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The Catalytic autoxidation of sulfite by supported water-soluble iron porphyrins

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Abstract

Water-soluble iron porphyrins $\text{Fe}(n\text{-TMPyP})$ ($n = 2, 3$ and 4), immobilized on a zeolite molecular sieve, have been used as catalysts and for the catalytic autoxidation of SO_3^{2-} to sulfate effectively in the presence of oxygen at room temperature in aqueous solutions. The catalytic reaction rate of the sulfite oxidation is affected by the amount of catalyst immobilized on the zeolite molecular sieve. The initial concentration of SO_3^{2-} influences the reaction rate. The pH value and ionic strength of the aqueous solution also very obviously influence the catalytic reaction rates. The catalysts are active in the pH range in which $\text{Fe(IV)}(n\text{-TMPyP})$ can be generated by electrochemical method and can influence the SO_3^{2-} catalytic autoxidation mechanism. Fe(2-TMPyP) is more catalytically active than Fe(3-TMPyP) and Fe(4-TMPyP) under the same conditions. Fe(2-TMPyP) and Fe(3-TMPyP) are robust catalysts, while Fe(4-TMPyP) deactivates significantly. The orientation of *N*-methyl-pyridinium groups at the *meso* position of the porphyrin ring exhibit strong effects on the catalyst stability.

1. Introduction

The oxidation catalyzed by supported metalloporphyrins is of interest to many field of study [1]. Supported metalloporphyrin can be used as an oxidation catalyst [2]. Metalloporphyrin oxidation catalysts have been developed which use organic or mineral supports, for example ion exchange resins [3–5], silicates [6,7], or zeolites [8,9] (de Vismes et al. used manganese porphyrin fixed on zeolite [8], Mallouk et al. used tris(bipyridine)ruthenium(II)-*N,N'*-dialkyl-2,29-bipyridinium complex at the surface of a zeolite L particle [10]). Zeolites are also used to support some metal complex catalysts [11–13].

The oxidation of SO_3^{2-} is an important reaction in flue gas desulfurization. A different process of absorbing and converting sulfur dioxide into sulfate is desired and must be promoted [14,15]. Some oxidation studies using different catalysts have been investigated concerning sulfite oxidation [16].

This paper describes the heterogeneous catalytic autoxidation of sulfite by water-soluble iron porphyrins $\text{Fe}(n\text{-TMPyP})$ ($n = 2, 3$, and 4) supported on a zeolite molecular sieve (see Fig. 1). This catalytic oxidation is in the presence of oxygen, in basic aqueous solutions. The catalytic autoxidation rate is influenced by the pH and ionic strength of the aqueous buffer solu-

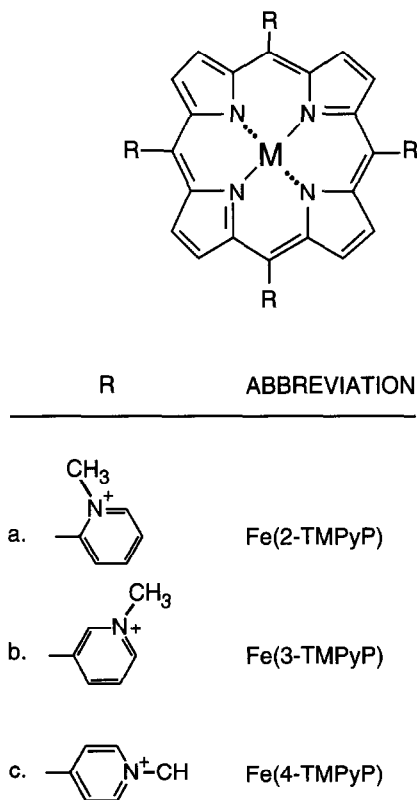


Fig. 1. Structure of Fe(2-TMPyP), Fe(3-TMPyP), Fe(4-TMPyP).

tion. This paper also reports the stability and catalytic activity for various catalysts of Fe(*n*-TMPyP) (*n* = 2, 3, and 4).

2. Experimental

A sample of Fe^{III}(2-TMPyP) was prepared according to a literature method [17,18]. Pyrrole and 2-pyridine carboxaldehyde were refluxed in propionic acid to obtain the *meso*-tetrakis(2-pyridyl)porphyrin(H₂(2-TPyP), C₄₀N₈H₂₆). Methylation was achieved by reacting H₂(2-TPyP) with neat dimethyl sulphate to form *meso*-tetrakis(*N*-methyl-2-pyridyl)porphyrin-([H₂(2-TMPyP)](SO₄CH₃)⁻). Metallation was achieved by refluxing H₂(2-TMPyP) with FeCl₂ · *x*H₂O in distilled water for 10 h. [Fe^{III}(2-TMPyP)]⁵⁺ was precipitated by drops of saturated NaClO₄ solution and recrystallized with water. The products were identified by their

UV-visible, IR, and NMR spectra. Fe(3-TMPyP) and Fe(4-TMPyP) were also synthesized by a literature method [17,18].

