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Short communication

Electroreduction of oxygen on mercury in the presence of titanium silicalite, TS-1

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1. Introduction

The use of titanium silicalites as catalysts for oxidation of organic compounds by hydrogen peroxide has received significant attention [1–5]. Such reactions are of practical importance as clean technological routes for industrially important oxidation schemes. In our laboratory, efforts were made to develop electrochemical routes for zeolite catalysed oxidation of organic compounds using electrogenerated hydrogen peroxide [6, 7]. The approach involves electrochemical reduction of molecular oxygen to hydrogen peroxide which oxidizes the organic substrate. Thus, unlike conventional anodic oxidations, here the oxidation is effected at the cathodic compartment. A number of organic compounds have thus been successfully oxidized [4, 5, 8]. However, the mechanism of these reactions is not fully understood. A logical approach to unravel the mechanism would be to first ascertain the mechanism of electroreduction of oxygen in presence of zeolite or its analogues. In this paper we discuss electroreduction of oxygen in presence of titanium silicalite, namely TS-1, employing mercury as the cathode using polarography as the technique of investigation.

2. Experimental details

Titanium silicalite, TS-1, prepared by reported procedures [9] was supplied by Dr S. Sivasankar, National Chemical Laboratory, Pune, India. The electrolyte was 0.1 M KNO_3 maintained at pH 5.6 using walpole acetate buffer. 0.01 g of the catalyst (crystal size 2 μm) was uniformly distributed into the electrolyte by continuous stirring for 6 h. Unless otherwise specified all chemicals used were E. Merck extra pure products. Triple distilled water was used in preparing the solution. All measurements were carried out at 298 ± 2 K. Constant potential macroelectrolysis of the electrolyte was carried out in a single compartment cell using mercury as the cathode (2.5×10^{-3} m^2 area) and a platinum gauze (7.5×10^{-3} m^2 area) as the anode. The cathode was maintained at a constant potential of 0.15 V vs SCE using Aplab (India) constant power supply unit. TS-1 (0.01 g) was dispersed into the electrolyte by continuous stirring. Oxygen (99.9% pure) was continuously bubbled through the electrolyte at a slow rate.

3. Results and discussion

The d.c. polarogram for the reduction of oxygen in 0.1 M KNO_3 (pH 5.6) is shown in Figure 1, curve 1. The polarogram is a two-step curve; each step being a $2e^-$ reduction. The first wave is a quasi-reversible reduction of oxygen to hydrogen peroxide and the second step is an irreversible reduction of hydrogen peroxide to water [10]. The corresponding d.c. polarogram in presence of TS-1 is shown in Figure 1, curve 2.

The important changes brought about by the presence of the catalysts are: (i) the second step of oxygen reduction, namely, that of $H_2O_2 \rightarrow H_2O$ is split up into two waves; and (ii) there is a considerable increase (about 10% increase) in the limiting diffusion current I_d of the first step, namely, $O_2 \rightarrow H_2O_2$.

The splitting up of the second oxygen wave is evidence that the intermediates of H_2O_2 reduction are stabilized at the electrode–electrolyte interface in the presence of the catalyst. It is an established fact that titanium and vanadium have the ability to form complexes with hydrogen peroxide [1, 11–13]. A species thus formed (a peroxide or an hydroperoxide) can undergo further reduction on the electrode surface which results in the splitting of the wave. Occasionally a post wave is seen at ~1.4 V (Figure 1). Its feature has been found to be that of adsorption by dependence of wave height on mercury column height [11]. The appearance of this wave is suggestive of a considerable degree of adsorption of hydrogen peroxide on the electrode surface.

It is of importance to note that a suppressor was not necessary to run the polarograms in presence of TS-1. The suppression effect of TS-1 indicates that the catalyst

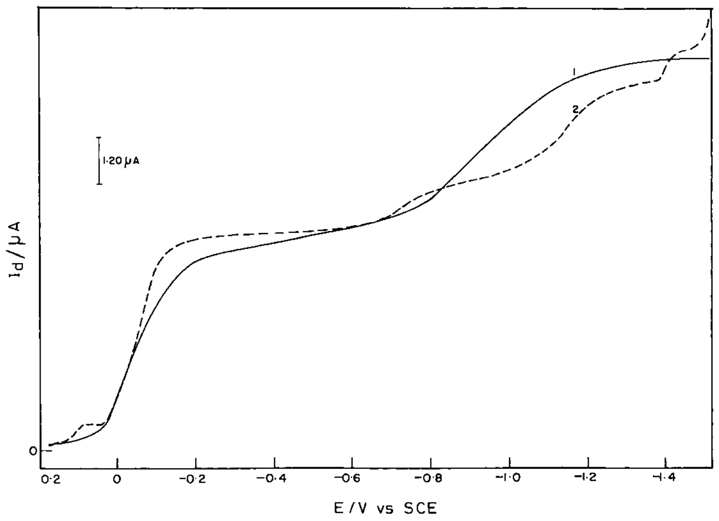


Fig. 1. D.c. polarogram for the reduction of oxygen in 0.1 M KNO_3 (pH 5.6) in presence (curve 1) and absence (curve 2) of TS-1.

