

Decomposition of H_2O_2 using ion exchange resin with a spacer containing α -nitroso- β -naphthol as a functional group

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Abstract

Catalytic activity of some transition metal complexes derived from crosslinked styrene–divinylbenzene copolymer with spacer containing α -nitroso- β -naphthol as a functional group (Ps-ANBN) have been used for the decomposition of hydrogen peroxide (H_2O_2). The decomposition of H_2O_2 was investigated by measuring evolution of oxygen at different time intervals. Kinetic and thermodynamic parameters have been evaluated. Various metal complexes were used to study the effect of the nature of metal ion on decomposition of H_2O_2 . Scanning electron microscopy (SEM) have been used to study the morphological variation between Ps-ANBN and Ps-ANBN-Cu^{II}. The Ps-ANBN-Cu^{II} is found to be thermodynamically more stable than Ps-ANBN. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: H_2O_2 ; α -Nitroso- β -naphthol; Scanning electron microscopy

1. Introduction

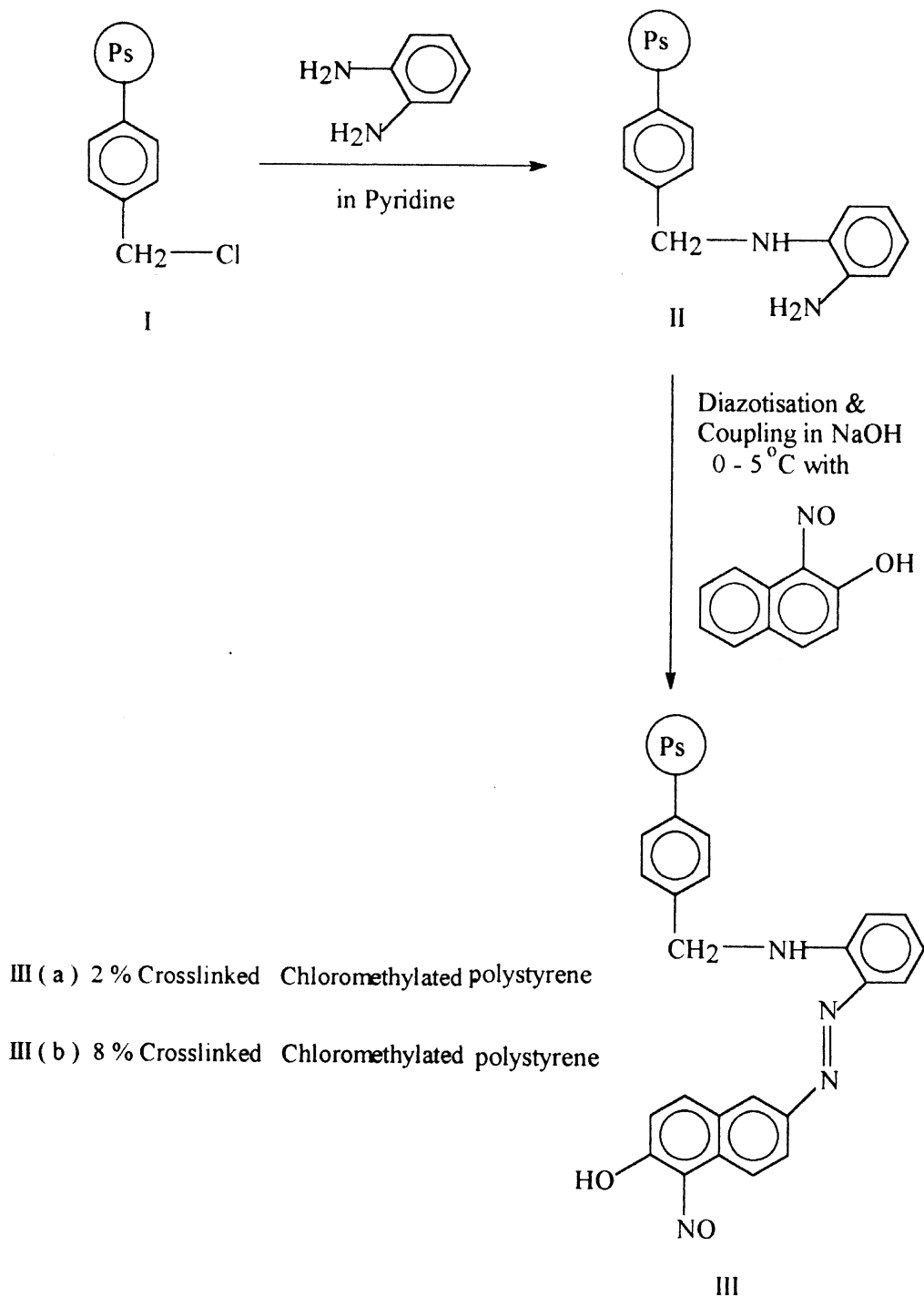
Hydrogen peroxide (H_2O_2), an important chemical used in various industries for chemical synthesis, environmental control, effluent treatment, bleaching, sterilization etc., provides a clean process without producing any harmful or environmentally unsafe product [1]. The use of chelating resin has been reported for a wide range of organic reactions. A common advantage in using polymer supported catalyst is found