All of the chemicals were of analytical grade. Aqueous solutions were prepared with doubly distilled deionized water. Solutions were deoxygenated by purging with pre-purified nitrogen gas. Buffer solutions were prepared from H₂SO₄, KHP, acetate, phosphate, borate, carbonate, and KOH for the pH range 0–14. The pH values were measured with a HANNA Model 8418 pH meter.

Fe(*n*-TMPyP) catalysts were immobilized on a zeolite molecular sieve by the strong interaction between zeolite and the tetracationic iron porphyrins. A typical experiment is a 12 g zeolite molecular sieve (Aldrich, 8–12 mesh, 4 Å) in water (90 ml), containing Fe(*n*-TMPyP) (10⁻⁴ M). The contents were shaken and left standing until the minimize absorbance can be measured for iron porphyrin in the aqueous solution. The immobilized catalysts were then washed with and immersed in a buffer solution.

Catalytic autoxidation of sulfite by supported Fe(*n*-TMPyP) in the presence of oxygen was performed in a flask into which enough air bubbles have been added, and the contents have been stirred. The sulfite content is quantified by measuring the absorbance at λ = 210 nm through the use of a flow system with a micro cell and a UV-visible detector. Throughout this paper the catalysts are supported on a zeolite molecular sieve. The temperature of the solutions are 25 ± 1°C.

Electrochemistry was performed with a Bio-analytical system (West Lafayette, IN) Model CV-27 potentiostat and a BAS X-Y recorder. Cyclic voltammetry was conducted with the use of a three-electrode cell in which a BAS glassy carbon electrode (area 0.07 cm²) was used as the working electrode. The glassy carbon electrode was polished with 0.05 μm alumina on Buehler felt pads and ultrasonicated for 1 min. The auxiliary compartment contained a platinum wire which was separated by a medium-sized glass frit. All cell potentials were taken

with the use of a Ag/AgCl/KCl (saturated KCl solution) reference electrode.

The ion chromatograph used in the experiments was a Dionex Instruments Ion chromatography DX-100 consisting of a pump, conductivity detector, an electrochemical detector, and a syringe loading system with 25 μ l sample loop. The IC chromatograms were recorded using a Spectra-Physics DataJet computing integrator. The columns used throughout were an IonPac AG4A guard column, an IonPac AS4A analytical column, and a self-regenerating suppressor column. Typical LC operational parameters were as follows: mobile phase was a Na_2CO_3 and NaHCO_3 buffer solution, mobile phase flow rate was 2 ml/min; the column temperature was at room temperature. These parameters were used analyzing sulfate, sulfite and thiosulfate. Thiosulfate and $\text{S}_2\text{O}_6^{2-}$ were analyzed by an MPIC-NG1 guard column, an MPIC-NS1 analytical column, and a suppressor column.

3. Results and discussion

3.1. The catalytic autoxidation of SO_3^{2-} by $\text{Fe}(n\text{-TMPyP})$ ($n = 2, 3,$ and 4) in homogeneous system

The reaction of SO_3^{2-} with $\text{Fe}(3\text{-TMPyP})$ in a pH 9.2 borate buffer aqueous solution in the presence of oxygen is quantified by measuring the amount of sulfite absorbance at $\lambda = 210$ nm by using a flow system with a micro cell and a UV-visible detector. Sulfite is oxidized to sulfate.

Fig. 2 shows the changes of absorbance at 210 nm during a continuous process with only sulfite present, or with both sulfite and $\text{Fe}(2\text{-TMPyP})$ present into which sulfite has been continuously added in intervals of a few minutes.

The first step (Fig. 2(a)) is only a borate buffer aqueous solution as a baseline for this

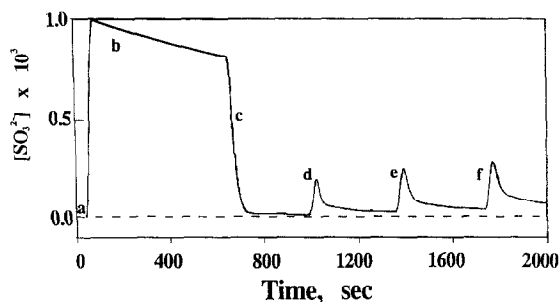


Fig. 2. Absorbance showing disappearance of sulfite at pH 9.2 borate buffer aqueous solution. The following processes is continuous from (a) to (f) by a flow system with a micro cell. (a) Only buffer solution, (b) added 1×10^{-3} M SO_3^{2-} , (c) added 5×10^{-7} M of $\text{Fe}(3\text{-TMPyP})$, (d) added 1×10^{-3} M SO_3^{2-} , (e) added 1×10^{-3} M SO_3^{2-} , (f) added 1×10^{-3} M SO_3^{2-} . Absorbance versus time scan wavelength set at $\lambda = 210$ nm.

system. When sulfite is added, the absorbance increases rapidly. The absorbance peaks (Fig. 2(b)), then comes down slowly. After $\text{Fe}(3\text{-TMPyP})$ is added, the absorbance decreases rapidly (Fig. 2(c)). Next, sulfite is added in intervals of several minutes and reoxidized rapidly by oxygen with $\text{Fe}(3\text{-TMPyP})$ present as a catalyst (Fig. 2(d), (e), (f)).

