrm{d}t = 2.0 \times 10^{6} \exp\,(-91.2 \pm 19\ \mathrm{kJ\ mol^{-1}}/RT)\,p_{NO}^{2}/p_{CO}\ \mathrm{molecules\ cm^{-2}\ s^{-1}} \qquad \text{(i)}$$

for p_{CO}/p_{NO} between 1 and 1.6. Over the ruthenium catalyst the rate is given by (ii) in the range 250—350 °C and

$$\mathrm{d}p_{CO_2}/\mathrm{d}t = 6.6 \times 10^{8} \exp\,(-82.4 \pm 15\ \mathrm{kJ\ mol^{-1}}/RT)\ p_{NO}^{0}\,p_{CO}^{0} \qquad \text{(ii)}$$

for p_{CO}/p_{NO} between 1 and 5. When p_{CO}/p_{NO} is greater than 5 for the ruthenium-catalyzed reaction the rate changes to $\mathrm{d}p_{CO_2}/\mathrm{d}t = kp_{NO}\,p_{CO}^{0}$. The kinetic behaviour agrees with the concept that, in the presence of CO–NO mixtures, palladium catalysts tend to favour adsorption of CO, whereas ruthenium catalysts favour adsorption of NO.

DETAILED kinetic and mechanistic studies of the reaction between nitrogen mono-oxide and carbon mono-oxide have taken on a new significance in the last few years because of the possibility of removing these gases from motor-vehicle emissions by catalytic methods. In this application the process is complicated by water vapour, hydrogen, and hydrocarbons also present in exhaust gases. Competing catalytic reactions include methanation, ammonia synthesis, and the water-gas reaction. Relative rates of these reactions and the specificity of different catalytic systems must be understood if a viable catalytic method is to be devised which fulfills the desired objective.

In this paper we compare the kinetics of the reduction of NO by CO using palladium and ruthenium supported on alumina. These metals were selected because when used as catalysts they frequently represent extreme activities for the noble metal series Pd, Pt, Rh, Ir, and Ru. When used to reduce NO by hydrogen, for instance, platinum and palladium catalysts give mainly ammonia, whereas with a ruthenium catalyst nitrogen formation is predominant.[1,2] For the reduction of NO by CO,[3] the activity sequence is Ru > Rh > Pt > Pd. In the case of the methanation reaction between CO and hydrogen,[4] the activity sequence was Ru $\gg$ Ir, Rh > Pt, Pd.

Most published studies of the kinetics of reaction between CO and NO have been made in catalytic converters using flow techniques in the presence of diluant gases such as nitrogen. The paucity of fundamental data describing the reaction of pure gases over these noble metals for conversions approaching 100% has prompted this investigation.

EXPERIMENTAL

Apparatus and Procedure.—Reactions were carried out in an electrically heated, tubular, Pyrex glass reaction vessel (450 cm^3) provided with a central thermocouple well and was similar to that previously described.[5] The reaction vessel was connected to a pre-heat chamber (257 cm^3), gas mixing chamber (86 cm^3), and to the usual vacuum-line assembly comprising manometers, gas burettes, pressure gauges, and mercury-diffusion and rotatory backing pumps.

The change in gas composition was followed during catalysis by monitoring the reaction mixture with an M. S. 10 mass spectrometer which was coupled to the reaction vessel

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[1] R. L. Klimisch and K. C. Taylor, *Environ. Sci. Technol.*, 1973, **7**, 127.

[2] M. Shelef and H. S. Gandhi, *Ind. and Eng. Chem. Product Res. and Development*, 1972, **11**, 393.

[3] T. P. Kobylinski and B. W. Taylor, *J. Catalysis*, 1974, **33**, 376.

[4] D. W. McKee, *J. Catalysis*, 1967, **8**, 240.

[5] J. D. Butler, *J. Chem. Soc.* (*B*), 1968, 905.

through a 4F grade Metrosil leak. For most purposes the increase in instrument response due to the doubly charged parent ion of carbon dioxide (*m*/*e* 22) was used to follow the reaction. Independent experiments had shown that the cracking pattern of CO_2 in the mass spectrometer gave an *m*/*e* 22 response of intensity 2% of that of the parent ion at *m*/*e* 44. In a mixture of CO_2, CO, NO, and dinitrogen oxide this ion is unique to carbon dioxide. Calibrations were also made by admitting known amounts of NO, CO, and CO_2 into the reaction vessel in the absence of the catalyst in order to establish that fractionation through the gas leak did not occur at the pressures and time durations of the present rate experiments. At the beginning of an experiment the mass spectrometer was tuned manually to the *m*/*e* 22 signal. This signal was displayed on a Servoscribe moving-pen chart recorder so that the trace obtained corresponded to the production of carbon dioxide with time from the start of an experiment. The duration of a run varied between 3 and 45 min depending on temperature, gas composition, and quantity of catalyst employed.

