Effect of electron exchange on the catalytic behaviour of MgV$_2$O$_4$-Mg$_2$VO$_4$ systems in methanol oxidation

B H Sakakini

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

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Methanol oxidation has been carried out in a flow system over a series of vanadium spinel solid solutions MgV$_2$O$_4$-Mg$_2$VO$_4$, in which the average oxidation state of vanadium in the catalysts changes from V$^{3+}$ to V$^{4+}$. Characterization of the catalysts used involved surface area and conductivity measurements. Results obtained show that the catalytic activity of the catalysts used change with the average oxidation state of vanadium in the catalysts. A reaction scheme based on the conductivity measurements and kinetic data has been proposed, for the selective oxidation of methanol to formaldehyde.

The importance of formaldehyde in the chemical industry has prompted extensive studies on the selective oxidation of methanol to formaldehyde$^1-8$. Earlier studies$^9$ on heterogenous oxidations of hydrocarbons seem to indicate that high selectivity to partial oxidation products is associated with relatively easy charge transfer or conductivity through the catalyst. It has been established that in some vanadium systems electrical conductivity depends upon vanadium being present in different valency states, and it is accepted that in these materials the conduction process involves the exchange of electrons between vanadium ions of different oxidation state$^{10-12}$. In the present study MgV$_2$O$_4$-Mg$_2$VO$_4$ system, where the vanadium oxidation state changes from 3$^+$ to 4$^+$, was chosen to test the relationship between the electrical properties of these solids and their catalytic behaviour in methanol oxidation.

Materials and Methods

Preparation of the samples

Solid solutions of MgV$_2$O$_4$-Mg$_2$VO$_4$ were prepared by mixing and grinding of the appropriate oxides to give the required average oxidation state of vanadium, pressing into pellets and heating in Pt bucket in vacuum for 24 hr at 1223-1373 K (ref. 13). Formation of spinel solid solution was confirmed by X-ray diffraction.

Catalyst characterization

After the preparation, catalysts were characterized by means of gas adsorption measurements (BET) and conductivity measurements. Specific surface areas of the samples were determined by BET adsorption measurements using nitrogen at liquid nitrogen temperature.

For conductivity measurements about 1 g of catalyst was pressed under a pressure of 10 ton/cm$^2$ to make a pellet and sintered at 1173 K for several hours in vacuum. The pellet was clamped between two platinum electrodes which were connected to a stabilized power supply of 2.26 V. The current passing through the pellet was measured by a digital voltmeter using a current shunt. Conductivity measurements were carried out under constant flow of 50 cm$^3$ min$^{-1}$ of Ar at atmospheric pressure. The conductivity ($\sigma$) was calculated and log $\sigma$ was plotted against $1/T$ where $T$ is the temperature in Kelvin. The slopes of the lines gave values of $E$ which correspond to the activation energy of the conduction.

Methanol oxidation

The oxidation of methanol was carried out using a continuous flow system. The reactor was a silica tube placed concentrically in the furnace. The catalyst was supported on a silica sinter. The temperature of the catalyst was measured by a Chromel-Alumel thermocouple in a silica sheath with the tip of the thermocouple just immersed in the catalyst bed. The reaction gases passed downward through the reactor and out to gas sampling of a Pye Unicam gas chromatograph. A by-pass enabled the reactant stream to be sampled by the gas chromatograph in order to determine the initial concentration of the components.

Compressed helium and oxygen from cylinders were dried by passing through molecular sieve traps and were separately passed through flowmeters before mixing. Methanol was introduced by
bubbling helium through a glass saturator filled with anhydrous methanol supplied by BDH Chemicals Limited. The saturator was immersed in a thermostat which was kept at 22°C. To avoid condensation of reactants and products, the tubing between the reactor outlet and the gas sampling valve was heated to 110°C. In each case, 0.5 g of catalyst was used and pretreatment consisted of heating the catalyst for 1 h in oxygen/He atmosphere at 773 K and flushing with He for 10 min. After the pretreatment a mixture of oxygen, methanol and carrier gas helium was passed over the catalyst at a total flow rate of 70 cm$^3$ min$^{-1}$. Normally the reaction mixture consisted of oxygen at a partial pressure of 0.30 atm and methanol at 0.05 atm.