$\text{Fe}(2\text{-TMPyP})$ and $\text{Fe}(4\text{-TMPyP})$ also have similar catalytic activity in pH 9.2 borate aqueous solutions. $\text{Fe}(4\text{-TMPyP})$ is deactivated more easily than $\text{Fe}(2\text{-TMPyP})$ and $\text{Fe}(3\text{-TMPyP})$.

From the results, $\text{Fe}(n\text{-TMPyP})$ ($n = 2, 3,$ and 4) are all able to perform catalytic autoxidation of sulfite in a homogeneous system.

3.2. $\text{Fe}(n\text{-TMPyP})$ ($n = 2, 3,$ and 4) supported on zeolite molecular sieve

$\text{Fe}(n\text{-TMPyP})$ catalysts were immobilized on a zeolite molecular sieve by the strong interaction between zeolite and the tetracationic iron porphyrins. Iron porphyrin was dissolved in water, then a zeolite molecular sieve was added to the solution. The absorbance of the solutions at 350–700 nm are shown in Fig. 3. The results show that the iron porphyrin can be adsorbed onto a zeolite molecular sieve. The results also show that $\text{Fe}(4\text{-TMPyP})$ seems to interact with

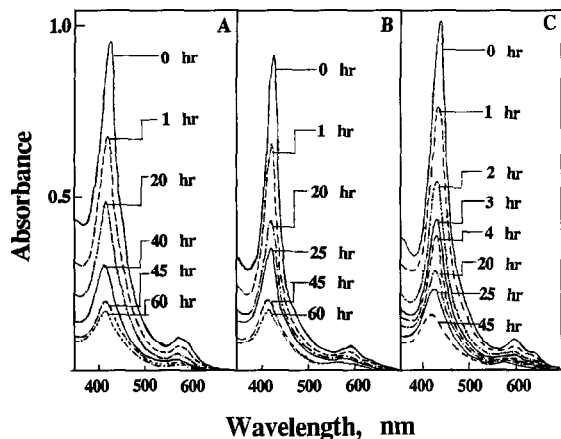


Fig. 3. Absorbance showing disappearance of $\text{Fe}(n\text{-TMPyP})$ in aqueous solution (30 ml) supported on zeolite molecular sieve (5 ml). (path length = 0.1 cm) (A) $\text{Fe}(2\text{-TMPyP})$, (B) $\text{Fe}(3\text{-TMPyP})$, (C) $\text{Fe}(4\text{-TMPyP})$.

the zeolite molecular sieve easier than $\text{Fe}(2\text{-TMPyP})$ and $\text{Fe}(3\text{-TMPyP})$ seemingly.

3.3. The catalytic autoxidation of SO_3^{2-} by $\text{Fe}(4\text{-TMPyP})$ supported on zeolite molecular sieve

Fig. 4(a) shows the SO_3^{2-} oxidation by oxygen in 0.05 M borate pH 9.2 buffer solution. Fig. 4(b) shows the same solution containing a 1 ml (dry weight 0.725 g) zeolite molecular sieve. Higher oxidation rates were obtained when the solution contained various volumes of

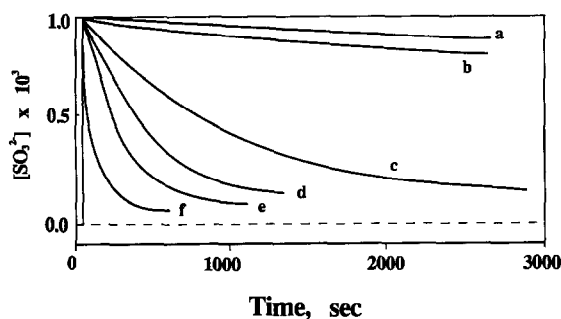


Fig. 4. Concentration of SO_3^{2-} versus time determine on $\lambda = 210$ nm of an oxygen present pH 9.2, 0.1 M borate buffer solution with different amount of $\text{Fe}(4\text{-TMPyP})$ supported on zeolite with concentration 2.7×10^{-7} mol/ml, $[\text{SO}_3^{2-}] = 10^{-3}$ M. (a) Only buffer solution, (b) add 1 ml zeolite molecular sieve without supporting catalyst, (c) 7×10^{-7} mol/l, (d) 1.4×10^{-6} mol/l, (e) 2.7×10^{-6} mol/l, (f) 5.4×10^{-6} mol/l.

catalyst ($\text{Fe}(4\text{-TMPyP})$ supported on a zeolite molecular sieve) (Fig. 4(c)–(g)). The catalytic reaction rate is obviously faster than when sulfite is present with oxygen only, or with oxygen and the unsupported zeolite molecular sieve. An initial reaction rate of about 9×10^{-6} M/s was obtained by measuring the change of the sulfite concentration.