Analysis of Data.—Experimental points from the chart trace were fed into a Digico Micro 16S computer programmed for a polynomial fit to six coefficients of the equation $t = \sum_{i=0}^{i=5} a_i x_i$, where x is the pressure of product at time t. The initial rate and time course of the reaction were obtained from the computer output which listed (*a*) the six coefficients, (*b*) the calculated pressure of product, (*c*) the rate of formation of product, (*d*) the logarithm of the rate of formation of product, and (*e*) the logarithm of the amount of unchanged reactant which was present in least concentration. Computed pressures fitted the experimental data within a standard deviation of ±0.6.

Catalysts.—Catalysts were prepared by impregnation of γ-alumina (8/16 mesh size, Fisons Ltd), with appropriate solutions of noble metal chloride (B.D.H.). Before impregnation, γ-alumina was treated with a stream of hydrogen (40 cm^3 min^{-1}) at 450 °C until hydrogen sulphide could no longer be detected in the effluant gas stream with lead acetate. Purified γ-alumina was treated with either a solution of palladium(II) chloride or ruthenium(III) chloride to give 0.5% w/w of the metal after drying and reduction in hydrogen at 450 °C.

Surface areas were determined by the BET method at liquid-nitrogen temperatures. The palladium–alumina and ruthenium–alumina catalysts used in this investigation had surface areas of 1.58×10^5 and 2.30×10^5 m^2 kg^{-1}, respectively. Between 0.1 and 0.6 g of catalyst gave convenient reaction rates for the temperatures and pressures used.

Materials.—Gases used were of lecture bottle quality from B.O.C. Nitrogen mono-oxide was purified by freeze–pump–thaw treatment using liquid nitrogen. Carbon mono-oxide was used without further purification.

RESULTS

Initial experiments showed that homogeneous reaction between CO and NO did not occur at 450 °C.

Palladium–Alumina Catalyst.—Figures 1 and 2 show logarithmic plots of initial rate against initial pressure of NO for a constant pressure of CO of 5.1 kN m^{-2}, and of initial rate against initial pressure of CO for a constant NO pressure of 5.1 kN m^{-2}. From the gradients of these plots the order of reaction at 400 °C was found to be two with respect to p_{NO} and −1 with respect to p_{CO}. Initial-rate data indicate, therefore, that under reducing conditions with excess of CO and NO pressures in the range 2—5 kN m^{-2} the rate law (1) is obeyed. The integrated form of this

$$\mathrm{d}p_{CO_2}/\mathrm{d}t = kp_{NO}^2/p_{CO} \tag{1}$$

equation is (2) where a and b represent initial pressures of

$$\frac{x(a-b)}{b(b-x)} + \ln\frac{b}{b-x} = kt \tag{2}$$

CO and NO, respectively, and x is the pressure of CO_2 at time t, and was used to test the validity of the rate law.

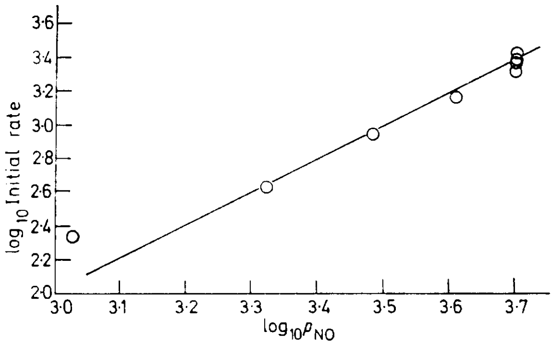

FIGURE 1 Plot of log initial rate against log initial pressure of NO, for the reduction of NO by CO over 0.5% w/w Pd–Al_2O_3 (0.21 g) at 400 °C. The CO pressure was held constant at 5.1 kN m^{-2}. The gradient of the plot is 2

