Charge transport and dielectric properties of vanadium oxide catalyst†

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Charge transport and the dielectric properties of vanadium oxide based sulphuric acid catalysts having different compositions and supports, have been investigated in the temperature range of 400-930 K. The activation energies for conduction have been calculated. Other physicochemical parameters such as porosity, total pore volume, along with the crushing strength and activity are also reported. An attempt has been made to correlate the catalytic activity in the light of charge transfer and space charge polarization and other physicochemical parameters.

The electrical conduction in vanadium pentaoxide, when heated with other oxides occurs1-2 by hopping of electrons from an ion of low valency state (V4+) to an ion of high valency state (V5+). It has also been suggested that the activation energy for conduction is the dominating factor and in many cases, preexponential factor has a great influence on conductivity. The catalytic action of V2O5 + K2SO4 system for SO2 oxidation have been studied by many workers3-10. Tamara et al.10 attributed the catalytic activity to two factors viz. (i) weakening of the V-O bond forming VO3S04 and (ii) increasing the effective active centres by lowering the melting point. Furthermore, Flood and coworkers11 have reported that the polarizing power of cation affected the solubility of S2O7(II) ion in molten salt.

In view of the above observations, the present study of V2O5 + K2SO4 catalyst systems of different compositions towards SO2 oxidation has been undertaken. The a.c. electrical conductivity and dielectric constant measurements and the activities of four catalyst systems A, B, C and D have been studied.

Experimental
All the catalyst samples were prepared by kneading a homogeneous mixture of vanadium pentaoxide, potassium sulphate, silica (natural kieselguhr) and other ingredients in distilled water. The kneaded mass was partially dried to a moisture level of about 10% by weight. The semi-dried cake was granulated and beads of 6 mm x 6 mm size were prepared. The beads were cured at 873 K for 7 or 8 hr.

The catalytic activity was measured in a continuous flow system at atmospheric pressure using fixed bed in an electrically heated reactor made of pyrex glass. The inlet gas of the composition SO2, 8%; O2, 10%; N2, 82% was fed from the top of the reactor. In each experiment the catalyst (-10 + 14 BSS; 5 ml) was charged and the activity of the catalyst was monitored at 723 K by the difference of SO2 concentrations in the inlet and outlet gases measured by iodometric titration.

The a.c. electrical conductivity (σ) and dielectric constant (e) were measured on a single bead of catalyst employing a Wayne-Kerr bridge model B-224 operating at internal frequency of 1.592 kHz and having an accuracy of 1%. Platinum disc electrodes connected by platinum wire passing through a silica tube were used. The experimental details and procedures of the measurement are described elsewhere12.

Results and discussion
(a) Electrical conductivity
The chemical composition, porosity and total pore volume of all the four catalysts A, B, C and D are given in Table 1. Table 2 presents the physicochemical properties like crushing strengths, catalyst activities at 723 K along with the activation energies for conduction, specific conductivities and dielectric constants at 723 K. The plots of log (conductivity) against 1/T for all the samples are presented in Fig. 1. The activation energies were obtained by the slopes of these curves at 723 K. It is found that all the samples show increase in conductivity with temperature showing a typical characteristic of a semiconductor. Ideally, this variation is given by Eq. (1)

\[ \sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \]  

where \( \sigma \) is the conductivity at \( T \), \( \sigma_0 \) is the characteristic constant and is a function of charge mass, mobility of individual charge carriers, \( k \) is the Boltzmann constant and \( E_a \) is the activation energy for conduction determined by the slopes of the tangents at some specific points on the log \( \sigma \) versus 1000/T curves. For an intrinsic semiconductor with a perfect crystalline system this plot should be linear giving rise to a single activation energy. However in
Table 1—Chemical composition, porosity and pore volume of the catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition (% W/W)</th>
<th>Porosity (ml/dl)</th>
<th>Total pore volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V$_2$O$_5$</td>
<td>K$_2$SO$_4$</td>
<td>Kieselguhr</td>
</tr>
<tr>
<td>Cat. (A)</td>
<td>5 15 76</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Cat. (B)</td>
<td>7 15 64</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Cat. (C)</td>
<td>7 15 64</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Cat. (D)</td>
<td>7 15 64</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Table 2—Crushing strength, catalyst activity, electrical conductivity and dielectric parameters of the catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crushing strength (Kg/cm$^2$)</th>
<th>Catalytic activity (%)</th>
<th>Activation energy (eV/K mole)</th>
<th>Sp. conductivity at 723 K (mho/cm)</th>
<th>log $\sigma_{ac}$ at 723 K</th>
<th>Dielectric constant at 723 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. (A)</td>
<td>99</td>
<td>62.0</td>
<td>0.73</td>
<td>6.87</td>
<td>0.84</td>
<td>25</td>
</tr>
<tr>
<td>Cat. (B)</td>
<td>91</td>
<td>19.7</td>
<td>1.16</td>
<td>19.96</td>
<td>1.30</td>
<td>45</td>
</tr>
<tr>
<td>Cat. (C)</td>
<td>139</td>
<td>50.0</td>
<td>0.95</td>
<td>50.12</td>
<td>1.70</td>
<td>46</td>
</tr>
<tr>
<td>Cat. (D)</td>
<td>112</td>
<td>55.4</td>
<td>0.85</td>
<td>16.44</td>
<td>1.22</td>
<td>110</td>
</tr>
</tbody>
</table>