The initial rate was found to increase with the rate of O_2 supply. It was also influenced by the stirring rate and the O_2 bubbling rate. In these experiments, the reaction rate appears nearly independent of stirring speed at more than 200 rev/min when the solution is just exposed to air. However, the experiments were performed with the stirring rate of more than 250 rev/min, and with sufficient gas bubbling.

3.4. The catalytic autoxidation of SO_3^{2-} by various iron porphyrins supported on zeolite molecular sieve

Fig. 5 shows the electrocatalytic autoxidation of SO_3^{2-} in the presence of oxygen by various supported catalysts ($\text{Fe}(n\text{-TMPyP})$, $n = 2, 3$, and 4) in a 0.05 M borate pH 9.2 buffer solution, when the substrate is added periodically. The results show that the catalytic reaction by $\text{Fe}(2\text{-TMPyP})$ is faster than when using $\text{Fe}(3\text{-TMPyP})$ or $\text{Fe}(4\text{-TMPyP})$ as a catalyst. The

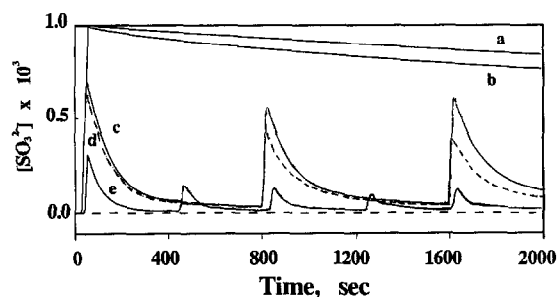


Fig. 5. Concentration of SO_3^{2-} versus time determine on $\lambda = 210$ nm of an oxygen present pH 9.2, 0.1 M borate buffer solution with various catalyst of 2.7×10^{-6} mol/l $\text{Fe}(n\text{-TMPyP})$ supported on zeolite molecular sieve (2.7×10^{-7} mol catalyst/ml support). 10^{-3} M of sulfite adds continuously after the prior addition sulfite have exhausted. (a) 0.0 mol/l, (b) add 1 ml zeolite molecular sieve without supporting catalyst, (c) $\text{Fe}(4\text{-TMPyP})$, (d) $\text{Fe}(3\text{-TMPyP})$, (e) $\text{Fe}(2\text{-TMPyP})$.

initial reaction rates are about 21×10^{-6} , 10×10^{-6} , and 9×10^{-6} M/s, respectively. Sulfite is added repeatedly some time after the substrate has mostly been exhausted. This figure shows that the sulfite added in intervals of several minutes is reoxidized rapidly by oxygen with Fe(*n*-TMPyP) (*n* = 2, 3, and 4) supported on a zeolite molecular sieve acting as the heterogeneous catalyst.

Ion chromatography determined the product of the catalytic oxidation performed on a pH 9.2 aqueous solution containing sulfite, supported catalyst, and the product. After the substrate is exhausted, the product is quantified by ion chromatography. The results show that the SO_4^{2-} is the only product of the catalytic oxidation of SO_3^{2-} by the supported catalysts (Fe(2-TMPyP), *n* = 2, 3 and 4).

3.5. The stability of the catalysts

Fig. 6 shows the reaction rate and the change after different turnover numbers, of the catalytic autoxidation of SO_3^{2-} in the presence of oxygen by various supported catalysts (Fe(*n*-TMPyP), *n* = 2, 3, and 4) in a 0.05 M borate pH 9.2 buffer solution. The results show the stability of various catalysts after different turnover numbers. The catalytic activity from the initial reaction rate of Fe(2-TMPyP) and Fe(3-TMPyP) are almost the same value after a turnover number of about 15,000. This is a sulfite to sulfate turn average of 7500 by each supported catalyst molecule. Fe(4-TMPyP) shows the activity decreasing by about 40% after a turnover number of 10,000. This is a turn average of 5000 sulfite to sulfate.

