Role of zinc oxide in $V_2O_5-K_2SO_4-ZnO-SiO_2$ catalyst in vapour phase oxidation of toluene to benzaldehyde

S K Chatterjee, A Das & Subodh K Ray*
Central Fuel Research Institute, Dhanbad 828 108, India
Received 2 May 1994; accepted 14 February 1995

Catalytic vapour phase oxidation of toluene to benzaldehyde has been studied to formulate optimal catalyst. $V_2O_5-K_2SO_4$ combination at 15:20 ratio on silica gel has been optimised. Method of preparation of support grade silica gel, specific for platforming the catalyst constituents for the controlled oxidation of toluene has been worked out. Incorporation of zinc oxide in the aforesaid combination confers the catalyst system improved activity, matching selectivity and adequate stability. The $V_2O_5-K_2SO_4-SiO_2$ system, provides a framework for the arrangement and strategic placement of Zn, hosted in prescribed manner so that their mutual electronic interaction can exhibit their desired catalytic functions.

Experimental Procedure
The support grade silica gel was prepared from sodium silicate by the reaction with dilute sulphuric acid. To a 25% (w/v) sodium silicate solution dilute sulphuric acid (1:1 by volume) was added with simultaneous stirring till the desired pH was attained. The solution was then allowed to set and the product was washed till free from $SO_4^{2-}$ ions. The gel was dried at 80-90°C in an air oven for 24 h and finally was calcined at 500°C for 5-6 h. The calcined silica gel was sized to -6 to + 14 mesh (BSS).

A R Grade $V_2O_5$, $K_2SO_4$ and $Zn(NO_3)_2$ were used for the preparation of catalysts. Vanadium pentoxide was converted to oxalate by the interaction of oxalic acid. The catalysts were prepared by impregnation technique and dried at 100°C for 10-12 h, followed by calcination at 500°C for 6-8 h.
The experimental setup as well as activity tests of the catalysts were carried out as described earlier. The reaction products were collected initially through a water condenser followed by a series of condensers cooled by ice-salt mixture. A series of U-tubes packed with active carbon to absorb toluene was introduced to the exit end and gaseous product that escaped through the active carbon adsorbent were collected occasionally to detect the presence of CO\textsubscript{2}. BZH and traces of benzene were extracted with m-xylene and subsequently analysed by GC using a column of 12\% Apiezon L grease on chromosorb-W (acid washed) maintained at 120°C with nitrogen as carrier gas.

Table 1 illustrates the effect of zinc oxide when incorporated in the V\textsubscript{2}O\textsubscript{5}-K\textsubscript{2}SO\textsubscript{4}/SiO\textsubscript{2} system. The proportion of Zn was varied from 1-5\%, keeping VK ratio constant at 15:20. It is observed that the maximum toluene conversion was achieved at 1.5\% loading of Zn and it either increases or decreases with ZnO loading. It is remarkable that with the incorporation of Zn, the product profile undergoes significant change, as virtually pure BZH is obtained. In the laboratory bench scale a consistent conversion of toluene to BZH, at the rate of 20 mol percent per pass with more than 90\% selectivity could be achieved.

The role of support being as important as that of the catalyst constituents, four silica gel samples were studied for this reaction. Samples A, C and D were prepared in the laboratory at pH 10, 5 and 7, respectively. Sample B was drawn from the commercial source. Fig. 1 indicates that maximum conversion was obtained from silica gel support which was precipitated at pH 7.

Effect of toluene feed rate on its conversion was studied by varying feed rate in the range 2.8-7 mL h\textsuperscript{-1}. The results are depicted in Fig. 2. A maximum was observed at feed rate 5.5 mL h\textsuperscript{-1} where as the conversion rate declines at both ends. K\textsubscript{2}SO\textsubscript{4} appears to play a significant role in controlling the degree of oxidation of vanadia catalyst.
Table 2—Effect of zinc oxide on the V$_2$O$_5$-K$_2$SO$_4$-SiO$_2$ system

<table>
<thead>
<tr>
<th>Conc. of ZnO percentage</th>
<th>Toluene converted to mol %</th>
<th>Unconverted toluene mol %</th>
<th>Total conversion mol %*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>Benzoic acid</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>Nil</td>
<td>16.7</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td></td>
<td>15.8</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>16.0</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.5</td>
<td>20.8</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>19.8</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>20.1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>3.0</td>
<td>12.4</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>12.8</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>13.6</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>5.0</td>
<td>6.5</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

*Includes error loss plus any other product not estimated.

