Metal oxide-support catalysis of the sucrose hydrolysis

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ABSTRACT

Using polarimetry technique we have investigated the acid – catalyzed inversion of sucrose in heterogeneous systems, and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} was selected as appropriate catalyst. This catalyst prepared by impregnation method. At the optimizing conditions the kinetic apparent parameters (A, E\textsubscript{a}, k) were calculated from data obtained from polarimeter with using the Arrhenius and Eyring method. The structure and particle size of catalyst has been studied with the use of XRD.

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INTRODUCTION

Investigation of the sucrose inversion plays an important role in the development of chemical kinetics because of its importance in food sweeteners industry especially for the fructose products\cite{1}. Although the industrial methods used nowadays for fructose type sweeteners are based on enzymatic hydrolysis of starch or sucrose with invertase enzyme, these technologies are laborious and expensive\cite{2}. Therefore, heterogeneous catalysis seems to be a good alternative for the sucrose hydrolysis reaction compared to the enzymatic or homogeneous procedures, because of its certain advantages like\cite{3-6}: the rigorous control of the reaction; the possibility of process automation; the higher purity of the reaction products, because of reducing the occurrence of secondary reactions; an easier separation of the catalyst from reaction medium; the absence of the equipment corrosion; the possibility to pilot the reaction at higher temperature than in the enzymatic process, which strongly favours the equilibrium displacement to the reaction products and also the possibility to re-use, several times, the catalyst. A number of catalysts have been reported for this reaction\cite{7-11}. In this article an attempt has been made to investigate the hydrolysis of sucrose by heterogeneous acid catalysis like TiO\textsubscript{2} and vanadium supported on titania. Thermodynamic and kinetic parameters are also reported. V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} is commonly used as a catalyst for a number of industrially important reactions, including the selective oxidation reactions of \textit{o}-xylene\cite{12-15} and ammoxidation of hydrocarbons\cite{16}.

EXPERIMENTAL

Catalyst preparation and conditions of the catalytic reaction

Sucrose, TiO\textsubscript{2}, NH\textsubscript{4}VO\textsubscript{3} and oxalic acid were of analytical grade (Merck) were used as received. Water was doubly distilled and degassed before use. The V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst was prepared by impregnation of TiO\textsubscript{2} with aqueous solution of NH\textsubscript{4}VO\textsubscript{3} in oxalic acid.
Excess water was evaporated while stirring, and solid thus obtained was dried at 343 K and calcined at 723 K for 3 h in air. Mass percent of V$_2$O$_5$ on TiO$_2$ (10 wt. %) was obtained according to the reported procedure$^{[17]}$. Hydrolysis of sucrose was investigated in the temperature interval of 50 to 80°C with 3, 5 and 7 g catalyst in 250 ml stirred solution of 0.3 M sucrose. Portions of the solution after centrifuging were taken out at known time intervals and the rotation of polarized light was noted with the help of a WXG-4 disk type polarimeter.

**Catalyst characterization**

XRD patterns were recorded on a D& ADVANCE diffractometer equipped with a Cu target and graphite monochromator, between $^\circ$10 and $^\circ$50 (2$\theta$) with radiation ($\lambda$=1.5406 A$^\circ$). The applied voltage and current were 40 kV and 80 mA, respectively.

**RESULT AND DISCUSSION**

**Inversion of sucrose**

The hydrolysis of sucrose to glucose and fructose, using the acid catalyst, proceeds according to the well-known equation:

$$[\text{H}]^+$$

C$_{12}$H$_{22}$O$_{11}$ + H$_2$O $\rightarrow$ C$_6$H$_{12}$O$_6$ + C$_6$H$_{12}$O$_6$

The reaction is irreversible and first-order with respect to the concentration of sucrose. For this reaction was used transition metal oxides TiO$_2$ and V$_2$O$_5$/TiO$_2$. Our experimental observation showed that the hydrolysis of sucrose did not occur by TiO$_2$. Hydrophilic character of TiO$_2$ may prevent the progress of hydrolysis. In this work the V$_2$O$_5$/TiO$_2$ (10 wt. %) was prepared and the progress of hydrolysis of sucrose was followed by the angles of rotation $r_t$ of the various sugar solutions at different temperatures with time (min). Typical results at 60$^\circ$C are graphically shown in Figure 1.

