

Kinetics of N₂O Decomposition on the Surface of γ -Al₂O₃ doped with Sodium Ions

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The kinetics of N₂O decomposition on a series of specimens prepared by doping γ -Al₂O₃ with various amounts of Na⁺ ions has been studied at various temperatures using a flow-bed reactor working under atmospheric pressure. This doping promotes the adsorption of oxygen anions produced from surface decomposition, presumably *via* the formation of surface species [Na⁺ ··· O⁻ ··· Na⁺], bringing about a transformation of the rate equation from $R = k$ into $R = kb_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}}/b_{\text{O}_2}^{\frac{1}{2}}P_{\text{O}_2}^{\frac{1}{2}}$ (where $b_{\text{N}_2\text{O}}$ and b_{O_2} are adsorption coefficients and $P_{\text{N}_2\text{O}}$ and P_{O_2} are partial pressures). Moreover, a decrease in catalytic activity, expressed either as fractional conversion or rate of reaction, was observed on increasing the surface coverage C , of γ -Al₂O₃ with Na⁺ ions determined by X-ray photoelectron spectroscopy. Specifically, the dependence of the catalytic activity on the surface coverage of γ -Al₂O₃ is described by the relationship $\ln(1/R) = 15.4 + (281/K)C$ (where K is a proportionality constant) and it was concluded that the deactivation observed is due to the promotion of the O₂ adsorption caused by the Na⁺ ions. Finally, the linear dependence of the surface coverage of γ -Al₂O₃ on the sodium content strongly suggests that the dispersion of the sodium supported species is constant irrespective of the surface concentration of sodium.

The decomposition of nitrous oxide has been extensively used as a probe reaction for studying many catalytic systems based on aluminas, such as solid solutions and supported metal-oxide catalysts.^{1–6} In most cases interest was focussed on the relationship between the nature of the active ion (its symmetry, valence, concentration *etc.*), which is a transition-metal cation, and the catalytic activity. Moreover, the elucidation of the mechanism of the title reaction, by performing detailed kinetics, helps establish relationships between the nature of the active phase and the kinetic parameters involved in the surface process. However, in the above-mentioned studies the possibility that impurities in the alumina, the most important of which are sodium ions, could influence its activity, and the kinetic law of N₂O decomposition has been completely disregarded. This possibility, at least concerning Na⁺ ions, must not be considered negligible because it has been recently observed that Li⁺ ions, like Na⁺ ions, considerably influence both the activity of Fe₂O₃/Al₂O₃ catalysts and the kinetics of N₂O decomposition.⁷

The purpose of the present work is to study the influence of sodium ions on the catalytic behaviour of alumina. This is attempted by studying the kinetics of N₂O decomposition on the surface of a series of specimens prepared by doping alumina with various amounts of sodium ions.

Kinetic experiments at various temperatures were performed using a flow-bed reactor working under atmospheric pressure. In addition X-ray photoelectron spectroscopy (X.p.s.) and specific surface area (B.E.T.) measurements were carried out to characterize the specimens used.

Experimental

Preparation of the Specimens

The doping of alumina (γ -Al₂O₃, Houdry Ho 415, 100–150 mesh) with various amounts of Na⁺ ions was performed by pore-volume impregnation with aqueous solutions of NaNO₃ [Merck p.a.] followed by drying at 110 °C for 2.5 h and air-calcination at 600 °C for 12 h.

Reference to the specimens prepared will be made using the formula Na-*X*-Al₂O₃, where *X* denotes the Na⁺ content in mmol g⁻¹ Al₂O₃ (*X*: 0.226, 0.309, 0.392 and 0.621). The sodium in the specimen with *X* = 0.226, which was prepared by impregnation with pure solvent (distilled water), originates from the γ -Al₂O₃ used.

X-Ray Photoelectron Spectroscopy

The surface of the catalyst was characterized by X.p.s. The X.p.s. spectra were recorded using a Vacuum Generators ESCA 3 spectrometer equipped with an aluminium anode [Al *K* α = 1486.6 eV] operating at 20 mA and 14 kV. The residual pressure inside the spectrometer was *ca.* 10⁻⁹ Torr.[†] All the X.p. spectra presented a small C(1s) contamination peak to which a binding energy of 285 eV was assigned. This peak served as a reference for determining the binding energies of all other peaks in the spectra.

