Role of Adsorbed Oxygen Species in Kinetics of Catalytic Decomposition of Nitrous Oxide

S LOUIS RAJ, B VISWANATHAN & V SRINIVASAN
Department of Chemistry, Indian Institute of Technology, Madras 600036

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The extent to which the adsorbed oxygen species affects the kinetics of nitrous oxide decomposition has been studied on a perovskite (LaMnO₃) catalyst. N₂O and N₂O + O₂ mixtures have been used with untreated (evacuated) and oxygen pretreated catalysts. The results confirm that (i) oxygen desorption is the rate-controlling step and (ii) the adsorbed oxygen species from N₂O decomposition is quite different from that obtained from the adsorption of molecular oxygen. Oxygen which normally inhibits the reaction, has been shown to accelerate the decomposition rate depending upon the nature of the adsorbed oxygen species.

Oxidation-reduction reactions on oxide catalysts have been shown to be influenced by the surface and adsorbed oxygen species. These species, depending upon their binding states, control the resulting rate-determining steps as well as the overall kinetics. A typical test reaction, viz. nitrous oxide decomposition, proceeding by suprafacial route, has been shown to be strongly influenced by the oxygen pretreatments given to the catalyst. The present investigation has been undertaken to elucidate in detail (i) the effect of pretreatment with oxygen on the decomposition rate and (ii) to identify the participation and nature of adsorbed oxygen species in the overall rate-limiting step of the decomposition reaction on a typical perovskite LaMnO₃ catalyst.

Materials and Methods

LaMnO₃ was prepared by the coprecipitation method. The kinetics of nitrous oxide decomposition was studied in a static recirculatory reactor. The catalyst (about 1.5 g) was normally evacuated at a final pressure of 10⁻⁶ torr at 500°C for 6 hr and cooled to reaction temperature. The catalyst so obtained has been termed "untreated". In some cases, after evacuation and cooling to reaction temperature, the catalyst was treated with 100 torr of oxygen and allowed to reach equilibrium for 10 hr. The gas phase and weakly adsorbed oxygen were removed by evacuating for 2 min. Catalyst that has undergone this treatment has been termed 'pretreated'. In either case, the subsequent measurements were found to be reproducible.

The reaction was studied at two initial pressures of nitrous oxide, namely 50 torr and 200 torr. A few kinetic runs were also taken with mixtures of N₂O and O₂ in the ratio 8:1 at a total initial pressure of 200 torr (the pressure of O₂ being nearly equal to that produced in the normal decomposition of N₂O in about 1 hr). The kinetics has been studied in the temperature range of 280-360°C for a period of 1 hr. The observed decomposition during this period was in the range of 5-15%.

Electrical conductivity measurements were carried out using sintered pellets of the catalyst in a two-probe cell, with provision for measurement in vacuo and ambient atmospheres.

Results

Cimino et al. proposed rate equations (1-3) for the catalytic decomposition of nitrous oxide,

\[ \ln \left( \frac{p_0 - x}{p_0 - x} \right) = k_1 t \]  \hspace{1cm} (1)

\[ \left( \frac{p_0}{2} \right)^{1/2} \ln \left( \frac{p_0^{1/2} + x^{1/2}}{p_0^{1/2} - x^{1/2}} \right) - (2x)^{1/2} = k_2 t \]  \hspace{1cm} (2)

\[ \ln \left( \frac{p_0 - x}{p_0 - x} \right) = b(2x)^{1/2} + b \left( \frac{p_0}{2} \right)^{1/2} \ln \left( \frac{p_0^{1/2} + x^{1/2}}{p_0^{1/2} - x^{1/2}} \right) = k_3 t \]  \hspace{1cm} (3)

which correspond to no inhibition, strong inhibition and weak inhibition by oxygen respectively. In Eqs. (1-3), \( p_0 \) = initial N₂O pressure; \( x \) = pressure of N₂O decomposed at any time \( t \); \( x/2 \) = pressure of oxygen produced; \( p_0 - x \) = pressure of prevailing N₂O; and \( b \) = adsorption coefficient of O₂.