The product gas was analyzed for oxygen, methanol, formaldehyde, carbon dioxide and water by periodic injection of the reactant gas mixture into a gas chromatograph. The gas chromatograph was operated using a thermal conductivity detector, He carrier gas and the product gases were separated on a column of 80-100 mesh Porapak T. A blank run without a catalyst gave no detectable conversion in the range of temperatures investigated and in all runs the % conversion did not exceed 10%. At each temperature the average of three measurements of steady state activity not differing by more than 5% was computed. For the total oxidation of methanol Arrhenius plots were plotted as log $C_T\%$/S vs 1/T, where $C_T\%$ is the percentage total conversion, S is the surface area of the catalyst and T is the temperature in Kelvin. For the selective oxidation to HCHO and the deep oxidation to CO$_2$, log $C\%$ was used where $C\%$ is the percentage conversion to either formaldehyde or carbon dioxide. Percentage total conversion was calculated from the relation,

$$C_T\% = \frac{\text{moles of CH}_3\text{OH reacted per min}}{\text{moles of CH}_3\text{OH fed per min.}} \times 100$$

$C\%$ for HCHO and CO$_2$ were calculated from the following relations:

$$C_{\text{HCHO}}\% = \frac{\text{moles of HCHO formed per min}}{\text{moles of CH}_3\text{OH fed per min.}} \times 100$$

$$C_{\text{CO}_2}\% = \frac{\text{moles of CO}_2\text{ formed per min}}{\text{moles of CH}_3\text{OH fed per min.}} \times 100$$

Selectivity in oxidation of methanol to HCHO was defined as,

$$S_{\text{HCHO}} = \frac{\text{moles of HCHO formed per min}}{\text{moles of (HCHO + CO}_2\text{) formed per min.}} \times 100$$

### Results and Discussion

#### Surface area

The results obtained are summarized in Table 1, where y denotes the average oxidation state of vanadium in the catalyst and S is the surface area.

#### Conductivity measurements

The conductivity data obtained for the samples used are included in Table 1. Both the end members show finite conductivity. Between the two end members, the maximum conductivity and the corresponding minimum activation energy of conduction occurs at the vanadium oxidation state of 3.12. This is in agreement with the results of Reuter et al.\textsuperscript{13} although there was some difference in the measured values of specific conductivity which may be attributed to particle and contact resistance. It was suggested that the increase in conductivity in the crystal mixture is due to V$^{3+}$ and V$^{4+}$ ions lying side by side on the octahedral sites which leads to easy electron exchange\textsuperscript{14}. This electron exchange will facilitate the bulk conductivity.

In comparison with other systems\textsuperscript{15,16}, one would expect the conductivity to go through a maximum when the ratio $\frac{V^{3+}/V^{4+}}{=} = 1$. However, the role of the Mg$^{2+}$ ion in the lattice should be considered. In MgV$_2$O$_4$, V$^{3+}$ ions occupy octahedral sites\textsuperscript{13}, and in forming the V$^{3+}/V^{4+}$ crystal mixture, each pair of octahedral sites vacated by two V$^{3+}$ ions will be filled by one Mg$^{2+}$ ion from a tetrahedral site and one V$^{4+}$ ion. This is to maintain charge neutrality and also to give a minimum in the crystal field stabilisation energy. The change in the proportions of the cations in the different sites can be seen in Table 2.

The Mg$^{2+}$ ion in the octahedral site has a noble gas electronic configuration, and the activation energy for conduction of these electrons is very high. More Mg$^{2+}$ will increasingly disrupt the electron exchange mechanism. Thus, there will be a balance of V$^{4+}$ and Mg$^{2+}$ to yield maximum conductivity. This seems to occur when the average oxidation state of vanadium in the crystal mixture is 3.12 and not 3.50 as expected when V$^{3+}$ and V$^{4+}$ are in the ratio of 1:1.

<table>
<thead>
<tr>
<th>y*</th>
<th>S/m$^2$g$^{-1}$</th>
<th>$E_p$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3.00</td>
<td>4.2</td>
<td>0.317</td>
</tr>
<tr>
<td>+3.02</td>
<td>3.7</td>
<td>0.259</td>
</tr>
<tr>
<td>+3.12</td>
<td>3.4</td>
<td>0.224</td>
</tr>
<tr>
<td>+3.50</td>
<td>1.2</td>
<td>0.274</td>
</tr>
<tr>
<td>+3.70</td>
<td>1.1</td>
<td>0.336</td>
</tr>
<tr>
<td>+4.00</td>
<td>1.1</td>
<td>0.445</td>
</tr>
</tbody>
</table>