to be in the ease of separation at any stage of reaction. Besides, an immobilized catalyst is sometimes more stable to atmospheric conditions, has greater bench stability and does not cause undesirable side reactions as is the case with homogeneous catalysts [2]. The catalytic efficiency of some transition metal complexed with Dowex-50W resin [3,4] on H_2O_2 decomposition has been studied. A radical chain mechanism was proposed for styrene–divinylbenzene immobilized-Cu(II) Schiff base complex in catalytic decomposition of H_2O_2 [5]. The main characteristics of the catalyst resulting from the polymeric structure are the insolubility, increased activity, stability and selectivity.

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It is also reported that the catalytic efficiency of metal ions increases by fixing them on to the

various supports [6–9], e.g., polymers, zeolites etc.



Scheme 1.

2. Experimental

2.1. Reagents and chemicals

Infra-red spectra (KBr disks) were recorded on FTIR (Perkin Elmer) spectrophotometer. Buffer solutions were prepared by using 0.2 M acetate buffers [10]. The metal ion content before and after complexation with modified polymer were determined spectrophotometrically by using Spectronic-20 [11]. Metal solutions were prepared by dissolving corresponding chlorides (reagent grade) in deionised water. Crosslinked polystyrene 2% and 8% (styrene–divinylbenzene copolymer) used as starting materials were obtained from Ion-Exchange, India. Galai Cis-1 was used to determine particle size of the resin.

2.2. Synthesis of resin

Resins II and III were prepared as per the reported procedure [12].

2.3. Preparation of metal complexes

The polymer supported ligand (200 mg) was stirred with metal salt solution (50 mg l^{-1}) for 24 h. The complexed resin was collected quantitatively. It was then purified by washing with deionised water and dried under vacuum. The difference between the initial and final metal contents gave the amount of metal ion complexed with resin [12].

2.4. Decomposition of H_2O_2

2.4.1. Gasometric measurements

The catalytic decomposition reaction of H_2O_2 in the presence of different metal complexes were studied by the conventional gasometric technique [13] by measuring the evolution of oxygen at different time intervals at different temperatures.

2.4.2. Kinetic measurements

A known amount of catalyst was stirred on a magnetic stirrer with H_2O_2 solution in a closed vessel at 35°C . The volume of oxygen gas evolved was measured at time interval using glass burette.

Similar experiments were also carried out at 40°C and 45°C . The value of specific reaction rate ' k ' was calculated from the plot of $\log(a-x)$ against time ' t ', where ' x ' is the volume of oxygen evolved, ' k ' of three different temperatures permitted the calculation of energy of activation (E_a) of the reaction by means of Arrhenius plot.

3. Results and discussion

The resin IIIa presented in this study was synthesized from chloromethylated styrene–divinylbenzene beads (2% and 8%) through the reaction steps shown in Scheme 1. IR spectrum of resin shows bands due to the nitroso group at 1350 , 1410 and 1510 cm^{-1} , a band between 1600 – 1700 cm^{-1} due to the tautomeric oxime

Table 1

Decomposition of H_2O_2 catalysed by Ps-ANBN-Cu^{II}; Catalyst: Ps-ANBN-Cu^{II}; Volume of H_2O_2 : 10 ml of 5 vol. H_2O_2 ; Weight of catalyst: 100 mg