Fig. 1—Variation of log (conductivity and (dielectric constant) as a function of temperature in K) [(a) (1) log $\sigma$ versus 1000/T plot of Cat. (A), (2) log $\sigma$ versus 1000/T plot of Cat. (B), (3) $\epsilon$ versus T plot of Cat. (A) (4) $\epsilon$ versus T plot of Cat. (B); and (b) (1) (O) log $\sigma$ versus 1000/T plot of Cat. (C), (2) log $\sigma$ versus 1000/T plot of Cat. (D), (3) $\epsilon$ versus T plot of Cat. (C), (4) $\epsilon$ versus T plot of Cat. (D)].

In order to confirm the above conclusion, the plot of catalytic activity against the activation energy was constructed which is linear with a negative slope (Fig. 2). However, Cat. (B) showed anomalous behaviour.

The present systems this ideal behaviour was not obtainable probably due to the presence of multi-component system with different phases.

Vanadium pentaoxide is an-type semiconductor at higher temperature$^{13}$, where the charge carriers are electrons which are transported by thermally activated hopping from (V$^{4+}$) site to a neighbouring (V$^{5+}$) site. The catalytic activity is the result of an increase in the population mobility of the charge carriers with temperature, facilitating the conversion between two valency states of vanadium. Therefore, the activation energy of conduction at the reaction temperature is associated with the reaction efficiency. While correlating the catalytic activity with the corresponding energy of activation included in Table 2, it is observed that Cat. (A) having the highest activity (62%) amongst the four samples has the lowest activation energy (0.73 eV/K mole) whereas Cat. (B) having the lowest activity (19.7%) has the highest activation energy (1.16 eV/K mole). When similar comparison is made for Cat. (C) and Cat. (D), the catalysts having medium catalytic activity of 50% and 55.4% respectively, the corresponding activation energies are 0.95 and 0.85 eV/K mole. This confirms our earlier conclusion$^{12-14}$ that the lower values of activation energy for conduction will give rise to higher catalytic efficiency.
In this case a significant deviation was observed. This deviation with respect to conductivity in the case of Cat. (B) appears to be due to some factors which could not be ascertained in this investigation.

(b) Dielectric constant

The variation of dielectric constant against temperature for all the four catalyst samples is presented in Fig. 1. The dielectric constant appears as a result of overall polarizability of the molecule, namely electronic, atomic, orientational and space charge polarizations. But in the present case, it is contributed mainly by the space charge polarization, arising from crystal defects, deformity and other anharmonic forces in the crystal. The space charge concentration increases with increase in temperature, because the thermal generation of both electrons and holes takes place. This is confirmed by the observed increase in dielectric constant with temperature for all the four samples. The relative increase in dielectric constant as a result of release of space charge by the increase in temperature should be associated with increase in catalytic efficiency. But in the present case this correlation is weak, Cat. (A) having the maximum activity (62%), the magnitude of increase of dielectric constant is low compared to that of the Cat. (B) having the minimum catalytic activity (19.7%). However the Cat. (D) having an activity of 55.4% shows a faster increase of dielectric constant with temperature than Cat. (C) having an activity of 50%.

On the basis of results obtained, it can be concluded that (i) lower values of activation energy for conduction contributes to higher catalytic efficiency and lower conductivity in the system (exception in the Cat. (B) systems) and (ii) the catalytic efficiency increases if the samples are prepared and cured in such a way so that there is increase in polarizability giving rise to higher dielectric constant.

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References

5. Tandy G H, J appl Chem, 6 (1956) 68.