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Catalytic activity of Pd(II) sorbed on an inorganic ion exchanger — zirconium molybdate

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Abstract

Zirconium molybdate has been used as a support on which Pd(II) has been sorbed. The materials have been characterised by elemental analysis, thermal analysis, spectral analysis (FTIR) and surface area measurements. The catalytic activity has been studied via hydrogen peroxide decomposition at different temperatures, using different concentrations of hydrogen peroxide and different amounts of catalyst. A probable mechanism for the reaction is suggested on the basis of the kinetic data obtained.

Keywords: Zirconium molybdate; Catalysis; Heterogenised homogeneous catalysis

1. Introduction

Heterogenising homogeneous catalysts [1–3] is a trend towards dissolution of the traditional disciplinary barriers between homogeneous and heterogeneous catalysis. Catalysis by supported metal ions and metal complexes is an area of intense interest [3,4]. Complexes have been affixed to polymers [3,5] formed in zeolite cavities [6] and affixed to silica or alumina surfaces [2]. Also complexes have been incorporated between the layers of a smectite clay (hectorite) by an ion exchange process [7,8]. However, there are a number of advantages in depositing catalytically active metals on a support. The metal can be highly dispersed as a result of which a large active metal surface is produced, relative to the weight of the metal used. This is especially advantageous with precious metals, if not recovered.

The ion exchange method of catalyst immobilization is simple when compared to procedures required for the attachment to polymers. The attractiveness of the method is further increased by providing temperature and solvent stable inorganic ion exchangers of known structures as supports.

Palladium and its complexes are versatile and extremely selective catalysts for a wide range of chemical reactions. They have been used for the hydrogenation of carbonyl and nitro groups at room temperature and atmospheric pressure, isomerisation of double bonds in olefins, allyl phenols, allyl benzene etc. and oxidation of primary and secondary alcohols at room temperature and atmospheric pressure [9–11].

The present work pertains to the study of a typical heterogenised homogeneous system. Zirconium molybdate (ZM) an inorganic ion ex-

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changer has been used as a support on which Pd(II) has been anchored by the method of ion exchange. The catalytic activity has been studied through hydrogen peroxide decomposition. The rate of chemical reaction and the factors influencing the rate, such as the amount of catalyst, substrate concentration and reaction temperature, are also discussed.

2. Experimental

2.1. Preparation of zirconium molybdate

Zirconium molybdate was prepared by the ammonium molybdate method as reported earlier [12].

2.2. Anchoring of Pd(II) onto zirconium molybdate

The acid treated ion exchanger (1 g) was placed in a glass conical flask fitted with a stopper. 25 ml of a known concentration of palladium chloride solution was added to this. The exchanger was kept in contact with the metal ion solution for 24 h with intermittent shaking. It was finally filtered, washed with conductivity water till the complete removal of the adhering metal ions and dried at 60°C. All washings were collected along with the filtrate to determine the quantity of Pd(II) ion remaining. The concentration of Pd(II) ion present on the exchanger was calculated from the difference between the initial and final concentration of the solution.

2.3. Kinetic studies

A weighed quantity of the catalyst was shaken with 10 ml (5 vol.) of hydrogen peroxide at 25°C. The desired concentration of hydrogen peroxide was obtained by successive dilutions of the stock solution. The volume of oxygen evolved was measured at various time intervals and also after complete decomposition of hydrogen peroxide using a gas burette. Experiments were carried out at different temperatures within the range of 25–40°C. The influence of various quantities of the catalyst used (0.025–0.075 g) was studied at 35°C. The effect of varying the concentration of hydrogen peroxide was also studied at 35°C.

2.4. Chemical and instrumental analyses

Zirconium was determined gravimetrically as zirconium oxide by precipitating with cupferron, molybdenum was determined gravimetrically using the α-benzoin oxime method while Pd(II) was estimated complexometrically using EDTA. The Na^+ exchange capacity of ZM was determined as usual by the column method [13]. The FTIR spectra of the samples were obtained on a Perkin Elmer, model 1720 X with Epson Hi 80 Printer/Plotter using the KBr disc technique. Thermogravimetric analysis of samples were performed on a Shimadzu DT = 30 thermal analyzer at a heating rate of 10°C/min. Surface areas of the samples were measured by the nitrogen adsorption BET method and recorded on a Carlo Erba sorptomatic series 1800, at −196°C.

3. Results and discussion

Chemical analyses indicate that the Zr:Mo ratio in zirconium molybdate is 1:1. Based on this the proposed formula for ZM is ZrO_2 $MoO_4 \cdot 15H_2O$. The number of water molecules were determined from the thermogram of the sample using Alberti's formula [14]. The Na^+ exchange capacity of ZM was found to be 1.02 milliequiv/g at room temperature.

The FTIR spectra of ZM shows broad bands in the region ca. 3400 cm^{-1}, attributed to asymmetric and symmetric hydroxo-(OH) and aqueous-(OH) stretches. A sharp medium band at ca. 1620 cm^{-1} is observed which is attributed to aqueous-(H–O–H) bending. A broad shoulder at ca. 935 cm^{-1} is attributed to the presence of

Zr–O stretching. FTIR of Pd(II) supported on ZM shows an additional band at ca. 620 cm^{-1} which may be attributed to Pd–O stretching.