The results show that Fe(2-TMPyP) is more catalytically active than Fe(3-TMPyP) and Fe(4-TMPyP) by about 2, and 2.3 times, respectively. Fe(2-TMPyP) and Fe(3-TMPyP) are robust catalysts while Fe(4-TMPyP) deactivates significantly after turning 10,000 sulfite to sulfate. The results show that the orientation of the *N*-methyl-pyridinium groups at the *meso* posi-

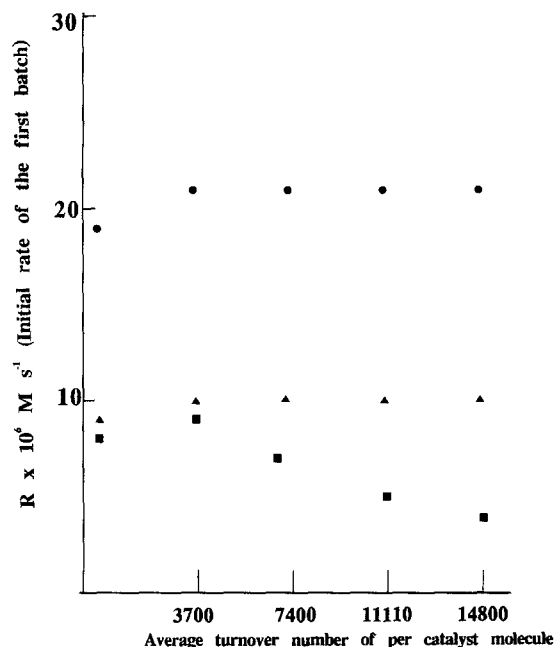


Fig. 6. Initial rate constant versus after different turnover number in various initial concentration of SO_3^{2-} in an oxygen saturated 0.1 M borate pH 9.2 buffer solution. (a) Fe(2-TMPyP), (b) Fe(3-TMPyP), (c) Fe(4-TMPyP).

tion of the porphyrin ring exhibit strong effects on the catalytic stability and activity.

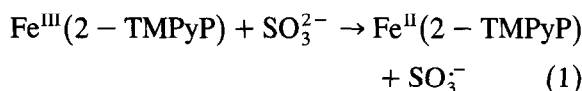
Elemental analyses have been performed before and after batch experiments. No back-exchange occurs during the oxidative reaction carried out in buffer solution by measuring the absorption spectrum of iron porphyrin or adding 1,10-phenanthroline and reducing reagent. Fe(4-TMPyP) easily deactivates after turning sulfite to sulfate, but no Fe(4-TMPyP) or decompositive product back-exchange to buffer solution.

3.6. The catalytic autoxidation mechanisms

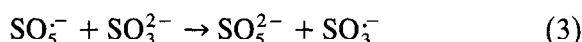
We have performed the electrocatalytic oxidation of sulfite in the absence of oxygen and the catalytic autoxidation in its presence [19]. The results show that $\text{Fe}^{\text{III}}(2\text{-TMPyP})$ oxidizes to $\text{Fe}^{\text{IV}}(2\text{-TMPyP})$ by either SO_5^{2-} without oxygen, or SO_3^{2-} in the presence of oxygen. We have proposed a mechanism for explaining the catalytic autoxidation of SO_3^{2-} by water-soluble iron porphyrin. The mechanisms include:

Fe^{III}(2-TMPyP) is reduced to Fe^{II}(2-TMPyP) by SO₃²⁻, and SO₃²⁻ is oxidized to SO₃⁻. In the presence of oxygen, SO₃⁻ reacts with O₂ to rapidly produce SO₅⁻. Fe^{II}(2-TMPyP) can reduce SO₅⁻ to SO₅²⁻, and SO₅²⁻ can oxidize Fe^{III}(2-TMPyP) to Fe^{IV}(2-TMPyP), then Fe^{IV}(2-TMPyP) can oxidize SO₃²⁻ to SO₄²⁻. In pH 9.2, the processes are as follows:

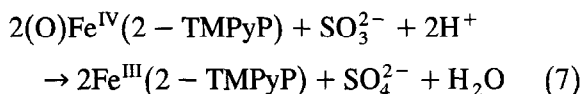
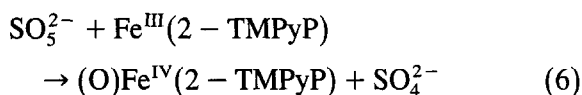
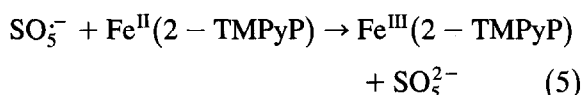
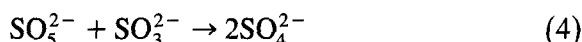
Initiation:



Propagation:



Termination:



The catalytic oxidation of sulfur dioxide by Fe³⁺ in aqueous solution in the presence of oxygen also has a reduction and an oxidation process [20].

Figs. 5 and 6 also show that in the first batch of the sulfite oxidation, the reaction rate is usually slower than the second or third batch. The reason may be that Fe^{III}(*n*-TMPyP) is reduced by sulfite and produces some intermediates, for example SO₃⁻, SO₅⁻, and SO₅²⁻. Fe^{III}(*n*-TMPyP) is also oxidized by SO₃²⁻; and produces Fe^{IV}(*n*-TMPyP). All of the above intermediates cause the catalytic oxidation rate of the second or third batch to have a faster initial reaction rate than the first batch.

