

Oxidation of SO₂ catalysed by Mn-zeolites in aqueous phase

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Abstract

Mn²⁺ was heterogenised over six different zeolites by ion exchange and their activity for SO₂ oxidation was studied by conductimetry. The activity of the heterogenised Mn²⁺ was compared with both, Mn²⁺ as a homogeneous catalyst and with a more conventional carbon based catalyst. Mn²⁺ was shown to be the only active phase, consequently the catalysts containing the higher content of ion exchanged Mn²⁺, were the most active ones. Additionally, the influence of the hydrophilia and the structure of the different zeolites used on the activity of the heterogenised Mn²⁺ were also analysed. Both the hydrophilia and the structure of the zeolites, which favour the interaction of the reaction intermediates and the Mn²⁺, were found to be the key parameters for the SO₂ oxidation activity of the catalysts. The combination of hydrophilia, a high Mn²⁺ ion exchange capacity, and a well-defined microporous structure, allows that almost all the zeolites studied present higher activity for aqueous phase SO₂ oxidation, than the homogeneous catalyst and significantly higher than the conventional carbon based catalyst for this reaction.

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1. Introduction

An important research effort is being made to design systems that are able to reduce SO₂ emissions, due to their pernicious impact on the environment. The most conventional desulfurization technology is based on the SO₂ retention on CaCO₃ at high temperature, which produces large amounts of a low valuable CaSO₄ [1]. Regenerable systems that will avoid such by-product are desirable alternatives [2]. Among these systems, the catalytic oxidation of SO₂ is specially promising [3–5] because it will transform a pollutant (SO₂) into a demanded chemical (H₂SO₄).

The oxidation of SO₂, usually in aqueous phase, is generally catalysed by activated carbons and activated carbon fibres [3–5]. A typical activity value for these materials is of the order of 0.01 mmol SO₂/g carbon min [4]. The porosity of the carbon material was found to be a key parameter because it favours the interaction of HSO₃[−] and O₂ to produce H₂SO₄ [4].

However, other materials, especially transition metal ions, are much more active catalysts for the oxidation of SO₂

[6–13]. These transition metal catalysts are also involved in the atmospheric SO₂ oxidation contributing to the acid rain formation. Mn²⁺ has shown to be a very active catalyst for SO₂ oxidation in aqueous phase [7,12,13]. Its activity for this reaction is around 1–15 mmol SO₂/g Mn²⁺ min, depending on the pH. The highest reaction rate is achieved when pH is between 3 and 6 [7]. At these conditions, HSO₃[−] is the most stable species. The heterogenisation of Mn²⁺ would be desirable due to the much easier separation of the catalyst from the solution.

In this sense, zeolites seem to be a suitable material to support Mn²⁺ due to their open structure and ion exchange capacities [14]. Thus, the goal of the present study is to heterogenise Mn²⁺ catalyst over different zeolites, which will favour the oxidation of SO₂ and the separation of the catalyst from the H₂SO₄ solution. Additionally, the influence of the structure and hydrophilia of these materials on the SO₂ oxidation activity will be analysed.

2. Experimental

A flow of 3000 ppm of SO₂ and 5% of O₂ in N₂ was bubbled into 250 ml of ultrapure water (1–2 μS/cm) in a two-necked round-bottomed flask until getting a constant

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conductivity value of 570 $\mu\text{S}/\text{cm}$, which corresponds to a HSO_3^- concentration of $1.65 \times 10^{-3} \text{ M}$ [5]. The conductivity variation during the SO_2 oxidation was followed by a precision conductivity cell, which was fitted in the second neck [5]. The temperature of the solution was controlled by a thermo-stabilised bath. All the experiments were carried out at $30.0 \pm 0.1^\circ\text{C}$ and stirred at 94 rad/s.