When Eqs (1-3) are written in the parametric forms, we have

\[ X = k_1 \]  \hspace{1cm} (1a)

\[ Y = k_2 \]  \hspace{1cm} (2a)

\[ X = k_3 - bY \]  \hspace{1cm} (3a)

A plot of \( X \) versus \( Y \) will indicate the rate law applicable for a particular situation.
Reactions at an initial pressure of 50 torr—At an initial \(\text{N}_2\text{O}\) pressure of 50 torr, plots of LHS of Eqs (1) and (2) versus time were not linear (Fig. 1), but showed a curvilinear trend of weak inhibition by oxygen. Values of \(k_1\) and \(k_2\) were calculated for various time intervals. Plots of \(k_2\) versus \(k_1\) (Fig. 2) were fairly linear having variations in the slopes and intercepts with temperature as the parameter. This regular variation is also significant in that it portrays the varying extents of inhibition with temperature. The kinetic parameters evaluated from these plots are given in Table 1. The activation energy \(E_a\) was calculated to be 15.6 kcal mol\(^{-1}\) and \(A = 1.16 \times 10^3\) mm\(^{1/2}\) min\(^{-1}\) m\(^{-2}\).

Reactions at an initial pressure of 200 torr: Untreated catalyst—At an initial \(\text{N}_2\text{O}\) pressure of 200 torr, the kinetics followed the rate Eq. (2). Typical kinetic plots after accounting for oxygen retention are shown in Fig. 3. The kinetic parameters were evaluated (Table 2) as in the case of the untreated catalyst. The value of activation energy was found to be 18.3 kcal mol\(^{-1}\). It will be seen that the rate constant at a particular temperature is higher than that observed on an untreated catalyst.

Reactions with \(\text{N}_2\text{O} + \text{O}_2\) mixture: Untreated catalyst—The kinetic data were found to fit in the integrated rate equation \(^6\) (4)

\[ (p_1 + p_2)^{1/2} \ln \left( \frac{(p_1 + p_2)^{1/2} + (p_1 + p)^{1/2}}{(p_1 + p_2)^{1/2} - (p_1 + p)^{1/2}} \right) - 2(p_1 + p)^{1/2} = k_4t \]  

In Eq. (4), \(2p_1 = \) initial pressure of \(\text{N}_2\text{O}\); \(p_1 = \) initial pressure of \(\text{O}_2\); and \(2p = \) pressure of \(\text{N}_2\text{O}\) decomposed at any time \(t\).
The evaluated kinetic parameters are given in Table 2. The activation energy was found to be 9.9 kcal mol⁻¹. It is observed that the rate constant at a particular temperature is higher than that observed for pure N₂O decomposition on untreated or pretreated catalyst.

Pretreated catalyst—The kinetic data were analysed using Eq. (4) and the derived kinetic parameters are given in Table 2. The activation energy was found to be 18.0 kcal mol⁻¹, the same value as that obtained for pure N₂O decomposition on a pretreated catalyst. The values of rate constants are comparable to those obtained for N₂O + O₂ mixture on untreated catalyst.

Oxygen adsorption measurements—Equilibrium oxygen adsorption measurements were carried out at the various reaction temperatures. The adsorption isotherms are shown in Fig. 4. It will be seen that the volume adsorbed at a given pressure increases with increase in temperature.

Table 2—Kinetic Parameters for N₂O Decomposition on LaMnO₃ at an Initial Pressure of 200 torr

<table>
<thead>
<tr>
<th>Reactant (state of catalyst)</th>
<th>Temp. (°C)</th>
<th>Rate constant (\times 10^4) (mm₁/₂ min⁻¹ m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O (untreated)</td>
<td>280</td>
<td>1.009</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2.600</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>6.618</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>9.882</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>21.320</td>
</tr>
<tr>
<td>N₂O (pretreated)</td>
<td>280</td>
<td>1.984</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.263</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>5.881</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>10.290</td>
</tr>
<tr>
<td>N₂O + O₂ (untreated)</td>
<td>280</td>
<td>7.718</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>9.386</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>13.350</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>17.783</td>
</tr>
<tr>
<td>N₂O + O₂ (pretreated)</td>
<td>280</td>
<td>5.416</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>8.822</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>14.577</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>16.240</td>
</tr>
</tbody>
</table>

Electrical conductivity measurements—In situ electrical conductivity measurements were carried out in different ambient atmospheres. The variation of conductivity is shown in Fig. 5. It is to be pointed out that on oxygen pretreated catalyst, conductivity did not change whether N₂O, O₂ or N₂O + O₂ mixture was admitted.

