



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_2O_5/TiO_2 was selected as appropriate catalyst. This catalyst prepared by impregnation method. At the optimizing conditions the kinetic apparent parameters (A , E_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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KEYWORDS

Hydrolysis;
Sucrose;
Heterogeneous catalyst;
X-ray diffraction
spectroscopy.

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^[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^[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^[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 displace-

ment 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^[7-11]. In this article an attempt has been made to investigate the hydrolysis of sucrose by heterogeneous acid catalysis like TiO_2 and vanadium supported on titania. Thermodynamic and kinetic parameters are also reported. V_2O_5/TiO_2 is commonly used as a catalyst for a number of industrially important reactions, including the selective oxidation reactions of *o*-xylene^[12-15] and ammoxidation of hydrocarbons^[16].

EXPERIMENTAL

Catalyst preparation and conditions of the catalytic reaction

Sucrose, TiO_2 , NH_4VO_3 and oxalic acid were of analytical grade (Merck) were used as received. Water was doubly distilled and degassed before use. The V_2O_5/TiO_2 catalyst was prepared by impregnation of TiO_2 with aqueous solution of NH_4VO_3 in oxalic acid.

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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_2O_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 7g 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.

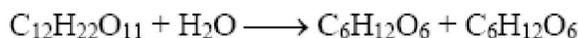
Catalyst characterization

XRD patterns were recorded on a D& ADVANCE diffractometer equipped with a Cu target and graphite monochromator, between 10° and 50° (2θ) with radiation ($\lambda=1.5406\text{\AA}$). 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:



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_2O_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_2O_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°C are graphically shown in Figure 1.

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

$$R = kC_{suc} \cdot m_{cat}^n \quad (1)$$

Here k is the rate constant, m is catalyst concentration ($g \cdot lit^{-1}$) and n is reaction order of catalyst. As the

catalyst weight is always constant in each experiment, so the rate law will be as follows:

$$R = k' \cdot C_{suc} \quad (2)$$

Where

$$k' = k \cdot m_{cat}^n \quad (3)$$

or

$$\ln k' = \ln k + n \ln m_{cat} \quad (4)$$

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

$$[\ln(r_\infty - r_t)/(r_\infty - r_0)] = -k' \cdot t \quad (5)$$

The value of $r_\infty = 6.5$ was calculated by the Guggenheim method^[18,19] with data for 3 g of catalyst at 60 °C. It is clear that the plots of $[\ln(r_\infty - r_t)/(r_\infty - r_0)]$ vs. $t(\text{min})$ 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 °C, the results are presented in Figure 2.

The linearity shown in Figure 2, supported a first order dependence on sucrose.

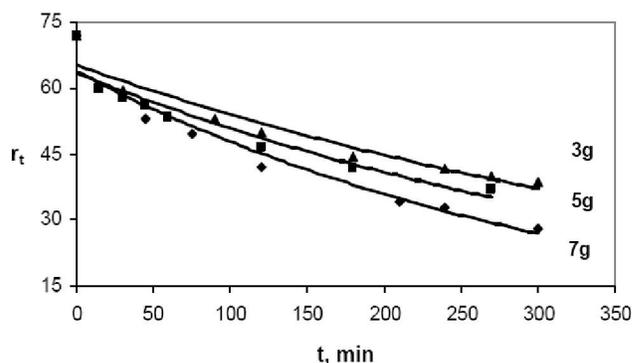


Figure 1 : Angle of rotation vs. time at 343 K

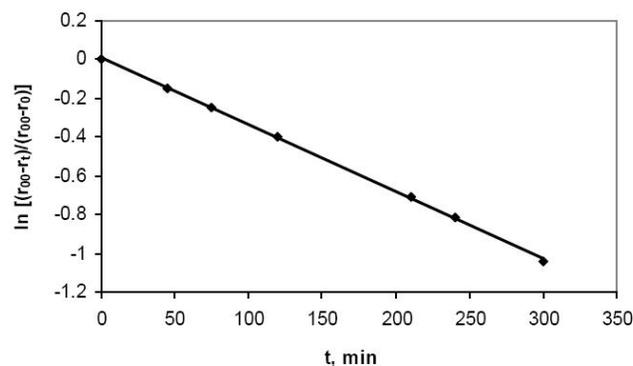


Figure 2 : $[\ln(r_\infty - r_t)/(r_\infty - r_0)]$ vs time for 7 g of catalyst at 343 K

The plots of $\ln k'$ vs. $\ln m_{cat}$ should be linear. From the intercept and slope value, the rate constant k and the reaction order n were evaluated at different tem-

peratures 50-80 °C. The values being reported in TABLE 1.