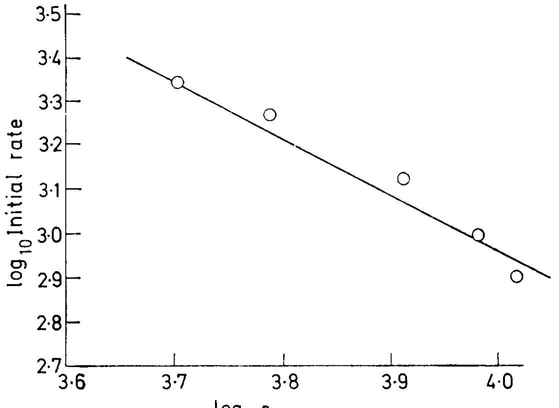

FIGURE 2 Plot of log initial rate against log initial pressure of CO, for reaction catalyzed by 0.5% w/w Pd–Al_2O_3 (0.21 g) at 400 °C. The NO pressure was held constant at 5.1 kN m^{-2}. The gradient of the plot is −1

Confirmation was obtained from linear plots of equation (2) for over 80% completion of reaction for CO pressures of 5.1 kN m^{-2} and NO pressures in the range 3.1—5.1 kN m^{-2}. For 1 : 1 stoicheiometric mixtures of CO to NO the equation predicts that first-order kinetics will be found. This was confirmed and this form of the equation has been used to determine the reaction rate constants in the temperature range 300—450 °C for equal pressures of CO and NO of 5.0 kN m^{-2}. An Arrhenius plot of this data (Figure 3) gave an activation energy of 91.2 ± 12 kJ mol^{-1}.

A few experiments were made with NO pressures greater than those required for stoicheiometry. As reported previously,[6] N_2O and CO_2 were produced under these

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[6] M. Shelef, K. Otto, and H. S. Gandhi, *J. Catalysis*, 1968, **12**, 361.

conditions. Since N_2O was not detected in the absence of CO, we conclude that decomposition of NO alone is not responsible. Carbon mono-oxide must participate mechanistically in the formation of N_2O. Detailed kinetic analysis in this pressure range was not attempted.

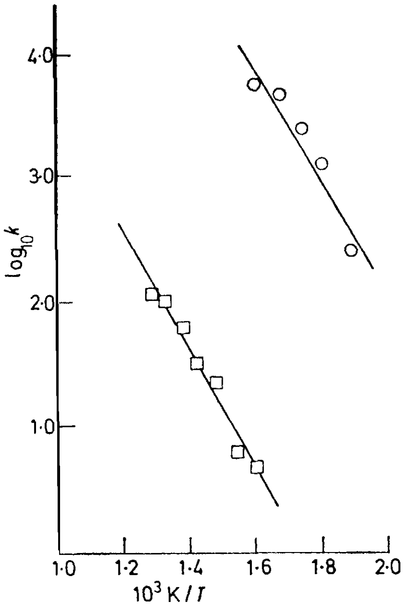

FIGURE 3 Arrhenius plots for the reduction of NO by CO over 0.5% w/w $Pd-Al_2O_3$ (□) and over 0.5% $Ru-Al_2O_3$ (○)

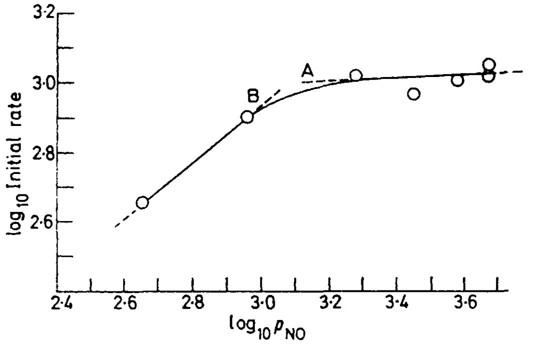

FIGURE 4 Plot of log initial rate against initial pressure of NO, for reaction catalyzed by 0.5% w/w $Ru-Al_2O_3$ (0.59 g) at 275 °C. The CO pressure was held constant at 4.6 kN m^{-2}. Gradient A = 0.04; B = 0.8