Table 1 shows the formal potential of Fe(*n*-TMPyP) in various oxidation states. Fe(2-TMPyP) has a more positive formal potential of

Table 1

The formal potential of various iron porphyrins in pH 9.2 borate buffer solution

	Fe[(IV/III)]	[Fe(III/II)P]	[Fe(II/I)P]
Fe(2-TMPyP)	+0.57 ^b	-0.15 ^a	-0.76 ^b
Fe(3-TMPyP)	+0.59 ^c	-0.23 ^c	-0.93 ^c
Fe(4-TMPyP)	+0.60 ^a	-0.24 ^c	No

^a Ref. [21].

^b Ref. [22].

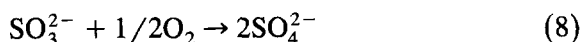
^c This work.

Fe(III/II)P than Fe(3-TMPyP) and Fe(4-TMPyP). The formal potential of Fe(2-TMPyP) is also less positive than Fe(3-TMPyP) and Fe(4-TMPyP). This is because the Fe^{III}(2-TMPyP) is reduced by SO₃²⁻ more easily than Fe^{III}(3-TMPyP) and Fe^{III}(4-TMPyP). Also, Fe^{III}(2-TMPyP) is oxidized by SO₅²⁻ more easily than Fe^{III}(3-TMPyP) and Fe^{III}(4-TMPyP). The catalytic reaction by Fe(2-TMPyP) is faster than Fe(3-TMPyP) or Fe(4-TMPyP). The initial reaction rates of the catalytic oxidation by Fe(3-TMPyP) and Fe(4-TMPyP) are similar.

Table 1 also shows the formal potential of Fe(II/I)P. Fe(2-TMPyP) and Fe(3-TMPyP) have a Fe(II/I)P redox couple but Fe(4-TMPyP) does not. The electrochemistry of Fe(2-TMPyP) and Fe(3-TMPyP) both involve metal central reduction, but the Fe(4-TMPyP) shows ring decomposition in the potential near -0.7 V (versus Ag/AgCl). The main cause of the deactivation of the sulfite oxidation by water-soluble iron porphyrin is the destruction of the porphyrin ring by sulfite and/or its intermediates. Both Fe(2-TMPyP) and Fe(3-TMPyP) are more robust than Fe(4-TMPyP) due to the lack of ring destruction.

3.7. Effects of pH

The catalytic autoxidation of SO₃²⁻ in the presence of oxygen by Fe(2-TMPyP) is not effected by pH according to the following equation:



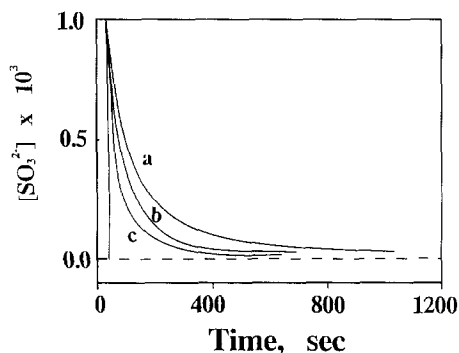


Fig. 7. Absorbance showing disappearance of sulfite in different pH buffer aqueous solution with ionic strength 0.1. (a) pH 11.5 $\text{Na}_3\text{PO}_4 + \text{Na}_2\text{HPO}_4$. Concentration of SO_3^{2-} versus time determine on $\lambda = 210$ nm of anbuffer, (b) pH 9.2 borate buffer, (c) pH 7.2 $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$. Oxygen present buffer solution with 10^{-3} M sulfite. $[\text{SO}_3^{2-}] = 10^{-3}$ M, [supported $\text{Fe}(4\text{-TMPyP})] = 2.7 \times 10^{-6}$ mol/l.

If the catalytic oxidation is through an electron transfer process, an increase in pH will favor the sulfite oxidizing to sulfate.

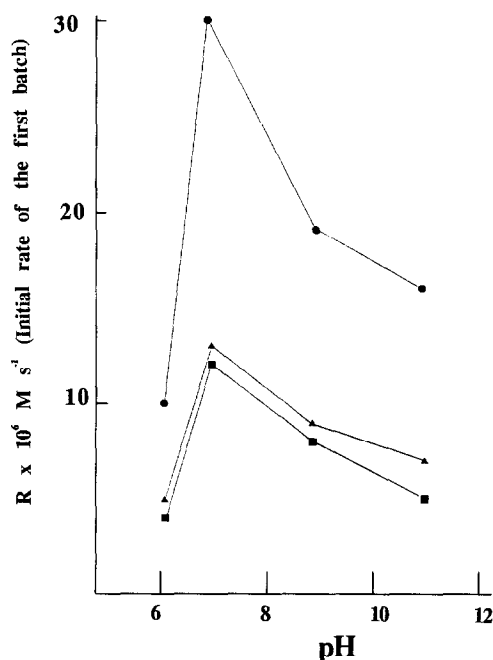
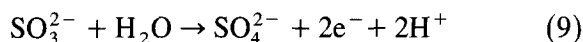