The surface coverage of γ -Al₂O₃ by Na⁺ ions, denoted by *C*, is defined as the ratio of the surface area covered by the supported ion, *s*, to the total surface area, *S*:

$$C = s/S \quad (1a)$$

Moreover, the dispersion of the supported Na⁺, denoted by *D*, is defined as the ratio of the surface area to the amount of supported Na⁺:

$$D = s/X \quad (1b)$$

On the other hand, in a recent publication⁸ it was demonstrated that the dispersion of the Na⁺ ions is given by the following relationship:

$$D = [(I_{\text{Na}(1s)}/I_{\text{Al}(2p)}) (\text{Al}/\text{Na})] K \quad (1c)$$

where $I_{\text{Na}(1s)}/I_{\text{Al}(2p)}$ is the true intensity ratio of the X.p.s. signals from the Na(1s) and Al(2p) photoelectrons, Al/Na denotes the atomic ratio of these elements and *K* is a proportionality constant. By combining the above relationships the following equation is derived:

$$C = K \frac{X [I_{\text{Na}(1s)}/I_{\text{Al}(2p)}] [\text{Al}/\text{Na}]}{S} \quad (1d)$$

Surface Area and Pore Volume Determination

The specific surface areas of the samples studied were determined by the B.E.T. method. The experimental details were described in a previous paper.⁹ The total pore volume of the specimens studied was determined by measuring the amount of water necessary for filling the pores.

Catalytic Tests

The catalytic tests were carried out in a plug-flow reactor working under atmospheric pressure. The catalyst sample, 400 mg, was placed on a perforated-glass bed occupying a volume of *ca.* 0.35 cm³ and having a depth of 0.2 cm. A mixture of He and N₂O was

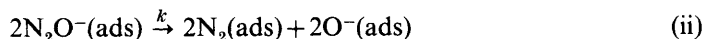
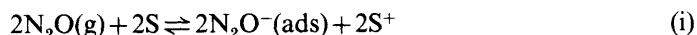
[†] 1 Torr = 101 325/760 Pa.

passed through the bed at a rate of $180 \pm 5 \text{ cm}^3 \text{ min}^{-1}$. Of this mixture two-thirds was He and one-third was N_2O . Under these conditions the contact time corresponds to 0.12 s.

A Varian 3700 gas chromatograph equipped with a thermal conductivity detector was used to analyse both reactants and products. Two gas valves with 1 cm^3 loops were used for sampling. The column (dimensions $0.5 \text{ m} \times \frac{1}{8}$ in i.d.) was of stainless steel and filled with molecular sieve 5A. Preliminary tests showed that no decomposition took place up to a temperature of $700 \text{ }^\circ\text{C}$ in the reactor without catalyst. The temperature range examined was from 525 to $625 \text{ }^\circ\text{C}$.

Determination of the Kinetic Laws

The conventional description of the whole process on the surface of most oxides and solid solutions includes the following steps:^{1-4, 6, 7, 10-16}



Here S represents a surface site.

The rate of the surface reaction depicted by step (ii) can be described by the following equation:

$$R = \frac{d[\text{N}_2\text{O}^-(\text{ads})]}{dt} = k\Theta_{\text{N}_2\text{O}^-(\text{ads})} \quad (2)$$

where R represents the reaction rate, k is the intrinsic rate constant and $\Theta_{\text{N}_2\text{O}^-(\text{ads})}$ is the fraction of catalytically active sites on the surface occupied by N_2O . Provided that the adsorption of the reactant, products and carrier gas follow a Langmuir type isotherm, $\theta_{\text{N}_2\text{O}^-(\text{ads})}$ is given by