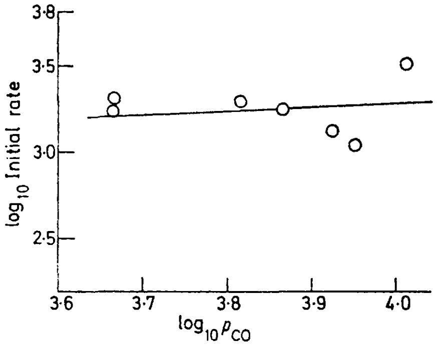

FIGURE 5 Plot of log initial rate against log initial pressure of CO, for reaction catalyzed by 0.5% w/w $Ru-Al_2O_3$ (0.59 g) at 275 °C. The NO pressure was held constant at 4.6 kN m^{-2}

Ruthenium–Alumina Catalyst.—Figures 4 and 5 show logarithmic plots of initial rates against initial pressures of NO and CO, respectively. As in the case of the palladium–alumina catalyst, these experiments were made with excess of CO. The results in Figure 4 indicate that at 275 °C a change in order occurs. Portion A represents a pressure range between 1.0 and 4.7 kN m^{-2} and portion B pressures of NO below 1.0 kN m^{-2}. The gradients of these two regions show that in region A the order with respect to p_{NO} approaches zero, and in region B the order becomes one. Figure 5 shows that a wide scatter occurs when attempting to find the dependence on p_{CO}. This was typical and despite repeated efforts no strong dependence on p_{CO} was discernible. The line of best fit through the experimental points given in Figure 5 indicates an order of 0.22 ± 0.12 for the reaction with respect to p_{CO}. These results, together with the pressure limits employed, are summarized in the Table. In region A the Table shows that the reaction approximates to zero order with respect to the pressures of both reactants. This was confirmed by the plot shown in Figure 7 where the zero-order relation is shown to hold for over 85% completion of the reaction for NO pressures in the range 1.9—4.6 kN m^{-2}. An activation energy of 82.4 ± 15 kJ mol^{-1} was found in this zero-order region between 250 and 350 °C (Figure 3). At pressures of less than 0.9 kN m^{-2} of NO (region B), Figure 4 indicates that a change in reaction order with respect to NO occurs. The gradient of the plot in region B suggests that this order approaches unity with respect to p_{NO}. The results of another series of experiments in which the logarithm of the rate of formation of CO_2 is plotted against the logarithm of unchanged NO are shown in Figure 6. Curve (*a*) of this plot corresponds to stoicheiometric pressures of CO and NO of 5.1 kN m^{-2},

Summary of reaction orders found for the reaction between CO and NO over 0.59 g of 0.5% $Ru-Al_2O_3$ catalyst at 275 °C

Pressure limit kN m^{-2}	Pressure of gas kept constant kN m^{-2}	Order with respect to NO	CO
CO 4.7—13.3	NO 4.7		0.22 ±0.12
(A) NO 4.7—0.9	CO 4.7	0	0.22 ±0.12
(B) NO 0.9—0.4	CO 4.7	*ca.* ~1	0.22 ±0.12

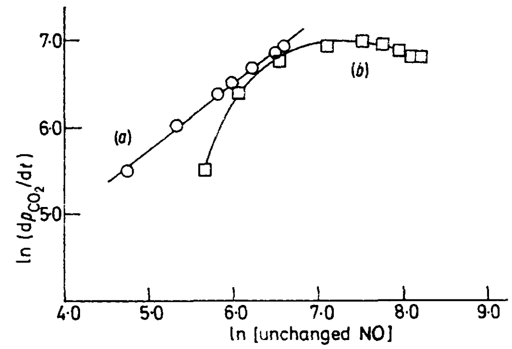

FIGURE 6 Plot of ln rate against ln unchanged NO over 0.5% w/w $Ru-Al_2O_3$ (0.59 g) at 275 °C, for (*a*) $p_{CO} = p_{NO}$ = 5.1 kN m^{-2}, and (*b*) p_{CO} = 5.1 kN m^{-2} and p_{NO} = 930 N m^{-2}

and curve (*b*) to pressures falling in the region B, *viz.* CO pressure 5.1 kN m^{-2} and NO pressure 930 N m^{-2}. Plot (*b*) of Figure 6 has a gradient of 0.8. This evidence indicates that at these NO pressures the rate law can be expressed by equation (3) where the order with respect to p_{NO} has

$$dp_{CO_2}/dt = kp_{NO}\,p_{CO}^{0} \qquad (3)$$

been taken to the nearest whole number. Figure 8 shows that a good linear plot for *ca.* 90% completion of the reaction was obtained on the assumption that the reaction was first order with respect to p_{NO}.