Six different zeolites (Na-A, Na-X, Na-Y, Na-USY, Na-beta, Na-ZSM-5) were prepared by conventional hydrothermal treatment following the different synthesis described in the literature and compiled in [15]. All the materials prepared are well-crystallised one-phase zeolites, as shown by XRD analysis. These zeolites were ion exchanged twice in a 1 M $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ for 24 h at 60°C and shaking at 200 cycles/min. The final materials were analysed by N_2 adsorption at 77 K and CO_2 adsorption at 273 K, XRD, FTIR, SEM, TG and atomic emission spectroscopy.

3. Results and discussion

3.1. Characterisation of the catalysts

From the characterisation of the materials carried out by XRD, FTIR and SEM it can be confirmed that all the zeolites prepared show high purity and crystallinity. No contamination by other phases or amorphous material was observed.

Table 1 compiles the molecular composition of the ion exchanged zeolites deduced from atomic emission spectroscopy, whereas Table 2 summarises the chemical and structural characteristics of the zeolites studied.

Hydrophilia (h) is an important parameter that was also studied. This can be properly estimated, as described in the literature [16], by dividing the amount of water loss at 423 K

Table 3

Hydrophilia and pore volumes of the different zeolites studied

Zeolite	Hydrophilia	$V_{\text{DR}} (\text{N}_2)$ (cm^3/g)	$V_{\text{DR}} (\text{CO}_2)$ (cm^3/g)
Na-A	0.17	<0.01	0.22
Na-X	0.21	0.32	0.37
Na-Y	0.14	0.30	0.37
USY	0.08	0.28	0.33
Na-beta	0.12		
Na-ZSM-5	0.07	0.17	0.20

(weakly adsorbed) by the total amount of water loss at 673 K and subtracting this value to 1, as described by the following equation:

$$\text{hydrophilia} = h = 1 - \left(\frac{M_0}{M_t} \right) \quad (1)$$

where M_0 is the amount of water loss at 473 K and M_t the total amount of water loss at 673 K. So, very hydrophilic materials will adsorb water strongly giving a h value close to 1, whereas poorly hydrophilic materials will have h values close to 0.

These experiments were carried out by thermogravimetry (TG-DTA Stanton-Redcroft STA-780). As an example the thermogram of the zeolite Na-A is shown in Fig. 1. The water losses at 473 and 673 K can be clearly observed. Additionally, the values of hydrophilia, estimated as described previously, are compiled in Table 3. For zeolites with the same structure, hydrophilia increases as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio decreases (as observed for FAU type zeolites, i.e. Na-X, Na-Y and USY). Comparison between different structures is not trivial. Na-ZSM-5 is clearly the less hydrophilic material. Hydrophilic zeolites, such as Na-A and Na-X show high Mn^{2+} ion exchange, probably due to the better diffusion of this cation in solution. The most hydrophobic

Table 1

Molecular composition and ion-exchange percentage of the Mn-zeolites prepared deduced from the emission atomic spectroscopy results

Sample	Molecular composition	Mn exchanged (wt.%)	Level of Na exchange (mol%)
Mn-A	$(\text{Na}_2\text{O})_{0.05}(\text{MnO})_{0.85}\text{Al}_2\text{O}_3(\text{SiO}_2)_{2.51}$	14.6	95
Mn-X	$(\text{Na}_2\text{O})_{0.17}(\text{MnO})_{0.76}\text{Al}_2\text{O}_3(\text{SiO}_2)_{2.46}$	13.3	82
Mn-Y	$(\text{Na}_2\text{O})_{0.31}(\text{MnO})_{0.64}\text{Al}_2\text{O}_3(\text{SiO}_2)_{4.78}$	7.8	67
Mn-USY	$(\text{Na}_2\text{O})_{0.35}(\text{MnO})_{0.65}\text{Al}_2\text{O}_3(\text{SiO}_2)_{11.5}$	4.2	65
Mn-Beta	$(\text{Na}_2\text{O})_{0.23}(\text{MnO})_{0.77}\text{Al}_2\text{O}_3(\text{SiO}_2)_{25.0}$	2.5	77
Mn-ZSM-5	$(\text{Na}_2\text{O})_{0.41}(\text{MnO})_{0.57}\text{Al}_2\text{O}_3(\text{SiO}_2)_{30.3}$	1.6	58