$$\Theta_{\text{N}_2\text{O}^-(\text{ads})} = \frac{b_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}}}{1 + b_{\text{He}}P_{\text{He}} + b_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}} + b_{\text{N}_2}P_{\text{N}_2} + b_{\text{O}_2}^{\frac{1}{2}}P_{\text{O}_2}^{\frac{1}{2}}} \quad (3)$$

where b_{He} , $b_{\text{N}_2\text{O}}$, b_{N_2} and b_{O_2} represent the adsorption coefficients and P_{He} , $P_{\text{N}_2\text{O}}$, P_{N_2} and P_{O_2} the partial pressures of these components in the reaction mixture. Since adsorption of He and N_2 is generally accepted to be negligible, the products $b_{\text{He}}P_{\text{He}}$ and $b_{\text{N}_2}P_{\text{N}_2}$ in the denominator of the right-hand side of eqn (3) can be neglected. Thus eqn (3) is reduced to

$$\Theta_{\text{N}_2\text{O}^-(\text{ads})} = \frac{b_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}}}{1 + b_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}} + b_{\text{O}_2}^{\frac{1}{2}}P_{\text{O}_2}^{\frac{1}{2}}}. \quad (4)$$

According to the magnitude of adsorption of the N_2O^- and O^- on the surface of the catalysts the following extreme cases may be considered: (i) weak adsorption of both N_2O^- and O^- , (ii) strong adsorption of N_2O^- and weak adsorption of O^- , (iii) strong adsorption of O^- and weak adsorption of N_2O^- . For each case eqn (4) is reduced to a certain simpler equation. By combining each of the resulting equations with eqn (2), we derive the following kinetic equations corresponding to the above-mentioned cases:

$$\text{(i)} \quad R = kb_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}} \quad (5)$$

$$\text{(ii)} \quad R = k \quad (6)$$

$$\text{(iii)} \quad R = \frac{kb_{\text{N}_2\text{O}}P_{\text{N}_2\text{O}}}{b_{\text{O}_2}^{\frac{1}{2}}P_{\text{O}_2}^{\frac{1}{2}}}. \quad (7)$$

Taking into account the stoichiometry of the reaction, the fact that under our experimental conditions the total pressure in the stream is equal to $3P_{N_2O}^o$ (where $P_{N_2O}^o$ is the partial pressure of N₂O in the feed) and the molar ratio of He to N₂O = 2, we derive the following relationships between the partial pressures P_{N_2O} and P_{O_2} in the reaction mixture and the degree of conversion:

$$P_{N_2O} = 6P_{N_2O}^o \frac{1-x}{6+x} \quad (8)$$

$$P_{O_2} = 3P_{N_2O}^o \frac{x}{6+x}. \quad (9)$$

The kinetic equations (5) and (7) are transformed into eqn (10) and (11) by substitution of P_{N_2O} and P_{O_2} from eqn (8) and (9):

$$(i) \quad R = kb_{N_2O} \frac{6P_{N_2O}^o(1-x)}{6+x} \quad (10)$$

$$(iii) \quad R = \frac{3.46kb_{N_2O}P_{N_2O}^{o\frac{1}{2}}}{b_{O_2}^{\frac{1}{2}}} \frac{1-x}{(6x+x^2)^{\frac{1}{2}}}. \quad (11)$$

The kinetic results are analysed using the well known equation of the plug-flow reactor:

$$F dx = R dS \quad (12)$$

where F is the reactor feed in N₂O (mol s⁻¹) and S the surface area of the catalyst used (m²). Substitution of the rate obtained from eqn (6), (10) and (11) into eqn (12) and integration of the resulting relationships gives the expressions (13), (14) and (15), respectively:

$$(i) \quad -[7 \ln(|1-x|) + x] = k \frac{6P_{N_2O}^o S b_{N_2O}}{F} \quad (13)$$

$$(ii) \quad x = k S / F \quad (14)$$

$$(iii) \quad 4 \ln \{ [2[x(6+x)]^{\frac{1}{2}} - 2x - 6] \} + \sqrt{7} \ln \left(\left| \frac{2[7x(6+x)]^{\frac{1}{2}} + 8x + 6}{1-x} \right| \right) - \{ [x(6+x)]^{\frac{1}{2}} - 11.91 \} = k \frac{b_{N_2O}}{b_{O_2}^{\frac{1}{2}}} \frac{3.46 P_{N_2O}^{o\frac{1}{2}} S}{F}. \quad (15)$$