Temperature (°C)	Specific reaction rate $k \times 10^{-3}$	E_a by graph (kJ mol^{-1})	E_a by calculation (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})
35	10.9					
40	9.94	13.780	13.290	10.691	81.360	-14.776
45	9.77					

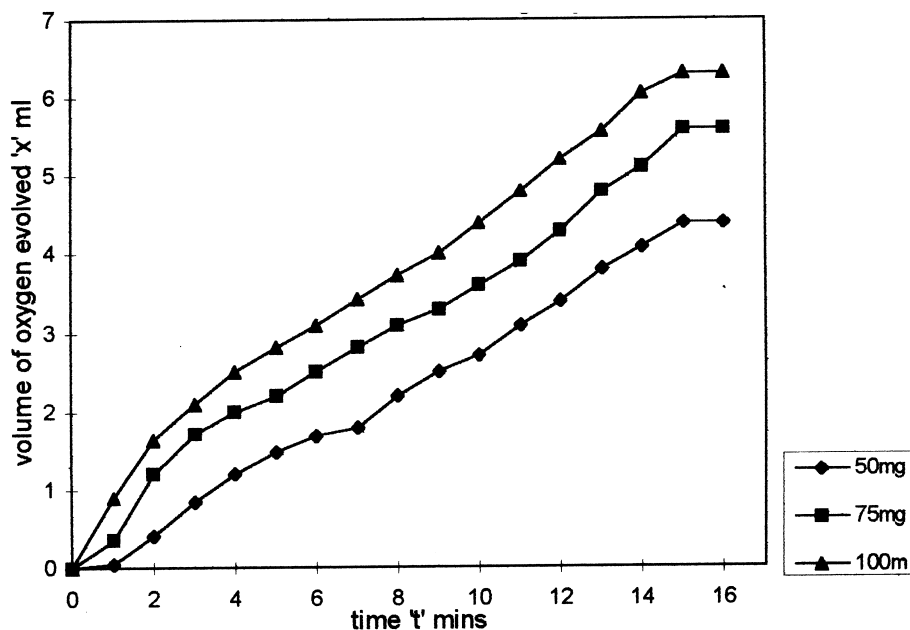


Fig. 1. Effect of concentration of catalyst on decomposition of H_2O_2 .

group and a band at 3150 cm^{-1} due to O–H stretching frequency of the phenol group. It is well known that some compounds containing

nitroso group and adjacent phenolic hydroxyl group forms complexes with transition metals. H_2O_2 contains the peroxy (–O–O–) linkage

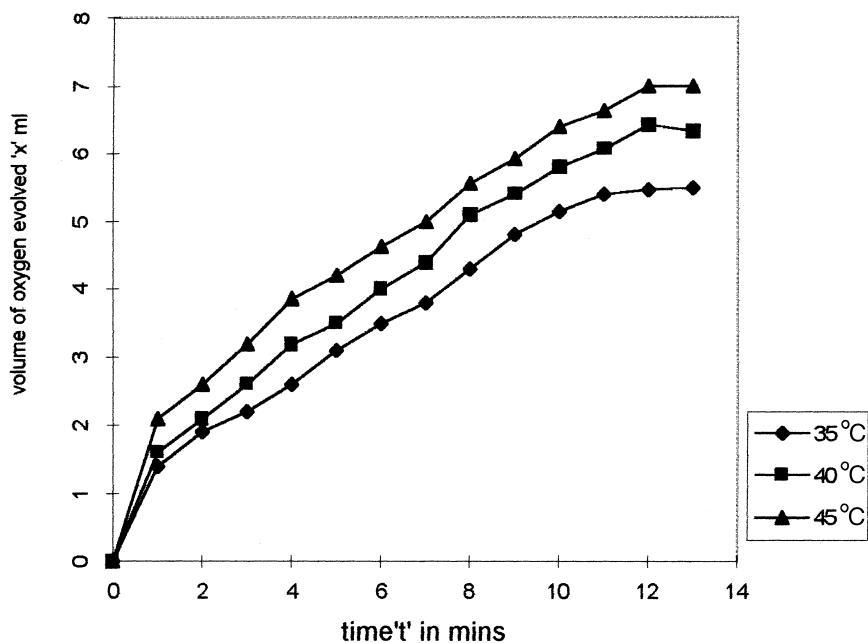


Fig. 2. Effect of temperature on decomposition of H_2O_2 .