In contrast to the palladium–alumina catalyst, the ruthenium–alumina system did not produce detectable quantities of N_2O when excess of NO was present in the reaction mixture. Although the kinetics were not studied under these conditions, we did establish that, unlike palladium, the ruthenium catalyst did decompose N_2O at temperatures as low as 300 °C and that a first-order rate law was obeyed.

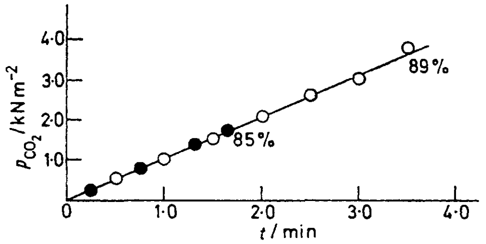

FIGURE 7 Zero-order plot for reaction catalyzed by 0.5% w/w Ru–Al_2O_3 (0.59 g) at 275 °C. The CO pressure was held constant at 4.6 kN m^{-2}. The initial pressures of NO were 1.9 (●) or 4.6 kN m^{-2} (○) respectively

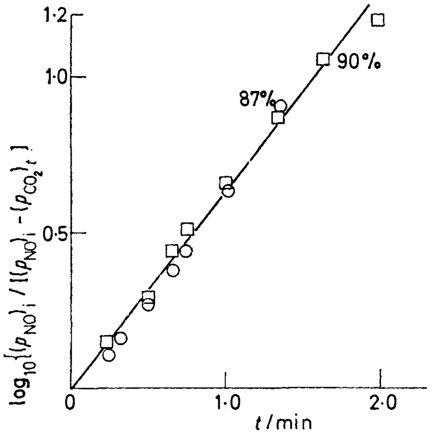

FIGURE 8 First-order plot for reaction catalyzed by 0.5% w/w Ru–Al_2O_3 (0.59 g) at 275 °C. The CO pressure was held constant at 4.6 kN m^{-2}. The initial pressures of NO were 933 (○) and 400 N m^{-2} (□) respectively

DISCUSSION

Palladium–Alumina catalyst.—The empirical rate law (1) in which the production of carbon dioxide is inversely proportional to p_{CO} implies a high surface coverage by CO. This result is consistent with that of Taylor and Klimisch [7] who also observed that the reduction of NO by CO over palladium–alumina was inhibited by CO. The classical i.r. study of Eischens *et al.*[8] on palladium–carbon mono-oxide surface interactions, together with the later work by Palazov *et al.*,[9] has established that CO is readily adsorbed by palladium. Adsorption of NO by palladium, on the other hand, also occurs but is known to be weaker.[10] In the presence of both gases, Unland [10] showed by i.r. studies that when CO is in excess isocyanate species are formed on palladium–alumina surfaces. Ruthenium supported on alumina also forms surface isocyanates although less readily.

This evidence indicates that during reaction under the conditions of excess of CO that we have employed, the catalyst surface is largely covered by CO. The second-order dependence on p_{NO} suggests that two NO molecules are associated with one adsorption site as in (4). Furthermore,

$$2NO + S \longrightarrow S\text{–}(NO)_2 \qquad (4)$$

the kinetics imply that the surface coverage by NO is low, as indeed would be expected for a surface mainly covered by CO. Although i.r. studies have indicated the possibility of NO being adsorbed as a dimer,[11–13] this seems unlikely at catalytic temperatures. A more reasonable route would be a rapid reaction between adjacently adsorbed molecules of CO and NO to give carbon dioxide and an adsorbed nitrogen atom [equation (5)]. Rapid reaction [equation (6)] of the adsorbed nitrogen atom with another molecule of NO would account for the second-order rate law with respect to p_{NO}. The fate of adsorbed N_2O will be dependent on

$$S\text{–}CO + S\text{–}NO \longrightarrow \underset{\underset{S\,+\,CO_2}{\Updownarrow}}{S\text{–}CO_2} + S\text{–}N \qquad (5)$$

$$S\text{–}N + NO \longrightarrow S\text{–}N_2O \qquad (6)$$

the extent of surface covered by carbon monoxide, θ_{CO}. A surface covered by CO will reflect a high probability that this adsorbed N_2O will react with an adjacently adsorbed CO molecule to produce carbon dioxide and nitrogen [equation (7)]. When less CO exists in the system, so that θ_{CO} no longer approaches unity, N_2O may desorb from the surface as a product.