The optimal combination of V$_2$O$_5$ and K$_2$SO$_4$ at V:K = 15:20 facilitates partial oxidation of toluene to BZH (Table 1). The promotive action of K$_2$SO$_4$ is adducible to the fact that V=O present in the V$_2$O$_5$ entity is believed to get loosend by the effect of alkalimetal sulphate and this weaken V=O, in effect, govern the oxidation. Further, potassium doped vanadia showed a shift from 1025 to 1000 cm$^{-1}$ band in IR absorption spectrum to signify promotive action of potassium in the oxidation of hydrocarbons.

Development of needle type entity of V$_2$O$_5$ in presence of K$_2$SO$_4$ was identified by electron microscopy and this particular type of V$_2$O$_5$ was assumed to be crucial for the catalytic oxidation of hydrocarbon. It is also claimed that the population of needle shaped species is influenced by the relative ratio of V:K. The desired type of vanadia is maximum at V:K = 15:20. It is apparent from Table 1 that the conversion of toluene to benzaldehyde at V:K 15:20 is maximum and this is in quite agreement with the above observations.

In their detailed review on oxidation of toluene in presence of wide number of metal oxides, Godedet et al. have reported that BZH was detected only in traces in case of ZnO. During a study of base catalysed adsorption of toluene by ZnO it has been observed that toluene is readily chemisorbed on ZnO surface, and with time undergoes dissociation resulting in benzyl radical alongwith OH species. The former may be looked upon as a precursor of BZH.

Many hydrocarbons including toluene having C-H bonds are amenable to polarization due to hyperconjugation effect. This polarization effect induces splitting of hydrogen from the hydrocarbon molecule to release a proton. This reaction takes place at the nucleophilic centres available in the catalyst surface. The number of such centres, it may be assumed, is enhanced in the catalyst surface by the introduction of ZnO. The mechanism of interaction between hydrocarbon and nucleophilic centre may be shown as:

The formation of carbanion has been confirmed by the spectral data during adsorption of toluene on the surface of ZnO. Carbanion thus formed is subsequently transformed into benzyl type (C$_6$H$_5$CH$_2$) surface radical when an electron is transferred to the catalyst. The benzyl radical thus formed is just the intermediate of BZH and with further depletion of one more electron carboxation (C$_6$H$_5$CH$_2$)$^+$ is formed and finally this carboxation takes up one oxygen ion, resulting in C$_6$H$_5$CHO.

The precise role of ZnO in combination with V$_2$O$_5$-K$_2$SO$_4$-SiO$_2$ may be adduced from the fact
that ZnO promote a nucleophilic addition of surface oxide ion which could be extracted from the surface in case of desorption of oxygenated species. In the present study a consistent conversion of toluene to BZH at the rate of 20 mol % per pass with more than 90% selectivity was achieved. It is worthwhile to mention here that the most difficult step of eliminating the formation of benzoic acid which happens to be the next immediate product following BZH in this controlled oxidation route, could successfully be avoided. Further, the absence of CO₂ at the exit end clearly suggest the environment friendliness of the reaction.

Support material is used primarily to disperse the active material and requires to be both chemically mechanically stable under the reaction conditions. But XPS investigation reveal that small crystallites of V₂O₅ having increased concentration of vanadium (IV) is possible when vanadyl oxalate was loaded on silica gel support. This vanadium (IV) is-believed to be the active constituent for catalysing this reaction. For preshaped inert support the obvious choice was silica gel. A large body of information is available on V₂O₅ loaded silica gel and the studies reveal that the pore texture including its geometry is crucially dependent upon the pH of precipitation of the silica gel. Fig. 1 indicates that the activity was maximum when the same catalyst loaded on the surface of the preshaped silica gel, precipitated at pH 7, and its declines at the either end of pH scale. Non optimum performance of the catalyst sample represented by A and C (Fig. 1) may be ascribed to the non ideal dispersion of the metal oxides on the available pores of the support. The pore radii of the samples A and C as implied by their respective pH of precipitation are either narrower or wider than the pore radius of the support D. It is probable, therefore, that the dispersion profile of the catalyst constituents in the case of A and C are different, in contrast to sample D. The commercial silica gel B, the study indicates, is not suitable support for this reaction.

The information that glean through this bench scale operation leaves impression that V₂O₅-K₂SO₄-ZnO-SiO₂ formulation may be suitable for developing industrial catalyst for vapour phase selective oxidation of toluene to BZH.

**Acknowledgements**

The authors thank Director, Central Fuel Research Institute, for his interest in the work and
Dr. Asit Bhattacharya for his technical assistance in GC analysis.

References