Table 2

Chemical and structural characteristics of the zeolites studied

Zeolite	Si/Al	Type of structure ^a	Pore size (\AA) ^a	Type of pores ^a
Mn-A	1.26	LTA	4.1×4.1	Cages
Mn-X	1.23	FAU	7.4×7.4	Cages
Mn-Y	2.39	FAU	7.4×7.4	Cages
Mn-USY	5.75	FAU	7.4×7.4	Cages
Mn-BEA	12.5	BEA	5.6×5.6 and 6.6×6.7	Cylindrical
Mn-ZSM-5	15.15	MFI	5.1×5.5 and 5.3×5.6	Zig-zag and cylindrical

^a Obtained from [20].

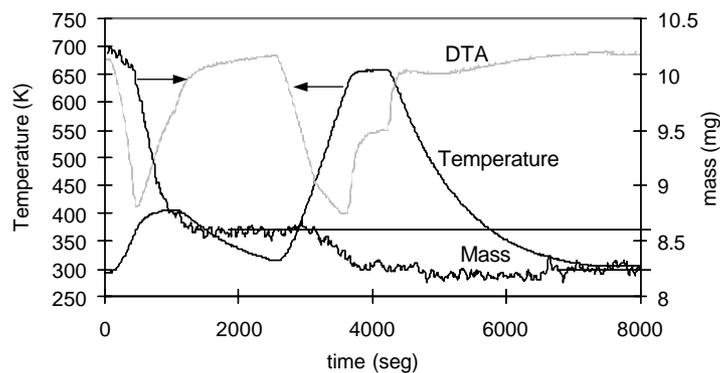


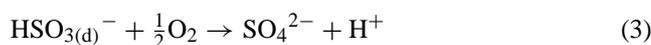
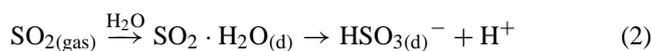
Fig. 1. TG-DTA of the zeolite Na-A. Temperature profile is also shown.

zeolites, specially Na-USY and Na-ZSM-5, present low Mn^{2+} ion exchange. Zeolite Na-beta shows a high Mn^{2+} ion exchange despite its high Si/Al ratio.

The textural properties of the different zeolites prepared were studied by N_2 adsorption at 77 K and CO_2 adsorption at 273 K. The equipment used was a volumetric system (Autosorb-6 from Quantachrome) which permits to obtain the adsorption isotherms up to a maximum pressure of 0.1 MPa. The samples were degasified at 523 K for 4 h in vacuum before the adsorption measurements. The pore volumes of the zeolites, estimated by applying the Dubinin–Radushkevich equation [17] are also compiled in Table 3. All the materials analysed show high pore volumes, as expected by their open structures. However, it is clear that N_2 adsorption at 77 K underestimates this value, especially for small pore size zeolites (Na-A), in which the CO_2 adsorption at 273 K is a much more suitable alternative to characterise materials with this narrow microporosity, as described elsewhere [18].

3.2. Catalysts activity

The SO_2 oxidation reaction has been done in aqueous solution. Under these conditions SO_2 is present as HSO_3^- , which is the chemical species to be oxidised by the O_2 , as shown in the following reactions:



The kinetics of the reaction (3), catalysed by the Mn-zeolites prepared, was followed by conductimetry. The initial conductivity ($570 \mu\text{S}/\text{cm}$) keeps constant if no zeolite is added, showing that the uncatalysed SO_2 oxidation reaction does not occur or is too slow to be measured.