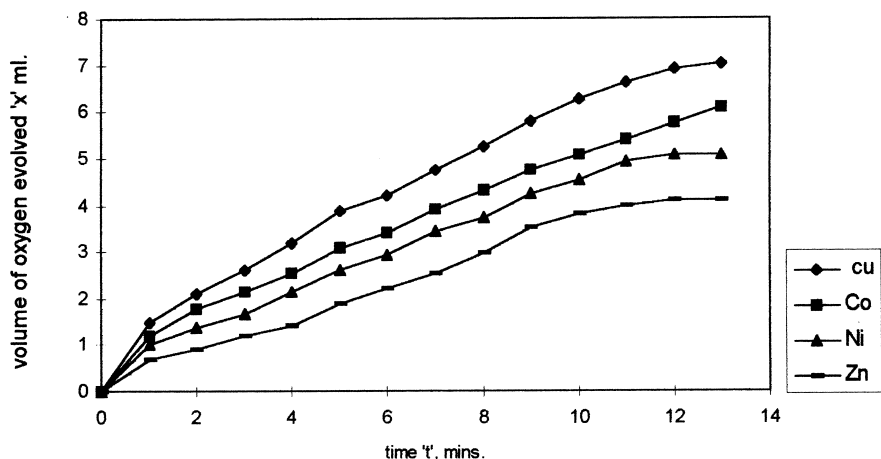


Fig. 3. Effect of various metal complexes on decomposition of H_2O_2 .

that get decomposed to H_2O and can be broken by liberating one atom as an active oxygen. The active oxygen is obtained by the controlled decomposition of hydrogen with H_2O as a product.

The results of our study on decomposition of H_2O_2 are presented and discussed below.

3.1. Effect of concentration of the catalyst and temperature on the decomposition of H_2O_2

The catalytic decomposition of H_2O_2 was studied at three different temperatures (35°C,

40°C and 45°C). The method adopted consisted essentially of following the kinetics of catalysed decomposition of H_2O_2 using a gasometric technique involving the measurements of the volume of oxygen evolved. The changes in entropy of activation ΔS^\ddagger , enthalpy of activation ΔH^\ddagger and free energy of activation ΔG^\ddagger have been calculated. The values are represented in Table 1.

The results suggests that the reaction rate ' k ' is governed by the entropy of activation. It has been suggested that when a system passes through a transition state, accompanied by a

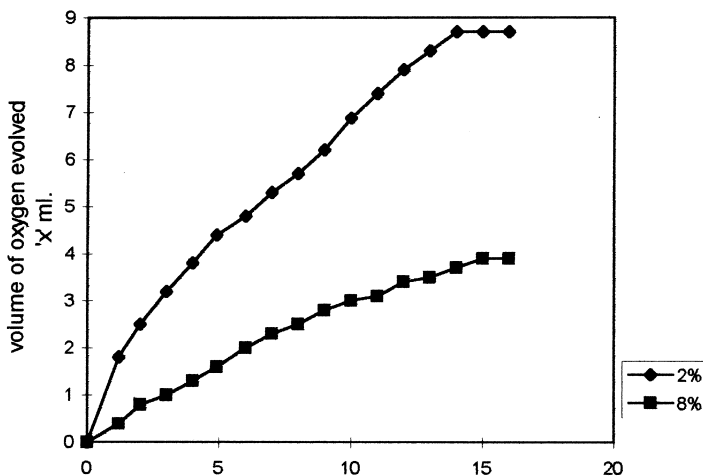


Fig. 4. Effect of crosslinking on decomposition of H_2O_2 .

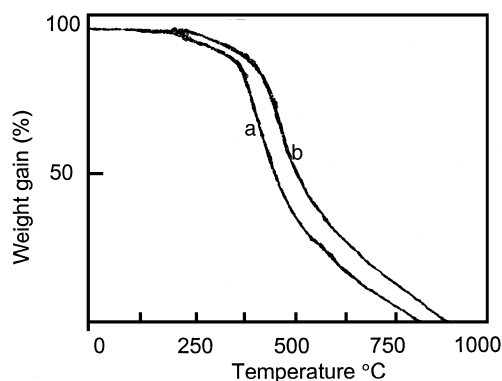


Fig. 5. TG curves of (a) Ps-ANBN and (b) Ps-ANBN-Cu^{II}.

large increase in entropy withstanding the large activation E_a , the reaction rate (k) will proceed at a high rate. Large positive entropy of activation, therefore appears to be an important factor contributing for the observed catalytic efficiency of the complex.