particles finely dispersed in the electrolyte decrease the surface tension of mercury through adsorption on the electrode surface. In other words, the catalyst has the ability to assume its role as a part of the electrode that is, as an electrocatalyst.

In general, the wave heights of both the steps of oxygen reduction are expected to be equal because both are $2e^-$ reductions. However, even in the absence of TS-1, the first wave is about 6% higher than the second. A similar effect has been observed by several workers [14,15] meaning that there is some natural tendency for H_2O_2 to be decomposed on the mercury surface. The following mechanism is generally ascribed to the reaction.

$$O_2^{\bullet -} + H_2O_2 \rightarrow O_2 + OH^- + OH^\bullet$$

The fact that there is an additional increase in wave height in the presence of TS-1 indicates facilitated retention of H_2O_2 on the electrode surface, which allows the above reaction to take place. However, this disproportionation does not seem to be a major reaction route for H_2O_2 on titanium silicalite as indicated by a rather smaller amplitude of wave height increase. A small prewave is also observed at potentials in the vicinity of +0.05 V vs SCE. This may be ascribed to the adsorption of products in the $O_2 \rightarrow H_2O_2$ step in presence of titanium silicalite. The products could be either O_2, OH^-, OH or H_2O_2 because the zeolites have affinity for all oxygen species. This proposition is supported by the fact that the pre-wave does not appear in the absence of the titanium silicalite (Figure 1). The dependence of the polarographic reduction on TS-1 content is shown in Figure 2. There is a progressive decrease in wave height of the H_2O_2 reduction wave with increase in TS-1 content. Thus, the H_2O_2 absorbing property of TS-1 is proven beyond doubt.

When more and more of H_2O_2 is being generated in the solution by electrolysis, the disproportionation reaction diminished and absorption of H_2O_2 on the

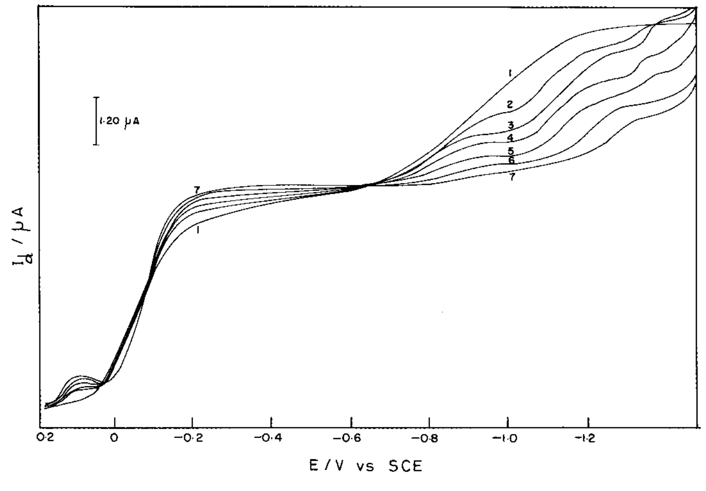


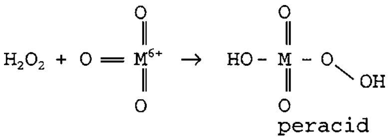
Fig. 2. Dependence of TS-1 content on the polarographic reduction of oxygen in 0.1 M KNO_3 (pH 5.6). Curve: (1) 0, (2) 0.005, (3) 0.01, (4) 0.025, (5) 0.05, (6) 0.06 and (7) 0.08 g.

titanium silicalite surface assumes significance. It is because of this absorption that there is a drastic decrease in the wave height of the second step (Figure 3, curve 2). The remaining hydrogen peroxide in solution undergoes stepwise reduction in two 1e regimes (as discerned by log analysis of the curve). The splitting of this $H_2O_2 \rightarrow H_2O$ step is an interesting observation which suggests that the intermediates of electroreduction of H_2O_2 are stabilized to a polarographically detectable level. The role of titanium silicalite in the stabilization is evident because the splitting is not observed in its absence (Figure 1, curve 1). When the electrolysis was continued beyond 0.5 h the wave heights increase owing to higher quantity of H_2O_2 accumulating in the solution.