As shown in Eq. (3), the products of the oxidation of HSO_3^- are SO_4^{2-} and H^+ . In this case, the anion is completely dissociated, due to its very high $\text{p}K_a$ value. Consequently, during the reaction one proton is liberated (reaction 3). Because the concentration of all the species are low and the molar conductivity of the H^+ is much higher than those

of the rest of the ions, the conversion of the SO_2 can be directly related to the change in conductivity [5]. So, the rate of the reaction can be calculated from the following equation [5]:

$$\begin{aligned} \text{reaction rate (mmol/min)} \\ = F (\text{mmol cm}/\mu\text{S}) \frac{\Delta k}{\Delta t} (\mu\text{S}/\text{cm}) \end{aligned} \quad (4)$$

where F is a constant which relates the mmol of SO_2 oxidised to the conductivity and is equal to $0.724 \text{ mmol cm}/\mu\text{S}$ [5]. This value was obtained dividing the moles of SO_2 dissolved in 250 ml of water by the conductivity of the initial concentration of SO_2 . The ratio $\Delta k/\Delta t$ is the slope of the linear part of the conductivity versus time plot.

As an example, Fig. 2 shows the evolution of the conductivity of the $1.65 \times 10^{-3} \text{ M HSO}_3^-$ solution when different amounts of Mn-beta zeolite were added (the sample amount used is shown above the curves in mg). In all the cases, a linear trend is observed. The same kind of behaviour is observed for the rest of the Mn-zeolites studied. Additionally, blank experiments with Na-zeolites were carried out. No increase in the conductivity of the solution was observed when no Mn^{2+} is present, showing that the zeolite has no activity and, hence that the transition metal is the only active phase.

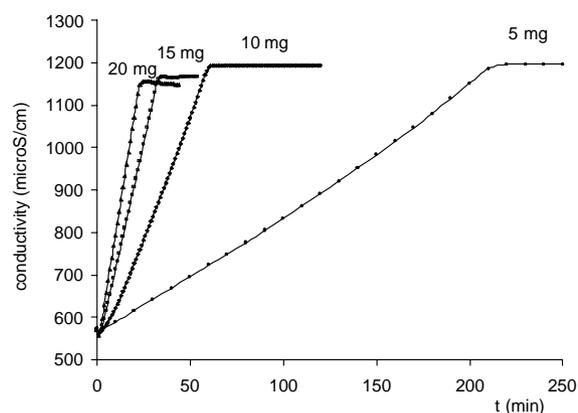


Fig. 2. Conductivity variation for different amounts of Mn-beta catalyst (included in the figure).

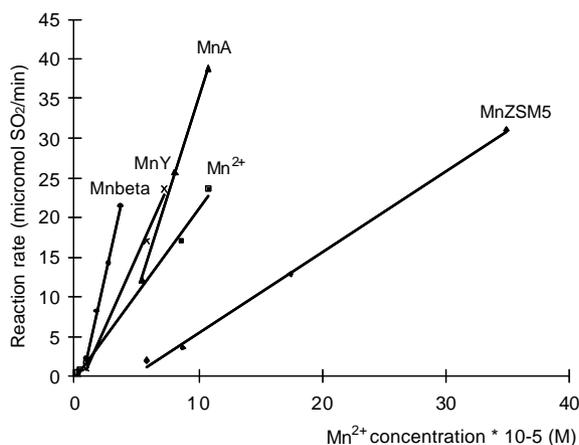


Fig. 3. Reaction rate of five different zeolites vs. the concentration of Mn^{2+} present by adding increasing amounts of zeolite.

As an example Fig. 3 presents the SO_2 oxidation rate versus Mn^{2+} concentration for five Mn-zeolites. Not only in these cases, but in all of the Mn-zeolite studied, the rate of the reaction is proportional to the amount of catalyst (as shown in Fig. 3) being the reaction rate per gram of catalyst mostly independent of the amount of catalyst, in the range of catalyst concentration studied. Only at high concentrations of catalyst the rate of the reaction versus catalyst concentration is not linear.