The reaction exhibits a first-order dependence with the following rate law:

$$ R = k \cdot C_{\text{suc}}$$  \hspace{1cm} (2)

Where

$$ k' = k \cdot m_{\text{cat}}^n$$  \hspace{1cm} (3)

or

$$ \ln k' = \ln k + n \ln m_{\text{cat}}$$  \hspace{1cm} (4)

By knowing $r_t$ we can determine the value of $k'$ using the following equation:

$$ [\ln (r_\infty - r_t)/(r_\infty - r_0)] = -k' \cdot t$$  \hspace{1cm} (5)

The value of $r_\infty = 6.5$ was calculated by the Guggenheim method$^{[18,19]}$ with data for 3 g of catalyst at 60$^\circ$C. It is clear that the plots of $[\ln (r_\infty - r_t)/(r_\infty - r_0)]$ vs. $t$(min) should be linear. Such plots were obtained in the present study and from the slope the value of $k'$ was evaluated. As a typical for 3 g catalyst 80$^\circ$C, the results are presented in Figure 2.

The linearity shown in Figure 2. supported a first order dependence on sucrose.
The Eyring equation may be suitably applied in the following form:
\[ \frac{RT}{HST} \exp(\Delta S^\neq) = k \]
\[ \Delta S^\neq = \Delta H^\neq / T \]
\[ \frac{\Delta H^\neq}{\Delta S^\neq} = \frac{RT}{k} \]
\[ k = \frac{RT}{\Delta H^\neq} \exp(-\Delta S^\neq / T) \]

The Arrhenius equation may be suitably applied in the following form:
\[ k = A \exp(-\frac{E_a}{RT}) \]
and as such a plot of \( k \) vs. \( 1/T \) will give a straight line. From the slope and intercept of this plot, the activation energy \( (E_a) \) and frequency factor \( (A) \) may be calculated, respectively. Results are given in TABLE 2 and also displayed graphically in Figure 3.

**TABLE 1**: Rate constants for hydrolysis of sucrose by \( \text{V}_2\text{O}_5/\text{TiO}_2 \) at different temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Rate constant ((k \times 10^4 \text{ s}^{-1}))</th>
<th>(\ln k) (\ln (k/T))</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>30.95</td>
<td>1.2</td>
<td>3.71</td>
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**TABLE 2**: Activation parameters for hydrolysis of sucrose by \( \text{V}_2\text{O}_5/\text{TiO}_2 \)

<table>
<thead>
<tr>
<th>(\Delta H^\neq) (\Delta S^\neq)</th>
<th>(E_a) (A \times 10^{-8})</th>
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<td>76.84 -0.0825</td>
<td>79.55 9.32</td>
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Structural characterization of the catalyst

Figure 5 shows the XRD patterns of the supported vanadia catalyst. On the basis of Scherrer's equation

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

particle size of synthesized catalyst \( (D) \) approximately was obtained 60 nm. Where \( \lambda \) is the wavelength, \( \beta \) is the full width at half maximum intensity of the peak and \( \theta \) is the diffraction angle.

**CONCLUSION**

For achieving hydrolysis is not to be feasible for such reaction, the following equation has recently been given by Bond:

\[ E_{app} = E_{tru} - \Delta H_A + \Delta H_B \]

The above equation refers for a binary system in which one of the components, \( A \) makes a strong bond with the surface \( \Delta H << 0 \). Hence, we suggest that for hydrolysis of sucrose one may select at suitable catalyst in which the magnitude of \( \Delta H_{ads} \) for \( \text{H}_2\text{O} \) should not be so high, which may be evaluated by theoretical or ex-

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Experimental methods. So that in spite of TiO$_2$ which are hydrophilic catalysts the V$_2$O$_5$ /TiO$_2$ has less tendency to the adsorption of water, and therefore could hydrolysis sucrose. The advantage of this catalyst is that after repeating the experiments with used catalyst, there was no decrease in reactivity. The another advantage is simplicity of production, suitable reactivity for hydrolysis and low cost in preparation of catalyst.

REFERENCES