$$S\text{–}N_2O + OC\text{–}S \rightleftharpoons \underset{\underset{S\,+\,N_2}{\Updownarrow}}{S\text{–}N_2} + \underset{\underset{S\,+\,CO_2}{\Updownarrow}}{S\text{–}CO_2} \qquad (7)$$

The scheme outlined will account for the formation of surface isocyanate if adsorbed atomic nitrogen reacts with CO rather than NO [equation (8)]. Surface isocyanates

$$S\text{–}N + CO \longrightarrow S\text{–}NCO \qquad (8)$$

are only formed under reducing conditions when excess of CO is present.

Ruthenium–Alumina Catalyst.—Both CO and NO are

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[7] K. C. Taylor and R. L. Klimisch, *J. Catalysis*, 1973, **30**, 478.

[8] R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.*, 1956, **60**, 194.

[9] A. Palazov, C. C. Chang, and R. J. Kokes, *J. Catalysis*, 1975, **36**, 338.

[10] M. L. Unland, *J. Catalysis*, 1973, **31**, 459.

[11] J. B. Peri, *J. Phys. Chem.*, 1974, **78**, 588.

[12] E. L. Kugler and R. J. Kokes, *J. Catalysis*, 1975, **36**, 142.

[13] E. L. Kugler and J. W. Gryder, *J. Catalysis*, 1975, **36**, 152.

considered to be strongly adsorbed on ruthenium, particularly when the surface is in a reduced condition.[4,14] At 275 °C, the predominant form of NO adsorption on ruthenium is molecular and at 350 °C or above dissociative adsorption occurs.[15] From the rate laws given in the Table, it appears that NO is more strongly adsorbed than CO. For reaction mixtures up to a 5 : 1 ratio of CO to NO (region A), a zero and a fractional order obtain for p_{CO} and p_{NO}. This result indicates that, even though the reaction has been carried out in excess of CO, NO can still compete effectively for the available surface sites. Only when the composition of the reaction mixture exceeds the 5 : 1 ratio does the order with respect to p_{NO} tend to one (region B).

Voorhoeve and Trimble [16] showed that a catalyst of ruthenium supported on alumina can have different states with characteristic conversion patterns in the reduction of NO with a mixture of CO and hydrogen. This work showed that in the reduced state the ruthenium catalyst produced high yields of ammonia, whereas in the oxidized condition only low conversions to ammonia occur. A correlation between the reduced state and the formation of surface isocyanates has been suggested by Unland.[10] He found that isocyanates could be formed on freshly prepared ruthenium samples but not on aged samples. Freshly prepared ruthenium behaves like palladium and produces ammonia. Aged ruthenium, on the other hand, does not form ammonia or isocyanate but favours the formation of molecular nitrogen.

This concept is in accord with our kinetic study if we consider that the catalyst used was in the aged, probably oxidized, state. Selectivity for nitrogen formation may readily be appreciated if adsorption of NO is favoured even in the presence of excess of CO. Then relative surface coverage will produce a high probability of NO molecules adsorbed on adjacent sites. This proximity of NO molecules will ensure selectivity for formation of molecular rather than atomic nitrogen on severance of nitrogen–oxygen bonds. Although not completely conclusive, we do not think that this bond-rupture stage occurs during adsorption of NO because a half-order pressure dependence indicative of dissociative adsorption was not found. Our evidence suggests that bond-rupture is induced by CO either in a one- or two-stage process which involves transient N_2O or accommodation of oxygen in the surface layer of the catalyst. Both these possibilities are in agreement with the known properties of ruthenium which may be contrasted with those of palladium. In the former instance N_2O is decomposed by ruthenium but not palladium at these temperatures, and in the latter ruthenium is less noble than palladium towards oxygen. This aspect of N_2O decomposition and reaction with CO over these catalysts will be the subject of a separate investigation.

[6/734 *Received*, 14*th April*, 1976]

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[14] M. Kobayashi and T. Shirasaki, *J. Catalysis*, 1974, **32**, 254.

[15] H. P. Bonzel and T. E. Fischer, *Surface Sci.*, 1975, **51**, 213.

[16] R. J. H. Voorhoeve and L. E. Trimble, *J. Catalysis*, 1975, **38**, 80.