As observed in Fig. 3, the lines, which fit the results of the reaction rate versus catalyst concentration for the Mn-zeolite samples, do not cross the origin. For all the Mn-zeolite studied these lines cross the x -axis at positive values, being these values higher in the case of the zeolites Mn-A and Mn-ZSM-5. This observation could be related to some diffusional problems of the HSO_3^- ions in the zeolite framework or difficulties to reach some Mn^{2+} cations. In the case of the Mn-A (Table 2), the diffusional limitations could arise by

its narrow microporosity and, in the case of the Mn-ZSM-5, because its high hydrophobia (Table 3), which is related to its high Si/Al ratio (Table 2). Also, some Mn^{2+} ions could be in less accessible locations (e.g. type I sites) of the zeolite framework, being not active to the HSO_3^- oxidation. Interestingly, in the case of the homogeneous catalyst (Mn^{2+}), the line which fits the experimental data has a zero intercept.

The reaction rates of the different Mn-zeolites are shown in Fig. 4. For comparison, the reaction rates of Mn^{2+} in homogeneous phase and of a typical activated carbon optimised for SO_2 oxidation [4] are also included. The Mn^{2+} loading of the different zeolites as wt.% is shown above the bars. In the case of the homogeneous catalyst, the content of Mn^{2+} was obtained from the salt used ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$). As deduced from Fig. 4, the materials with more Mn^{2+} exchanged are the most active, showing that this is the active phase. Unfortunately, the most active zeolites (Mn-A and Mn-X) are also the less stable in acid media. Therefore, a balance between activity and stability must be found. Even so, very stable zeolites, such as Mn-USY and Mn-beta, are still significantly more active than the conventional carbon based catalysts. The selection of a more hydrophilic material and the incorporation of a well dispersed and very active species, Mn^{2+} , allowed us to increase notably the activity of the catalyst.

Fig. 5 shows the catalytic activities of the different Mn-zeolites prepared (expressed by gram of Mn^{2+}) in order to compare the influence of the zeolite properties in the activity of the Mn^{2+} . Interestingly, in almost all the cases the activity of the Mn-zeolite catalysts is higher than that of the Mn^{2+} in homogeneous phase. The dispersion of Mn^{2+} in precise locations of the microporous structure of the zeolites increases its activity due, probably, to the better interaction between the intermediates and the Mn^{2+} and the activation of the adsorbed species. So, the heterogenisation of the Mn^{2+} using zeolites, not only allows

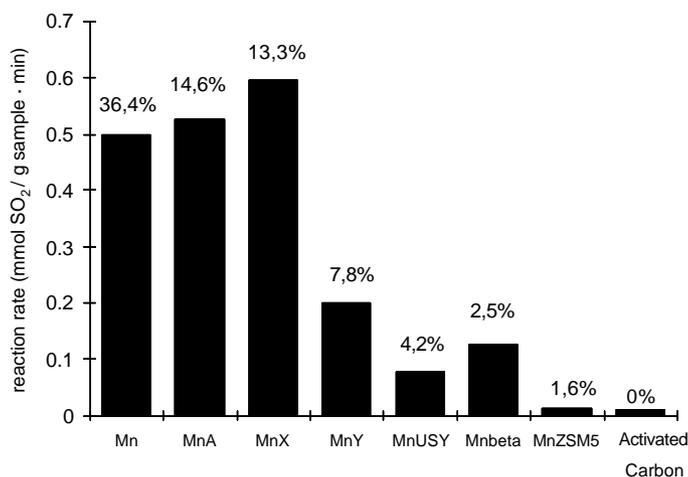


Fig. 4. Activity (per gram of catalyst) for SO_2 oxidation of the Mn-zeolites studied. Additionally, the activity of an active carbon optimised for this reaction is also included. The loading of Mn^{2+} of the different zeolites as wt.% is shown above the bars. In the case of the homogeneous catalyst, the content of Mn^{2+} in the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was considered.