TGA of ZM shows sharp changes within the temperature range of 100 to 180°C corresponding to the loss of external water molecules, after which slow change in weight is observed which may be due to the condensation of structural hydroxyl groups.

TGA of Pd ZM shows additional breaks within the temperature range of 400–460°C, which may probably be due to the loss of palladium from the surface of the support.

Further the value of surface area of Pd ZM is 60 m^2/g as compared to that of ZM, which is 25 m^2/g.

In the present investigation, the kinetic analysis is based on the initial rate data, since the reaction rate approaches an equilibrium after extended time intervals.

In the decomposition of hydrogen peroxide it was found that the rate was independent of the concentration of hydrogen peroxide (from 5 vol. to 7.5 vol. of H_2O_2, the rate was 1.2×10^{-4} min^{-1} (Fig. 1)) while an increase in the amount of catalyst from 7.0×10^{-4} to 2.1×10^{-3} g increased the rate of reaction from 9.5×10^{-5} to 1.6×10^{-4} K min^{-1} (Fig. 2) indicating that there is no dimerisation of the system in the range studied. An increase in the reaction temperature increases the rate of decomposition

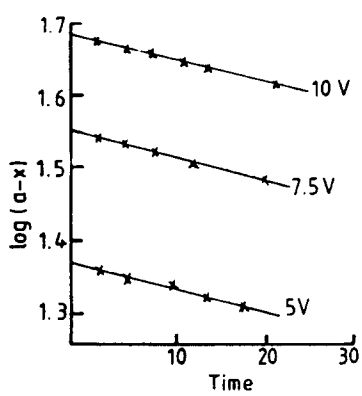

Fig. 1. Plot of log (a − x) vs. time for different concentrations of hydrogen peroxide.

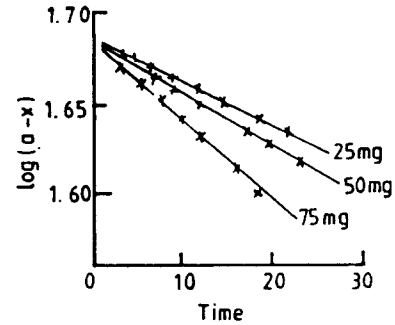

Fig. 2. Plot of log (a − x) vs. time for different amounts of the catalyst.

from 5.9×10^{-5} to 1.50×10^{-4} K min^{-1} (Fig. 3).

The colour of the surface adsorbed metal ion changed from light brown to yellowish brown when it came into contact with hydrogen peroxide. The colour persisted as long as any residual hydrogen peroxide remained in the system. After complete decomposition of the hydrogen peroxide, the catalyst regained its original colour. Similar results have been observed earlier [15–18]. This could be due to the formation of a peroxo species [19].

Based on the above observations the following reaction mechanism and rate equation have been suggested and proposed by us earlier [17,18].

It is known that H_2O_2 dissociates as

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad (1)$$

The metal ion bound to support may interact with HO_2^- ions to form an intermediate complex.

$$M^{2+} + HO_2^- \rightarrow [M(HO_2)]^+ \quad (2)$$

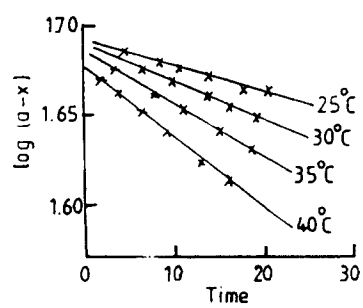

Fig. 3. Plot of log (a − x) vs. time for different temperatures.

A second molecule of H_2O_2 may then interact with the intermediate complex to form the products.

$$[M(HO_2)]^+ + H_2O_2 \rightarrow M^{2+} + H_2O + O_2 + OH^- \quad (3)$$

During the course of decomposition of hydrogen peroxide there is a continuous increase in pH which confirms the liberation of OH^- ions as per the suggested mechanism.

The activity of the surface metal ions is dependent on the availability of sites present on the surface of the support. Thus on increasing the amount of the catalyst, the rate constant should increase, which has been found so, as mentioned earlier in text.

The value of energy of activation for the decomposition of hydrogen peroxide is 11.0 kcal/mole (calculated from Fig. 4) suggesting that palladium sorbed onto zirconium molybdate is catalytically active. The activity may be explained by the formation of a stable complex between the metal and an oxygen donor, i.e., to the formation of an intermediate peroxo species.

The above work suggests the use of Pd ZM as a promising hydrogenation catalyst.

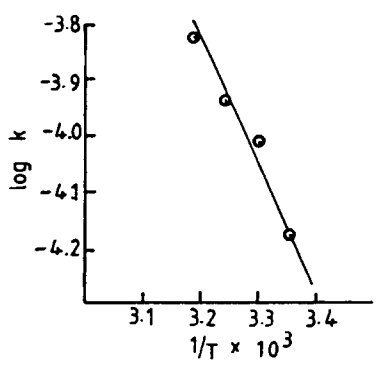

Fig. 4. Arrhenius plot.

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