In polymer supported complexes, the active metal complex sites may be distributed evenly through out the particle surface and therefore the specific surface area is less important [14]. Moreover, the rate of reaction was found to be sensitive to the concentration of the catalyst, as shown in Figs. 1 and 2 and in Table 1. The rate was found to increase with the increase in the quantity of catalyst from $50 < 75 < 100$ mg. The same data also make a constructive statement that the catalytic decomposition is found to be favoured by higher temperature and quantity of catalyst.

3.2. Effect of various metal complexes on catalytic decomposition of H_2O_2

The decomposition of H_2O_2 was followed in the presence of Cu (II), Co(II), Ni (II) and Zn

(II) complexes of resin to study the effect of particular metal ion on the decomposition of H_2O_2 . The catalytic efficiency is found to decrease in the order of Cu (II) > Co (II) > Ni (II) > Zn (II) complexes. The chelating resin complexes are found to be active in catalytic decomposition of H_2O_2 . The extent of decomposition is found to be maximum with Cu (II) complexes, whereas catalytic efficiency of Zn (II) complexes is minimum as shown in Fig. 3.

3.3. Influence of extent of the crosslinking on the decomposition of H_2O_2

The extent of crosslinking agent in polymeric matrix influences the reactivity. Therefore, the influence of the extent of the crosslinking on the decomposition of H_2O_2 was studied by using 2% and 8% divinylbenzene-crosslinked styrene copolymers shown in Fig. 4. The less catalytic activity at higher crosslinking is due to the reduced accessibility of the reactive sites used for the complexation. Generally, a highly crosslinked system restricts the diffusion of the reducing species into the matrix [15] (Fig. 4).

3.4. Thermodynamic stability of the catalyst

Thermogravimetry of polymer metal complexes can reveal the variation of thermal stability by complexation with metal ions. Thermal stabilities of Ps-ANBN and Ps-ANBN-Cu^{II} were analysed by thermogravimetric analysis (TG) in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$. The TG curves of Ps-ANBN and Ps-ANBN-Cu^{II} are shown in Fig. 5.

Table 2
Thermal behaviour of Ps-ANBN and Ps-ANBN-Cu^{II}

No.	Polymer sample	IDT* (°C)	Weight loss (%) at temperatures shown					
			250°C	375°C	500°C	625°C	750°C	900°C
1	IIIa	300	2	12	60	78	92	100
2	IIIa-Cu ^{II}	250	5	10	43	69	86	97

Table 2 shows thermal behaviour of Ps-ANBN and Ps-ANBN-Cu^{II}. It is seen that both the resins almost decompose (95%) at 800°C.

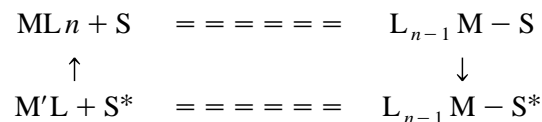
The initial decomposition temperature (IDT*) for Ps-ANBN is 300°C, whereas for Ps-ANBN-Cu^{II} it is 250°C. It is seen that Cu-complex of Ps-ANBN (IIIa) starts decomposing earlier than its resin IIIa. The reason for the early IDT is not clear. The second stage for both Ps-ANBN and Ps-ANBN-Cu^{II} is a major decomposition stage. In the case of Ps-ANBN, the stage starts from 375°C to 650°C; for the Ps-ANBN-Cu^{II} complex, it starts from 375°C to 500°C. Resin Ps-ANBN-Cu^{II} complex starts decomposing earlier but it remains thermodynamically more stable than Ps-ANBN after 400°C.

3.5. Reusability of the polymer supported metal complex in catalytic decomposition of H₂O₂

The extent of the decomposition of H₂O₂ in the presence of Cu(II) complexes were estimated for four cycles. After each use of the polymer, metal complex was collected and washed with water and dried. The complexes

are found to retain the catalytic property for repeated use.

The catalyzed cycle of metal complex catalyzed reaction may take place as follows



where M = metal atom, L = ligand, S = substrate, S* = activated substrate.