* Average oxidation state of vanadium

<p>| Table 1—Surface area and conductivity data for MgV$_2$O$_4$-Mg$_2$V$_2$O$_4$ system |
|-----|----------------|----------|</p>
<table>
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<tr>
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<td>0.336</td>
</tr>
<tr>
<td>+4.00</td>
<td>1.1</td>
<td>0.445</td>
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</table>

* Average oxidation state of vanadium
Table 2—Distribution of cations in tetrahedral and octahedral sites in MgV₂O₇·Mg₂VO₄ system

<table>
<thead>
<tr>
<th>Cations distribution on</th>
<th>V⁺⁺·V⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral sites</td>
<td>Octahedral sites</td>
</tr>
<tr>
<td>+3.00 Mg⁴⁺</td>
<td>V⁴⁺</td>
</tr>
<tr>
<td>+3.02 Mg⁴⁺</td>
<td>V₅⁺</td>
</tr>
<tr>
<td>+3.50 Mg⁴⁺</td>
<td>V₉⁺</td>
</tr>
<tr>
<td>+4.00 Mg⁴⁺</td>
<td>V₁₄⁺</td>
</tr>
</tbody>
</table>

Table 3—Activation energies for the oxidation of methanol over MgV₂O₄·Mg₂VO₄ series

<table>
<thead>
<tr>
<th>Activation energies (Eₐ)/kJ mol⁻¹</th>
<th>Total oxidation</th>
<th>Selective oxidation</th>
<th>Deep oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3.00</td>
<td>105.3</td>
<td>105.3</td>
<td>—</td>
</tr>
<tr>
<td>+3.02</td>
<td>94.5</td>
<td>94.5</td>
<td>—</td>
</tr>
<tr>
<td>+3.12</td>
<td>103.8</td>
<td>103.8</td>
<td>—</td>
</tr>
<tr>
<td>+3.50</td>
<td>106.5</td>
<td>106.5</td>
<td>—</td>
</tr>
<tr>
<td>+3.70</td>
<td>104.8</td>
<td>97.4</td>
<td>159.2</td>
</tr>
<tr>
<td>+4.00</td>
<td>151.2</td>
<td>138.8</td>
<td>210.4</td>
</tr>
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</table>

Catalytic results

The reaction was carried out at different temperatures for each catalyst. Results obtained are summarized in Table 3 and Figs. 1-5. All catalysts used, except for the last two specimens, were 100% selective towards formaldehyde formation within the temperature range studied. Fig. 5 shows the variation of the catalytic activity towards formation of formaldehyde from methanol as a function of the average oxidation state of vanadium at 473 K for catalysts used. The observed activity behaviour can be divided into three parts:

Region 1: The average oxidation state of vanadium varies from 3.00 to 3.02 and this is accompanied by an increase in activity.

Region 2: The average oxidation state of vanadium changes from 3.02 to 3.12. In this region a decrease in activity is observed.

Region 3: The average oxidation state of vanadium changes from 3.12 to 4.00. In this region there is a steady rise in activity.

In order to account for the observed activity, we propose the following reaction scheme:

1. The methanol molecule is adsorbed onto the catalyst at V⁴⁺ site (A)

Fig. 1—Arrhenius plots for the total oxidation of methanol. The numbers indicate the average oxidation state of vanadium.

Fig. 2—Arrhenius plots for the selective oxidation of methanol. The numbers indicate the average oxidation state of vanadium.

Fig. 3—Arrhenius plots for the deep oxidation of methanol. The numbers indicate the average oxidation state of vanadium.
Busca et al.\textsuperscript{20} who investigated the adsorption of formaldehyde over $\sigma$-Fe$_2$O$_3$ surface using IR concluded that formaldehyde molecules exist on the surface coordinatively bonded through the carbonyl oxygen to Lewis acid sites (Fe$^{3+}$) in a manner similar to what is proposed here (B)

The V$^{4+}$ site where adsorption takes place becomes less positively charged due to the electron flow from the adsorbed formaldehyde to the adsorption site as indicated in the scheme. This creates a local electronic disturbance at the surface which is energetically unfavourable. The subsequent behaviour of the adsorbed formaldehyde is governed by the ability of the system to dissipate or minimize this electronic disturbance. In the case when electron exchange between the vanadium adsorption site and one or more neighbouring or adjacent site—which, we suggest to be V$^{4+}$—is possible, the local disturbance will be minimized relatively easily. In this case, the adsorbed form will be stabilized. Therefore, formaldehyde will be strongly adsorbed and it will effectively block the adsorption sites, thus decreasing the activity of the catalyst. If, on the other hand, electron exchange is difficult or inhibited for one reason or another, the only way by which the electronic disturbance could be dissipated is by desorption of formaldehyde. Thus, the vanadium adsorption site is brought again to V$^{4+}$ which can now be ready to adsorb a new methanol molecule and so on.