TABLE 1 : Rate constants for hydrolysis of sucrose by V_2O_5/TiO_2 at different temperatures

Temperature (K)	(1/T)×10 ⁴	Rate constant (k×10 ⁴ s ⁻¹)	(k/T)×10 ⁷	ln k	ln (k/T)	N
323	30.95	1.2	3.71	-9.03	-14.81	0.56
333	30.03	3.7	11.1	-7.91	-13.71	0.43
343	29.15	5.7	16.61	-7.47	-13.31	0.53
353	28.32	17.7	50.1	-6.34	-13.24	0.45

One can write the following Arrhenius equation

$$k = A \exp(-E_a / RT) \quad (6)$$

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 2 : Activation parameters for hydrolysis of sucrose by V_2O_5/TiO_2

ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (kJ.mol ⁻¹ .K ⁻¹)	E_a (kJ.mol ⁻¹)	$A \times 10^{-8}$
76.84	-0.0825	79.55	9.32

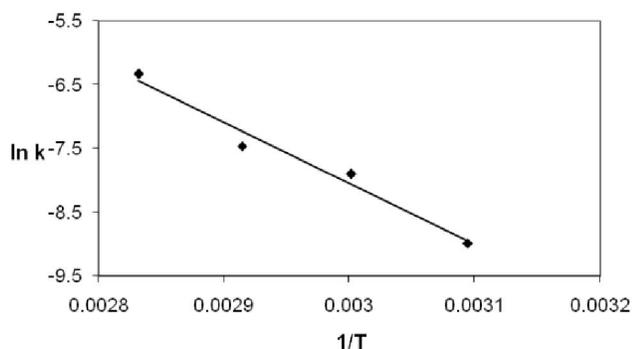


Figure 3 : Arrhenius plot ln k vs. 1/T

The Eyring equation^[20] may be suitably applied in the following form:

$$k = \frac{RT}{Nh} \exp(T \Delta S^\ddagger - \Delta H^\ddagger) / RT \quad (7)$$

where k is the rate constant and the order symbols have their usual significance. The equation leads to:

$$\ln(k/T) = \ln(R/Nh) + \Delta S^\ddagger / R - \Delta H^\ddagger / RT \quad (8)$$

Thus plot of $\ln(k/T)$ vs. $1/T$ should give a straight line, the slope and intercept of which may be used to compute enthalpy of activation, ΔH^\ddagger and entropy of activation, ΔS^\ddagger values, respectively. The values obtained are

also reported in TABLE 2 and displayed in Figure 4.

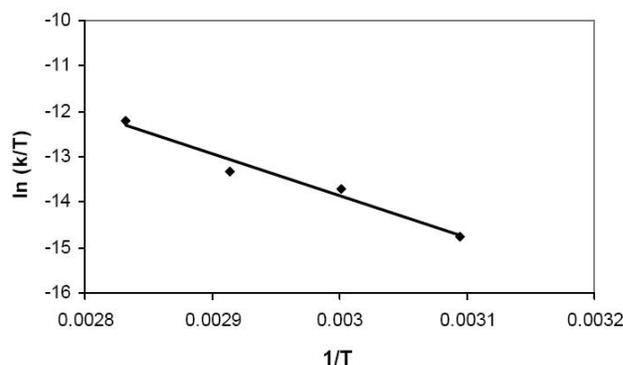


Figure 4 : Eyring plot of ln (k/T) vs. 1/T

Structural characterization of the catalyst

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

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (9)$$

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

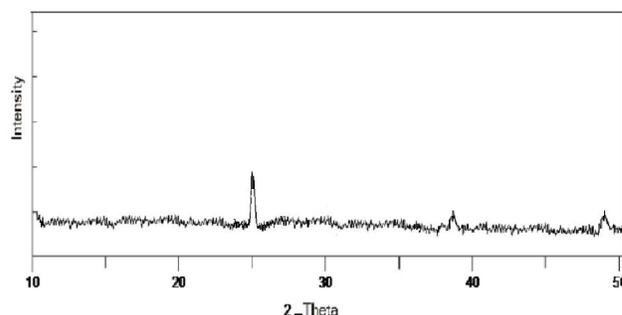


Figure 5 : XRD patterns of V_2O_5/TiO_2

CONCLUSION

For achieving hydrolysis is not to be feasible for such reaction, the following equation has recently been given by Bond^[21]:

$$E_{app} = E_{tru} - \Delta H_A + \Delta H_B \quad (10)$$

The above equation refers for a binary system in which one of the components, A makes a strong bond with the surface $\Delta H \ll 0$. Hence, we suggest that for hydrolysis of sucrose one may select at suitable catalyst in which the magnitude of ΔH_{ads} for H_2O should not be so high, which may be evaluated by theoretical or ex-

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perimental methods. So that in spite of TiO_2 which are hydrophilic catalysts the $\text{V}_2\text{O}_5/\text{TiO}_2$ 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.

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