The following well known relationships are valid for both N₂O and O₂:

$$b \equiv k^a / k^d$$

$$k^a = A^a \exp(-E^a / RT)$$

$$k^d = A^d \exp(-E^d / RT)$$

$$\Delta H^a = E^a - E^d$$

$$k = A \exp(-E_{a(t)} / RT)$$

$$E_{a(a)} = E_{a(t)} + \Delta H_{N_2O}^a$$

where (k^a , E^a , A^a) and (k^d , E^d and A^d) are the Arrhenius parameters for adsorption and desorption respectively, ΔH^a is the heat of adsorption and $E_{a(t)}$ and $E_{a(a)}$ are the true

and apparent activation energies of reaction, respectively. Using these relationships we can rearrange eqn (13), (14) and (15) into the expressions (16), (17) and (18), respectively:

$$(i) \quad (i) \quad \ln[-7 \ln(|1-x|) + x] = \ln\left(\frac{6P_{N_2O}^0 SAA_{N_2O}^a}{FA_{N_2O}^d}\right) - \frac{E_{a(a)}}{R} \frac{1}{T} \quad (16)$$

$$(ii) \quad \ln x = \ln \frac{AS}{F} - \frac{E_{a(t)}}{R} \frac{1}{T} \quad (17)$$

$$(iii) \quad \ln \left[4 \ln \{ [2[x(6+x)]^{\frac{1}{2}} - 2x - 6] \} + \sqrt{7} \ln \left(\left| \frac{2[7x(6+x)]^{\frac{1}{2}} + 8x + 6}{1-x} \right| \right) - x(6+x) - 11.91 \right] \\ = \ln \left[\frac{3.46 P_{N_2O}^0 SAA_{N_2O}^a}{A_{N_2O}^d F} \left(\frac{A_{O_2}^d}{A_{O_2}^a} \right)^{\frac{1}{2}} \right] - \frac{E_{a(a)} - (\Delta H_{O_2}^a/2)}{R} \frac{1}{T} \quad (18)$$

To decide which of the above models describes more satisfactorily the experimental data, plots of the left-hand side of eqn (15)–(17) *vs.* $1/T$ were constructed, and the standard errors of the slope and intercept as well as the correlation coefficients were determined. The model selected for each catalyst had the minimum percentage standard error in both the slope and intercept as well as the maximum correlation coefficient. The above procedure was performed using a BBC microcomputer.

Results and Discussion

Fig. 1 illustrates the variation with sodium content of the surface coverage of $\gamma\text{-Al}_2\text{O}_3$ and the specific surface area of the specimens studied. The specific surface area remains practically constant, whereas the surface coverage increases with the X . The lack of variation in the specific surface area suggests that the sodium doping does not provoke any considerable change in the $\gamma\text{-Al}_2\text{O}_3$ texture. This is corroborated by the values determined for the total pore volume. In fact, the total pore volume remains practically constant ($0.50 \pm 0.02 \text{ cm}^3 \text{ g}^{-1}$) irrespective of the Na^+ content.

The linear increase of the surface coverage of $\gamma\text{-Al}_2\text{O}_3$ with the concentration of deposited sodium demonstrates that the size of the crystallites of the supported Na species is constant irrespective of the sodium content. Furthermore, the slightly lower value of the surface coverage obtained for the sample with $X = 0.226$ compared to that predicted by the straight line simply reflects the fact that the repartition of the deposited Na^+ ions along the radius of an alumina grain favours the surface of the grain rather than the more uniform microdistribution of the Na^+ ions resulting from the original material used (undoped $\gamma\text{-Al}_2\text{O}_3$).