Fig. 8. Initial rate constant versus pH with ionic strength 0.1 by various catalyst supported on zeolite molecular sieve. $[\text{SO}_3^{2-}] = 10^{-3}$ M, [supported catalyst] = 2.7×10^{-6} mol/l. (●) $\text{Fe}(2\text{-TMPyP})$, (▲) $\text{Fe}(3\text{-TMPyP})$, (■) $\text{Fe}(4\text{-TMPyP})$.

Fig. 7 shows the influence of pH on the catalytic oxidation in the presence of oxygen. $\text{Fe}(n\text{-TMPyP})$ ($n = 2, 3$, or 4) all show the same result (Fig. 8), as the pH values of the aqueous solution decreases, the initial rate of catalytic oxidation increases significantly. If the $\text{pH} < 7$, the reaction rate of the catalytic oxidation decreases abnormally. The reason is that $\text{Fe}^{\text{IV}}(n\text{-TMPyP})$ can oxidize from $\text{Fe}^{\text{III}}(n\text{-TMPyP})$ only in basic aqueous solutions. This was determined from spectroelectrochemical method [21,22]. As the pH value of the aqueous solution decreases, the catalytic oxidation rate increases. The catalytic oxidation is performed through a $\text{Fe}^{\text{IV}}(n\text{-TMPyP})$ process. The effect of pH is significant on the sulfite autoxidation catalyzed by $\text{Fe}(n\text{-TMPyP})$ in the presence of oxygen. This may be explained by the interaction of support and counterion serving to sulfite, increasing its concentration near the catalyst site.

3.8. Effects of ionic strength

Fig. 9 shows the reaction rate of the catalytic autoxidation of SO_3^{2-} in presence of oxygen by supported catalyst [$\text{Fe}(4\text{-TMPyP})$] in different ionic strengths of borate pH 9.2 buffer solutions. The data shows that the effect of an ionic strength increase is to increase the reaction rate.

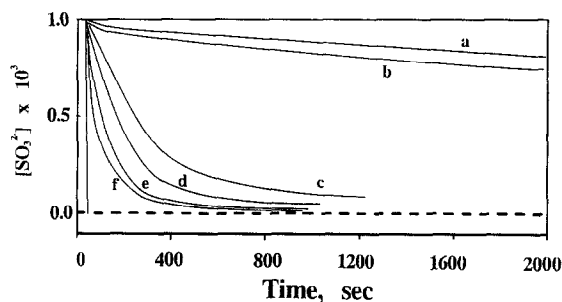


Fig. 9. Absorbance showing disappearance of sulfite in different ionic strength pH 9.2 borate buffer solution. (a) only buffer solution with ionic strength 0.1, (b) add 1 ml zeolite molecular sieve without supporting catalyst, ionic strength 0.1. ionic strength (c) 0.01, (d) 0.02, (e) 0.05, (f) 0.1. $[\text{SO}_3^{2-}] = 10^{-3}$ M, [supported $\text{Fe}(3\text{-TMPyP})] = 2.7 \times 10^{-6}$ mol/l.

The effect of the ionic strength is to increase the rate of ions with charges of the same sign, and to decrease it when the charges are opposite in sign. This is a variation of a reaction rate constant which is often called the primary salt effect [23]. Fig. 10 also shows the ionic strength effect of the reaction for different catalysts. Fe(2-TMPyP) and Fe(3-TMPyP) also have similar results.

The effect of ionic strength is obvious for the sulfite autoxidation catalyzed by Fe(*n*-TMPyP) in the presence of oxygen. Sulfite and a zeolite molecular sieve have charges of the same sign (negative charge), therefore the reaction rate constant increases when ionic strength is increased.

3.9. Effects of concentration of sulfite on reaction rate

We have determined the reaction rate of the catalytic autoxidation of SO_3^{2-} in the presence of oxygen by supported catalyst Fe(2-TMPyP)