Discussion
It has been shown⁷ that the decomposition of N₂O on oxides takes place in accordance with the mechanism shown in Scheme 1.

\[
\begin{align*}
N₂O & \rightarrow N₂O(ads) \quad \text{... (I)} \\
N₂O + e^- & \rightarrow N₂O(ads) \rightarrow N_2(g) + O(ads) \quad \text{... (II)} \\
N₂O(ads) & \rightarrow O(ads) + N_2(g) \quad \text{... (III)} \\
O(ads) + N₂O(g) & \rightarrow O_2(g) + N_2(g) + e^- \quad \text{(to the catalyst)} \quad \text{... (IV)} \\
O(ads) + O(ads) & \rightarrow O_2(g) + 2e^- \quad \text{(to the catalyst)} \quad \text{... (V)}
\end{align*}
\]

Scheme 1

Fig. 3—Kinetic plots for N₂O decomposition at 200 torr on LaMnO₃ (pretreated)

Fig. 4—Adsorption isotherms of oxygen on LaMnO₃
The fact that there is a weak inhibition by oxygen at an initial pressure of 50 torr indicates that the rates of \( \text{N}_2\text{O} \) adsorption (step-I) and oxygen desorption (step-V) are comparable and of the two steps, \( \text{N}_2\text{O} \) adsorption is faster than oxygen desorption. The increase in \( b \)-values with temperature indicates that oxygen adsorption is activated. Independent oxygen adsorption measurements as well as the values of oxygen retention computed by the least square regression method support this finding.

At 200 torr initial pressure of \( \text{N}_2\text{O} \), the rate of adsorption of \( \text{N}_2\text{O} \) is very much faster than the rate of desorption of oxygen and oxygen desorption has been shown to be rate-controlling\(^8\). On the untreated catalyst, the oxygen desorption step is given by Eq. (5),

\[
\text{O}(\text{N}_2\text{O}) + \text{O}(\text{N}_2\text{O}) \rightarrow 2\text{O}_2(a) + 2e^- \quad \ldots (5)
\]

where \( \text{O}(\text{N}_2\text{O}) \) refers to the oxygen that has been generated by the breakage of O—N bond in \( \text{N}_2\text{O} \) during decomposition and can be expected to be retained strongly on the surface. If one assumes \( R_1 \) and \( q_1 \) to be the rate and rate constant for the desorption step shown in Eq. (5), then

\[
R_1 = q_1 [\text{O}(\text{N}_2\text{O})]^2 \quad \ldots (6)
\]

On pretreatment with oxygen, a fraction of the active sites can be occupied by oxygen species from molecular oxygen. However, \( \text{N}_2\text{O} \) decomposition can still take place on the remaining active sites available on the surface. It is thus possible to visualise two different surface oxygen species, \( \text{O}_1(\text{N}_2\text{O}) \) one generated in the decomposition of nitrous oxide and another from the direct adsorption of oxygen \( \text{O}_2(\text{ads}) \). Of these two forms, it is probable that the \( \text{O}_1(\text{ads}) \) is held less strongly compared to \( \text{O}_2(\text{N}_2\text{O}) \). Under these circumstances, the desorption can be visualised to occur by Eq. (7)

\[
\text{O}_1(\text{N}_2\text{O}) + \text{O}_2(\text{ads}) \rightarrow \text{O}_2(a) + (1 + x)e^- \quad \ldots (7)
\]

If one assumes \( R_2 \) and \( q_2 \) to be the rate and rate constant for the desorption step shown in Eq. (7), then

\[
R_2 = q_2 [\text{O}(\text{N}_2\text{O})][\text{O}(\text{ads})] \quad \ldots (8)
\]