The absorption or better the chemisorption of H_2O_2 by the titanium silicalite was supported by the colour change induced in dispersion during polarographic analysis, at potentials >1.2 V vs SCE resulting in a brownish purple coloration on the catalysts around 1.4 V vs SCE.

The catalyst separated from the reaction mixture by terminating the experiment was in fact deep brown in colour. The colour was retained during drying at 353 K. However, upon heating at ~573 K the colour discharged with a mild cracking sound. Visual examination indicated absence of metallic mercury along with the spent catalyst indicating the absence of occlusion of mercury into the catalyst. However, the absence of ultralevels if any of mercury requires to be ascertained by suitable technique. The synergistic action of the titanium silicalite as an integral compound of the mercury cathode is discernible from the electrochemical modifications observed as above.

In general the catalysis of H_2O_2-mediated chemical oxidations on titanium silicalities has been suggested to take place through a mechanism involving peracids which closely resemble organic peracids [16]:



$$H_2O_2 + O{=}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{M^{6+}}} \rightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{M}}-O-OH$$

On the other hand, a homolytic catalytic reaction involving the following mechanism has also been proposed for H_2O_2 mediated reactions [12]:

$$M^{n+} + H_2O_2 \rightarrow M^{(n-1)} + {}^{\bullet}OOH + H^+ \qquad (1)$$

$$M^{(n-1)} + H_2O_2 \rightarrow M^{n+} + {}^{\bullet}OH + {}^{-}OH \qquad (2)$$

$$^{\bullet}OOH + {}^{\bullet}OH \rightarrow H_2O + O_2 \qquad (3)$$

In the present context it is therefore reasonable to presume that chemisorption of H_2O_2 proceeds via formation of the per acid. The stepwise reduction of the remaining hydrogen peroxide in solution can be expected to follow the homolytic catalytic route, as under [13, 17–19]:

$$\text{TS-1(Hg)} + HO_2^{\bullet} \rightarrow \text{TS-1(HgO)} + OH^{\bullet}$$

$$\text{TS-1(HgO)} + O_2H^{\bullet} \rightarrow \text{TS-1(Hg)} + HO^{\bullet} + O_2$$

4. Conclusion

In the present work polarographic reduction of oxygen in the presence of titanium silicalite, TS-1, has been investigated. In the presence of the catalyst, the second step of the oxygen reduction wave (i.e., the reduction of hydrogen peroxide) undergoes splitting, together with a considerable reduction in the wave height, and a postwave is also exhibited. Observations suggest that hydrogen peroxide is chemisorbed on the electrode

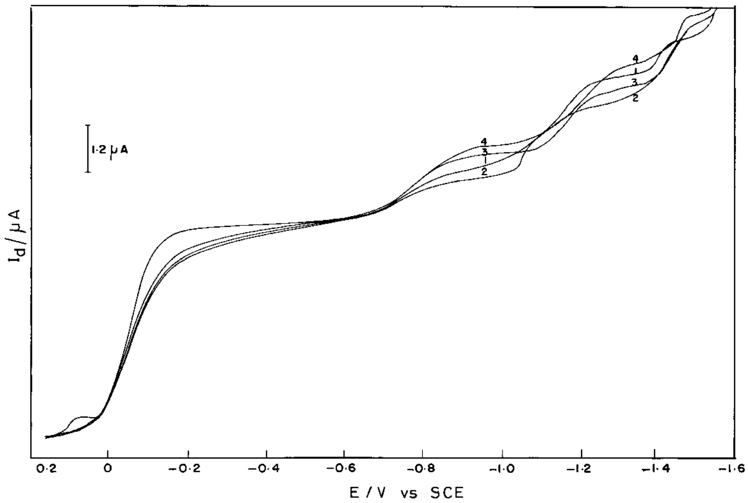


Fig. 3. Impact of electrolysis at −0.15 V vs SCE, on the polarographic reduction of oxygen in 0.1 M KNO_3 (pH 5.6). Duration of electrolysis: (1) 0, (2) 0.5, (3) 1.0 and (4) 1.5 h.

surface. The titanium silicalite finely dispersed in the electrolyte is responsible for the catalysis. Its role as an electrocatalyst rather than a catalyst is evident.

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