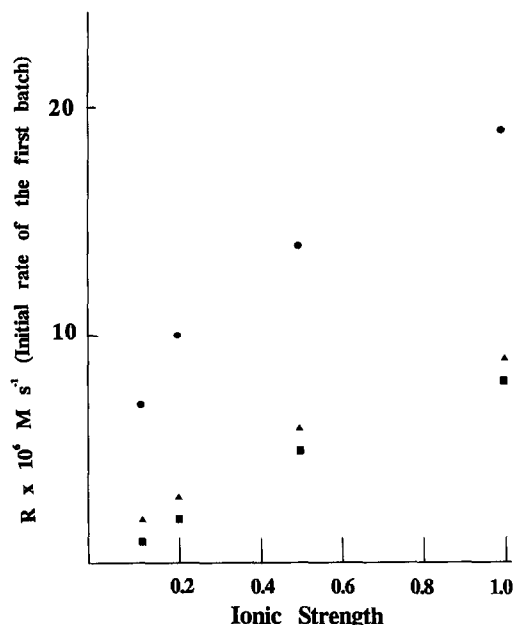


Fig. 10. Initial rate constant versus ionic strength in pH 9.2 borate buffer solution with various catalyst supported on zeolite molecular sieve. $[\text{SO}_3^{2-}] = 10^{-3} \text{ M}$, $[\text{supported catalyst}] = 2.7 \times 10^{-6} \text{ mol/l}$. (●) Fe(2-TMPyP), (▲) Fe(3-TMPyP), (■) Fe(4-TMPyP).

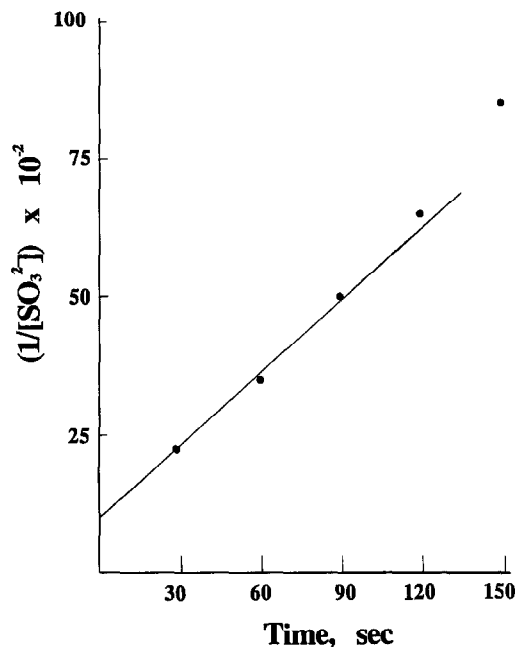


Fig. 11. $1/[\text{SO}_3^{2-}]$ versus time determine on $\lambda = 210 \text{ nm}$ of an oxygen saturated pH 9.2 borate buffer solution with 10^{-3} M of sulfite. $[\text{supported Fe(2-TMPyP)}] = 5.4 \times 10^{-6} \text{ mol/l}$.

with different concentration of sulfite in pH 9.2 buffer solution. The result of a plot of $1/[\text{SO}_3^{2-}]$ against time is nearly a straight line (Fig. 11). The half-life of the substrate is almost proportional to $1/[\text{SO}_3^{2-}]_0$ ($[\text{SO}_3^{2-}]_0$ is the initial concentration of sulfite). Therefore, the reaction rate law is nearly a second order when oxygen is in enough supply and the reaction is not influenced by the stirring rate.

4. Conclusion

This paper has shown that supported water-soluble iron porphyrin Fe(2-TMPyP), Fe(3-TMPyP), and Fe(4-TMPyP) on the zeolite molecular sieve, act as efficient catalysts for catalytical autoxidation of sulfite in the presence of oxygen. All the catalysts have shown catalytical activity for sulfite oxidation in the pH range in which $\text{Fe}^{\text{IV}}\text{P}$ can be produced by electrochemical method in the absence of oxygen.

The supported catalysts Fe(*n*-TMPyP) (*n* = 2, 3, and 4) have shown the catalytic activity of

sulfite oxidation. Fe(2-TMPyP) has a more catalytically active initial reaction rate than Fe(3-TMPyP) and Fe(4-TMPyP). The catalytic activity is influenced by the *N*-methyl-pyridinium group at the *meso* position. Fe(2-TMPyP) has a more positive formal potential of Fe(III/II)P than Fe(3-TMPyP) and Fe(4-TMPyP).

It was shown that Fe(2-TMPyP) and Fe(3-TMPyP) are very stable, but Fe(4-TMPyP) is easily deactivated. The porphyrin ring of Fe(4-TMPyP) is easily destroyed by sulfite and/or its intermediates, just as Fe(4-TMPyP) destruction is easier in the electrochemical reduction than Fe(2-TMPyP) and Fe(3-TMPyP).

Ionic strength and pH of the buffer solution also influence the catalytic autoxidation rate. In pH < 7, the catalytic reaction rate decreases abnormally because Fe^{IV}P only can be produced in basic aqueous solution. The catalytic autoxidation rate increases as the pH values of the aqueous solution decrease in the basic aqueous solution. In the weak basic solution, sulfite may more easily be near the catalytic site, compared to a stronger basic solution with the same ionic strength. These catalytical reactions obey the primary salt effect and show that increasing the ionic strength of the buffer solution increases the catalytic reaction rate.

Acknowledgements

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