In the initial step, a substrate coordinates to a metal catalyst and forms an intermediate mixed complex (LMS). The substrate is then activated by the metal ions and dissociates from the catalyst. The complex catalyst having accomplished its purpose gets regenerated to the original complex. The catalytic action of the metal ion depends substantially on the nature of the ligands in the intermediate mixed complex.

The decomposition of H₂O₂ in the presence of Cu(II)-complexes is reported to be proportional to [H⁺] [H₂O₂] [CuL₂] [16].

Based on the above experimental observations, the reaction mechanism as shown in

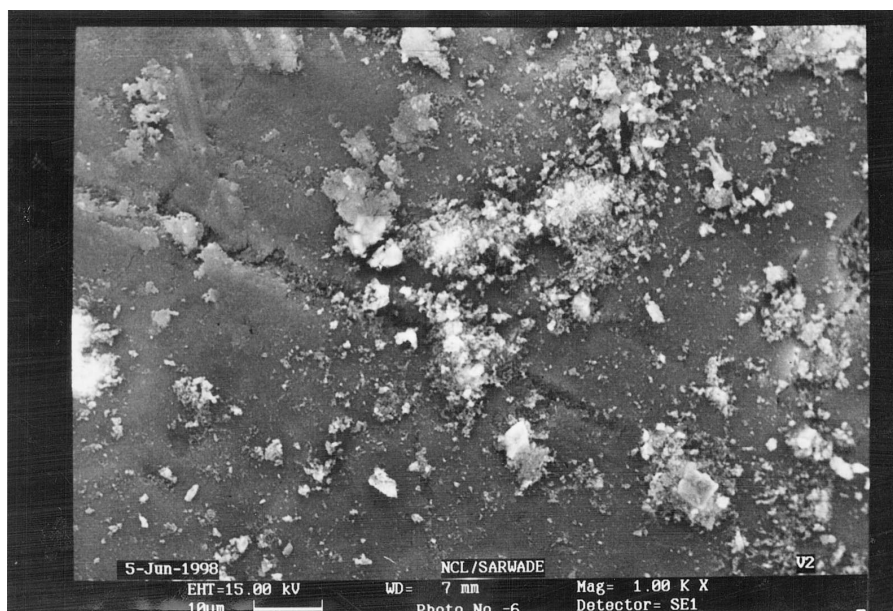
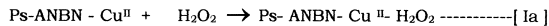


Fig. 6. Scanning electron microscopy (SEM) of Ps-ANBN-Cu^{II}.

Scheme 2 may be suggested and this involves interaction of H_2O_2 or ^-OOH ion on the surface complex.

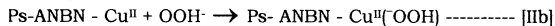
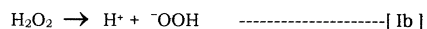


In second step H_2O_2 gets deprotonated;



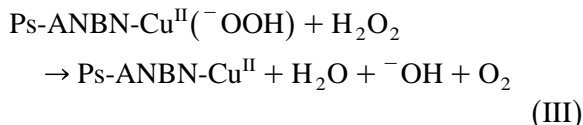
Scheme 2.

Alternatively the initial reaction may proceed through the formation of ^-OOH ion, as reported in decomposition of H_2O_2 catalysed by metal ion [17] (Scheme 3):



Scheme 3.

The reaction may then proceed through the common step III. The catalytic action in the decomposition of H_2O_2 may be attributed to the interaction of another molecule of H_2O_2 in this step.



The catalytic nature of the reaction was confirmed by recovering the complex catalyst unchanged at the end of the reaction. It was confirmed by IR spectra and SEM.

In order to delineate the morphological variation in resin IIIa (complexed and without complexed) and correlate them with their reactivity

and physical properties, SEM was employed. In the case of resin IIIa, the surface appears to be irregular and highly porous. The presence of large number of pores allows free and fair flow of solvents resulting in effective swelling and solvation. These cavities/voids disappear in case of resin IIIa– Cu^{II} complexed encapsulated species, suggesting that the encapsulation takes place at suitably sized cavities (Fig. 6). The FTIR spectra and the appearance of $\text{Cu}(\text{II})$ complexed catalyst before and after the reaction are found to be identical, showing that the catalyst used does not suffer any irreversible change in the structure.

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