**Interpretation of catalytic activity behaviour**

**Region 1:** The inherent catalytic activity of MgV$_2$O$_4$ can be interpreted by assuming that the 'pure' MgV$_2$O$_4$ is non-stoichiometric with some V$^{4+}$. Increasing the amount of V$^{4+}$ in the crystal mixture in the region V$^{3+}$ to V$^{3.02+}$ will increase the number of isolated V$^{4+}$ sites, i.e. there will be no V$^{4+}$ ions adjacent to each other and so charge stabilization will not occur. Therefore, the formaldehyde formed will be easily desorbed and thus activity will increase with increasing V$^{4+}$ ion concentration.

**Region 2:** In this region the probability of having V$^{4+}$ pairs sometime during adsorption will increase. The adsorbed formaldehyde will be stabilized by electron exchange and will stay on the surface longer, thus effectively blocking the active sites. If the V$^{4+}$ site

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**Fig. 4**—Activity for the total oxidation of methanol as a function of the average oxidation state of vanadium (X) at 473 K.

**Fig. 5**—Activity for the selective oxidation of methanol as a function of the average oxidation state of vanadium (X) at 473 K.

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The V$^{4+}$ sites are known to act as Lewis acid centres for the adsorption of ammonia in vanadium bronzes\textsuperscript{17}. So the suggested adsorption of methanol would be reasonable since methanol can act as an electron donating species. Similar scheme for the adsorption of methanol on acidic sites has been proposed by Ai\textsuperscript{4}. According to Pernicone et al.\textsuperscript{18} and Novakova et al.\textsuperscript{19} formaldehyde is formed via an alcoholate bound to an acidic site.

2. The adsorbed methanol loses hydroxy hydrogen and one of the methyl hydrogens attached to the lattice oxygen (shown in the previous scheme, as H atoms, which probably subsequently get oxidised to water at the surface). The formaldehyde produced, which is an electron-donating compound (basic) would still be adsorbed on the vanadium site.
where adsorption occurs can be considered as $V^{3+}$ site due to electron density donation by formaldehyde oxygen. Then correlation can be made between the decrease in activity with increasing $V^{4+}$ pairs and the increase in conductivity data; maximum conductivity and corresponding minimum activation energy of conduction occurs at the vanadium oxidation state of $+3.12$.

Region 3: In this region the $Mg^{2+}$ ion concentration in octahedral sites will increase. This will tend to destabilize the adsorbed formaldehyde in two ways:

(a) It will reduce the probability of $V^{4+}$ sites being on adjacent octahedral sites by competing with $V^{4+}$ for octahedral sites (see Table 2).

(b) It will tend to inhibit electron exchange between $V^{4+}$ and $V^{3+}$ by virtue of its noble gas electronic configuration.

It must be emphasised here that $V^{4+}$ sites are not localised but free to move through the lattice by electron exchange with $V^{3+}$.

If a $Mg^{2+}$ is between a $V^{4+}$ and a $V^{4+}$ adsorption site, then electron exchange cannot occur, the formaldehyde will not be stabilized and the activity would revert to region 1 behaviour.

Thus, the activity increases with the average oxidation state of vanadium in this region because of the effect of the octahedral $Mg^{2+}$ and also because the actual number of $V^{4+}$ sites available for adsorption also increases.

Specimens with $V^{2+}$ and $V^{4+}$ were 83% selective towards formaldehyde formation at 10% total conversion. The production of the deep oxidation product CO$_2$ on these specimens could be attributed to their high activity. Probably carbon dioxide is formed by the consecutive oxidation of the produced formaldehyde.

Although the proposed mechanism for the selective oxidation of methanol on the catalysts used seems to fit the results obtained, further experimental work is required to clarify and define the methanol adsorption process. Conductivity measurements during adsorption will give further insight into the electron transfer during the adsorption process, thereby clarifying the reaction pathway.

**Conclusion**

The catalytic activity of the catalysts used depends on facile electron exchange. Easy electron exchange stabilizes the adsorbed formaldehyde thereby effectively blocking the adsorption sites and decreasing the activity of the catalyst for further reaction.

**References**