Taking into consideration that (i) the initial concentration of \( \text{O}_1(\text{ads}) \) species can be expected to be higher on the surface due to the pretreatment given to the catalyst and (ii) \( \text{O}_2(\text{ads}) \) species can be expected to be less strongly held on the surface compared to \( \text{O}_1(\text{N}_2\text{O}) \), \( R_2 > R_1 \). The cumulative effect of the above two factors facilitating oxygen desorption is reflected (i) in the decrease in \( E_a \) value and (ii) increase in the value of the rate constant at a particular temperature for the pretreated compared to the untreated catalyst.

When a mixture of \( \text{N}_2\text{O} + \text{O}_2 \) is admitted to the untreated catalyst, there would be competition between \( \text{N}_2\text{O} \) and \( \text{O}_2 \) for sites and both of them get adsorbed on the surface. In this case, the oxygen desorption step can be represented by Eq. (9)

\[
\text{O}_1(\text{N}_2\text{O}) + \text{O}_1(\text{ads}) \rightarrow \text{O}_2(a) + (1 + y)e^- \quad \ldots (9)
\]

where \( \text{O}_2(\text{ads}) \) refers to the oxygen species that is getting adsorbed from molecular oxygen in the presence of \( \text{N}_2\text{O} \). This \( \text{O}_1(\text{ads}) \) species can be expected to be less strongly held on the surface compared to \( \text{O}_1(\text{N}_2\text{O}) \) species since the latter has unrestricted mobility on the surface and sufficient time for equilibration. The \( \text{O}_1(\text{ads}) \) species can be expected to be different from \( \text{O}_2(\text{ads}) \) species due to the restricted mobility of the former in the presence of adsorbed \( \text{N}_2\text{O} \). If one considers \( R_3 \) and \( q_3 \) to be the rate and rate constant for the desorption step shown in Eq. (9), then

\[
R_3 = q_3 [\text{O}(\text{N}_2\text{O})][\text{O}(\text{ads})] \quad \ldots (10)
\]

It is probable that \( R_3 > R_2 \) because \( \text{O}_1(\text{ads}) \) would be less strongly held on the surface than \( \text{O}_2(\text{ads}) \) and hence can easily get desorbed compared to \( \text{O}_1(\text{N}_2\text{O}) \). This is reflected in the lower value of activation energy and higher value of rate constant at a particular temperature observed for \( \text{N}_2\text{O} \) decomposition from \( \text{N}_2\text{O} + \text{O}_2 \) mixture on untreated catalyst than that observed for pure \( \text{N}_2\text{O} \) decomposition on untreated or pretreated catalyst.

The observation that the values of activation energy and rate constant for \( \text{N}_2\text{O} \) decomposition on pretreated catalyst either from pure \( \text{N}_2\text{O} \) or from \( \text{N}_2\text{O} + \text{O}_2 \) mixture are the same would indicate that the
desorption step is predominantly controlled by the surface oxygen species \( \text{O}^{\text{ads}} \) generated during pretreatment. The desorption step in this case would be governed by Eq. (11),

\[
\text{O}_2(\text{ads}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3 + (1 + x) e^-
\]

similar to the one observed for \( \text{N}_2\text{O} \) decomposition on pretreated catalyst. Since the sites available for oxygen adsorption are already saturated during pretreatment, further adsorption of gas phase oxygen from \( \text{N}_2\text{O} + \text{O}_2 \) mixture would become negligible.

Thus it is clear that the surface should contain a spectrum of sites capable of promoting various types of adsorbed oxygen species. This contention is supported by the observation that there is a compensation between \( \ln A \) and \( E_a \) values obtained under various treatments given to the catalyst (Fig. 6). Further, the posulate that there are different binding states of oxygen is confirmed by the technique of temperature programmed desorption (TPD) studies on oxide surfaces which show that the adsorbed oxygen species generated during the decomposition of \( \text{N}_2\text{O} \) is energetically different from that obtained by adsorption from gas phase oxygen.

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References