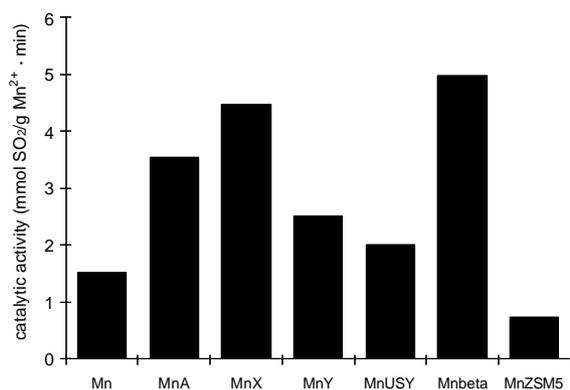


Fig. 5. Activity (per gram of Mn²⁺) for SO₂ oxidation of the Mn-zeolites studied.

reusing the catalyst and avoiding the separation step, but also increases notably its activity. It is worthy to remark that the activity of Mn-zeolites for SO₂ oxidation is ca. 5 mmol SO₂/g Mn²⁺ min, whereas conventional catalysts (activated carbons or activated carbon fibres) show activities of ca. 0.01 mmol SO₂/g carbon, i.e. 500 times smaller.

The influence of the different properties of the Mn-zeolites in the activity of the catalyst was also studied. Therefore, the series of the FAU zeolites (zeolites Mn-X, Mn-Y and Mn-USY), which share the same structure, clearly shows that the higher the hydrophilia (from Mn-X to Mn-USY, see Table 3) the more active the catalyst is (expressed per gram of Mn²⁺) as shown in Fig. 5. This observation is probably related to the higher diffusivity of the reaction intermediates, most of them electrically charged, in a hydrophilic structure. In this sense, the most hydrophobic material, the Mn-ZSM-5, is the least active catalyst. Moreover, the hydrophilic zeolites have the advantage of allowing to load more amount of Mn²⁺ by ion exchange.

The structure also influences strongly on the activity of these catalysts. So, the effect of the four different structures studied in the activity of the SO₂ oxidation reaction was analysed. Fig. 5 clearly shows that the Mn²⁺ localised in the beta structure is the most active, more than even the more hydrophilic zeolites, such as Mn-A and Mn-X and Mn-Y. The cylindrical shaped pores (see Table 2) of the BEA structure is likely to activate the reaction species more effectively than the cage shaped pore of the LTA and FAU type zeolite [19]. In the case of Mn-A zeolites, which has pore mouths of only 4.1 Å, accessibility limitations cannot be discarded. Finally, the zeolite Mn-ZSM-5, which has wider pore than Mn-A and cylindrical and zig-zag shaped zeolites, shows, however, low catalytic activity which is most likely related to its high hydrophobicity (see Table 2).

The significant increase in SO₂ oxidation catalytic activity showed by carbons with the suitable microporosity [4] is an additional evidence that SO₂ is activated in micropores with the appropriate pore size.

4. Conclusions

SO₂ oxidation in aqueous phase by O₂ catalysed by Mn-zeolites was studied by conductimetry. The combination of both a very active specie, i.e. Mn²⁺, and a hydrophilic support with a suitable open structure and with ion-exchange capability, i.e. zeolites, allowed us to prepared catalysts which are 500 times more active catalysts for the oxidation of SO₂ than the activated carbons and activated carbon fibres used for SO₂ conversion into H₂SO₄.

For the same zeolitic structure the activity of the Mn-zeolites increases with the hydrophilia of the material, probably, because the reaction intermediates are electrically charged.

The influence of the structure was also analysed. Medium pore size zeolites, such as Mn-beta seems to favour the oxidation of SO₂. Narrower pore sizes zeolites (Mn-A) or too large cages-based zeolites (Mn-FAU) show lower activity.

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