Kinetics of benzyl alcohol reaction on heteropoly molybdate and salts

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The kinetics of the parallel reaction of benzyl alcohol on heteropoly compounds has been analyzed through power rate law as well as on the basis of Langmuir and Hinshelwood and Eley and Rideal models. From the values of adsorption coefficients and rate constants the order of activity is deduced to be HPV$_2$Mo$_{10}$O$_{40} >$ HPMo$_{12}$O$_{40} >$ NH$_4^+ >$ Cs$^+ >$ K$^-$. Among the various catalytic organic transformations studied on heteropoly compounds, the catalytic reaction of benzyl alcohol is interesting since it undergoes different types of reactions like dehydration, dehydrogenation and disproportionation depending on the nature of the catalyst used

The kinetic data were analyzed with power law rate equation of the form

$$R = kp_A^n$$

where $k$ is the lumped (composite) kinetic apparent rate constant and $n$ is the order of the reaction.

Results and discussion

Benzyl alcohol undergoes disproportionation and dehydrogenation on heteropoly molybdates to give benzaldehyde, toluene and water. Dibenzyl ether was not detected as in the case of heteropoly tungstates. The parallel reaction scheme is given by

$$2C_6H_5CH_2OH \rightarrow 2C_6H_5CHO + H_2O \rightarrow C_6H_5CH_3 + C_6H_5CHO$$

The data on the conversion of benzyl alcohol on all these catalysts have been reported earlier. The selectivity and other aspects of this reaction have already been reported by Athilakshmi and Viswanathan. Figure 1 shows the rate of disappearance of benzyl alcohol over heteropoly acid catalysts. The rate of disappearance of benzyl alcohol increases with increase of its partial pressure and passes through a maximum. This indicates a depressive behaviour of the reactant at high partial pressures of the reactant. This type of behaviour can be rationalized by dual site mechanism.

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Fig. 1—The rate of disappearance of benzyl alcohol over heteropoly acid catalysts. [A, HPV$_2$Mo$_{10}$O$_{40}$; B, H$_2$PMo$_{12}$O$_{40}$; C, (NH$_4$)$_2$PMo$_{12}$O$_{40}$; D, K$_2$PMo$_{12}$O$_{40}$; E, Cs$_2$PMo$_{12}$O$_{40}$]
tion. The plot of the rate of disappearance of benzyl alcohol against the partial pressure was found to be linear. The kinetic parameters were obtained by linear regression analysis and are given in Table 1.

The value of $n$ varied between 0.65 and 1.40. This is expected because the reaction is bimolecular. Since the reaction is heterogeneous in nature the reaction order is expected to be less than 2. These are the general observations in the case of heterogeneous reactions, because the active sites are nearly saturated at high partial pressures of reactant and the reaction order will approach the value of 0 at saturated coverage of the surface. The decreasing order of $n$ on the catalysts is

$$\text{HPV}_2\text{Mo}_{10} > \text{NH}_4^+ > \text{Cs}^+ > \text{HPMo}_{12} > \text{K}^+$$

This indicates that the saturation partial pressure of the reactant on the $\text{K}^+$ salt is less than that on other catalysts. This catalyst can be expected to have a strong reactant catalyst interaction (with strong adsorption strength) and hence is less active. The order of activity is

$$\text{HPV}_2\text{Mo}_{10} > \text{HPMo}_{12} > \text{NH}_4^+ > \text{Cs}^+ > \text{K}^+$$

It has been suggested that power law should not be used for correlating kinetic data on heterogeneous solid surfaces because it fails to give proper interpretation to kinetic parameters. This power rate law equation failed to give an insight into the strength of the adsorption of the reactant on the catalyst surface because $k$ cannot be separated into the components of true reaction rate constant and the equilibrium constant for adsorption. However it should be noted that the analysis shows that the data fit fairly well with the power rate law.

Assuming a dual site mechanism, the rate equations have been deduced on the basis of both Langmuir and Hinshelwood (LH) and Rideal Eley (RE) mechanisms. In the case of LH mechanism, the surface chemical reaction between two adjacent adsorbed species is the rate determining step and the corresponding expression for the disappearance of benzyl alcohol is

$$R_B = k \cdot k_A \cdot P_A^2 \cdot (1 + K_A \cdot P_A)^2$$  \hspace{1cm} \text{(3)}$$

According to the RE mechanism, the surface reaction is the rate determining step and one benzyl alcohol molecule directly from the physically adsorbed state or from the gas phase reacts directly with another chemisorbed benzyl alcohol. The corresponding rate equation has to be derived using a model in which for every adsorbed alcohol molecule there is an adjacent vacant site. The rate of disappearance of benzyl alcohol is given by

$$R_B = k \cdot k_A \cdot P_A^2 \cdot (1 + K_A \cdot P_A)^2$$  \hspace{1cm} \text{(4)}$$

The above rate equations have been simplified by neglecting the reverse reaction terms and assuming that the contributions of the products ($K \cdot P$) to the adsorption term are negligible. Qualitatively these two kinetic expressions will predict a reaction order between 0 and 2.
The kinetic data were analyzed by using the linear forms of Eqs 3 & 4. It is seen that good linear relationship exists confirming the applicability of the models assumed (Fig. 2). The values of adsorption desorption equilibrium constants were deduced from the slope and intercept of these plots and are given in Table 2. The order of adsorption desorption equilibrium constant is

$$K^+ > HPMO_{12} > Cs^+ > NH_4^+ > HPV_2Mo_{10}$$

This shows the order of the strength of adsorption of benzyl alcohol on these catalysts. It also indicates that lower saturation partial pressure will be required for $K^+$ salt.

The confidence limit of the applicability of these two models was ascertained by regression analysis. Results show that these models fit the observed kinetic data better than the power rate law. This conclusion is in conformity with the observations of Boudart$^9$ and Weller$^{10}$. The slope and the linear plot of predicted rate versus the observed rate over all these catalysts was 0.99.

This further confirms the validity of the models for analyzing the observed kinetic data.

It is worth noting that it is not possible to distinguish between LH and RE models. Similar conclusion has been drawn by Yue and Olaofe$^8$. It is, therefore, suggested that a competitive reaction scheme has to be devised to discriminate between LH and RE mechanisms as has been reported in literature.

References