At this point it must be emphasized that the quantities C/K and X plotted in fig. 1 have been determined experimentally. According to the literature¹⁷ the deposited Na^+ ions can diffuse into the $\gamma\text{-Al}_2\text{O}_3$ lattice during calcination, neutralize the surface hydroxyls, forming $=\text{Al}-\text{O}-\text{Na}$ surface groups, and form islands of Na^+ compounds supported on the $\gamma\text{-Al}_2\text{O}_3$ surface. These islands are aggregates of sodium, *e.g.* NaNO_3 and NaNO_2 , or tridimensional compounds between Na and Al, *e.g.* $\text{Na}_2\text{Al}_2\text{O}_4$. In most cases these compounds are poorly defined by X-ray analysis, presumably because of their low concentration and/or their poor crystallinity. The relative extent of the above-mentioned surface processes depends on the concentration of sodium and the calcination temperature. The relatively low sodium concentration and temperature at which the specimens were calcined favour the neutralization of the surface hydroxyls.

Table 1 illustrates the models which follow from N_2O decomposition on the surface of the specimens examined. The experimental data are fitted better by model (ii) in the case of the undoped support, thus suggesting a zero-order kinetic law. This behaviour implies strong adsorption of N_2O and weak adsorption of oxygen. The doping of $\gamma\text{-Al}_2\text{O}_3$ with Na^+ ions causes a transformation of the model from (ii) to (iii).

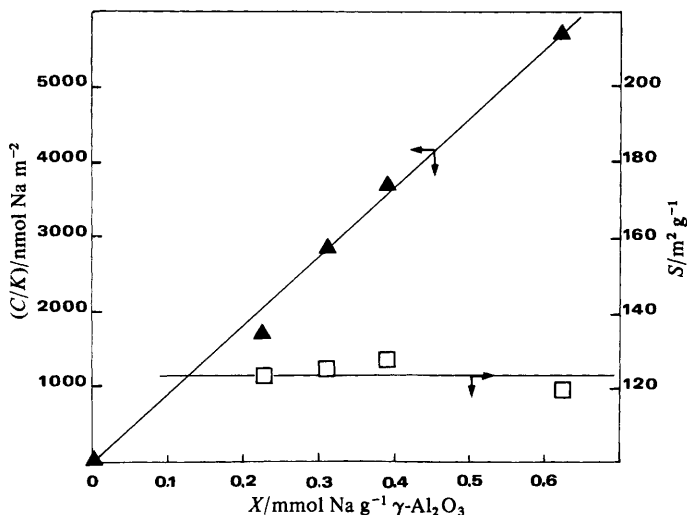


Fig. 1. Variation of the surface coverage, C , of γ -Al₂O₃ (\blacktriangle) and the specific surface area, S , of the specimens studied (\square) with the sodium content.

Table 1. Model selection

sample	model
Na-0.226-Al ₂ O ₃	(ii)
Na-0.309-Al ₂ O ₃	(iii)
Na-0.392-Al ₂ O ₃	(iii)
Na-0.621-Al ₂ O ₃	(iii)

The change in the kinetic law may suggest: (i) promotion of O₂ adsorption or (ii) promotion of N₂O adsorption but much stronger promotion of O₂ adsorption. In view of the fact that both N₂O and O₂ are retained on the surface as negative ions the second suggestion seems more realistic.

The catalytic activity, expressed as fractional conversion, is illustrated in table 2. One observes a continuous drop in activity with increasing dopant content. Moreover, fig. 2 shows the dependence of the rate of the N₂O decomposition, determined at a typical temperature (575 °C), on the surface coverage of γ -Al₂O₃ with Na⁺ ions. This rate has been calculated using the relation $Fx = RS$ resulting from eqn (12), for values of conversion lower than 0.15, where the reactor could be considered as a differential one. An inspection of fig. 2 shows that a good correlation is obtained between $\ln(1/R)$ and the surface coverage, C . This correlation is described by the following empirical relationship:

$$\ln(1/R) = 15.4 + 281 C/K \quad (19)$$

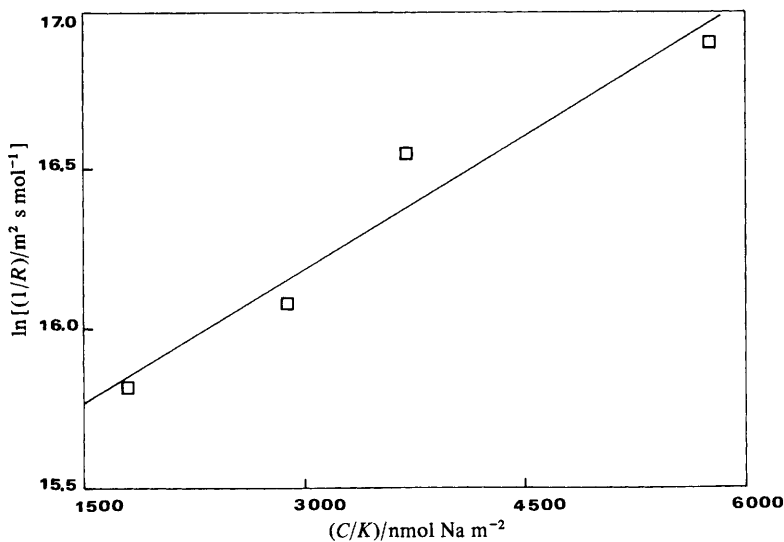
where K is the proportionality constant of eqn (1d). In order to explain this relationship we assume that the promotions of the O₂ and N₂O adsorption are described by the expressions

$$b_{O_2}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}} = a \exp(bC) \quad (20)$$

$$b_{N_2O} P_{N_2O} = a' \exp(b'C) \quad (21)$$

Table 2. Degree of conversion for the decomposition of N₂O

sample	temperature of reaction/°C				
	525	550	575	600	625
Na-0.226-Al ₂ O ₃	0.047	0.076	0.140	0.220	0.460
Na-0.309-Al ₂ O ₃	0.037	0.065	0.110	0.160	0.320
Na-0.392-Al ₂ O ₃	—	0.037	0.070	0.100	0.210
Na-0.621-Al ₂ O ₃	—	—	0.045	0.078	0.140

**Fig. 2.** Dependence of the rate of the N₂O decomposition determined at 575 °C on the surface coverage of γ -Al₂O₃ by Na⁺ ions.

where a , a' and $b \gg b'$ are proportionality constants. Based on these expressions eqn (22) is derived by combining eqn (2) and (4), provided that $1 \ll b_{\text{N}_2\text{O}} P_{\text{N}_2\text{O}} + b_{\text{O}_2}^{\frac{1}{2}} P_{\text{O}_2}^{\frac{1}{2}}$. The latter relation is implied in the assumptions already made for the derivations of eqn (6) and (7):

$$R = \frac{ka' \exp(b'C)}{a' \exp(b'C) + a \exp(bC)} \quad (22)$$

On the assumption that $1/k \ll (a/ka') \exp[(b-b')C]$, an expression similar to eqn (19) can be easily achieved by transforming eqn (22):

$$\ln(1/R) = \ln(a/ka') + (b-b')C. \quad (23)$$

The above equation clearly demonstrates that the stronger promotion of O₂ adsorption, compared to that of N₂O adsorption, caused by the doping is responsible for the decrease in the catalytic activity with Na⁺ concentration.

As to the mechanism whereby the Na⁺ ions promote oxygen adsorption it seems to us reasonable to assume, in agreement with assumptions for the Fe₂O₃/ γ -Al₂O₃-Li system,⁷ that the retention on the surface of the oxygen anions produced from the N₂O decomposition occurs *via* the formation of an unstable surface species between Na⁺ and O⁻ (Na⁺ ··· O⁻ ··· Na⁺).

In conclusion, the modification of $\gamma\text{-Al}_2\text{O}_3$ by sodium ions brings about a promotion of oxygen adsorption produced from the decomposition of N_2O , which in turn lowers the kinetic rate and decreases the catalytic activity. These effects must be taken into account when various aluminas containing different amounts of sodium ions have to be utilized as supports or matrices in catalytic systems where N_2O decomposition is used as a probe reaction.

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