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Catalytic oxidation of trichloroethylene over Fe-zeolites

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ABSTRACT

The activity of Fe loaded zeolites towards the oxidation of trichloroethylene (TCE) was evaluated by varying the preparation procedure and zeolite type. The activity of 2% Fe-ZSM-5 and Fe-beta were compared first, and after confirming that the activity over ZSM-5 catalyst was higher, modification in the preparation method was carried out. The catalysts prepared by impregnation or solid state ion exchange methods were also found to be active towards the oxidation of TCE, however, comprehensively less than the activity of the catalyst synthesised by ion exchange method. The influence of exchange time on the activity was studied and we found that increasing the duration of exchange time enhanced the catalytic performance. Catalyst characterization which include XRD, BET surface area analysis, NH_3 desorption studies and TEM were carried out for the catalyst samples and results were correlated to get better understanding of the catalytic performance. Finally the stability of the catalyst was tested and compared with H-ZSM-5.

1. Introduction

Chlorinated volatile organic compounds, such as trichloroethylene (TCE) constitute a major portion of the hazardous solvent wastes produced by air stripping and soil venting processes. TCE is among the widespread toxic chlororganic pollutants, which causes serious problems to human kind and also is responsible for the depletion of stratosphere [1]. Thus removal of chlorinated volatile organic compounds (CVOCs) becomes essential; thermal decomposition is one possibility, but requires high temperatures and also leads to polychlorinated aromatic compounds [2,3]. Hence, catalytic oxidation is considered as an effective, alternative method as comparatively low temperature (250–550 °C) is sufficient. Noble metal, metal complex oxides and metal-incorporated zeolites [4–7] have been used as catalysts for TCE removal. Though the former exhibits better performance their removal cost has pushed for more interest in zeolite based catalysts.

Fe incorporated zeolites have been extensively studied in various catalytic processes of oxidation and reduction, in particular for N_2O decomposition, selective catalytic reduction (SCR) of nitrogen oxides by NH_3 or hydrocarbons, i.e. for exhaust treatment [8,9], and selective catalytic oxidation (SCO) of ammonia [1] but only fewer studies on organic compounds oxidation has been carried out [10]. Iron can be incorporated in the extra-framework of zeolite by using various preparation procedures, which include traditional liquid ion exchange or solid state ion exchange or impregnation. In most cases, depending on the preparation method, various coexisting iron species are produced, ranging from isolated iron ions via dimers and small oligonuclear Fe_xO_y clusters inside the pores up to Fe_2O_3 particles on the external surface [11,12].

In this study, we evaluate the catalytic activity of supported iron zeolites which are prepared by different methods towards TCE catalytic oxidation. Also the influence of ion-exchange duration on the activity of the zeolite is studied. Later the stability of the catalysts was tested and compared with H-ZSM-5 to gain insight on the nature of transition metal incorporated into zeolites towards CVOC's destruction. Thus a complete picture on the nature of catalyst preparation and its influence on activity and stability towards TCE oxidation can be obtained.

2. Experimental

For this study Fe was incorporated on two different zeolites [ZSM-5(Si/Al = 50) and beta(Si/Al = 25)] by different procedures, namely ion exchange (IE), solid state ion exchange (SSIE) and impregnation (IMP). Two different time durations were used for ion exchange, namely 4 h and 24 h. Fe-ion exchange was carried out by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ required for 2% Fe in water. H-ZSM-5 or H-beta was added to this solution ($8\,g\,L^{-1}$) and was stirred for either 4 h or 24 h at 60 °C. The ion exchanged samples were then filtered, dried and calcined at 650 °C 4 h. For preparation using SSIE

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the required amount of Fe precursor ($Fe(NO_3)_3{\cdot}9H_2O$) was added to H-ZSM-5 or H-beta and ball milled for 1 h, later the mixture was taken out and heated at 500 °C for 1 h with a ramp of 50 °C min^{-1}. The resulting sample was washed twice in deionised water and was calcined at 650 °C for 4 h. Fe-zeolite was prepared by the wet impregnation method; the required amount of the precursor dissolved in water was added slowly to H-beta or H-ZSM-5 and well stirred until the solvent evaporated. The samples were dried and later calcined at 650 °C for 4 h. In all cases the nominal loading of iron was maintained at 2%. The amount of Fe in the solution before and after impregnation was determined by ICP-AES to know the exact amount of Fe exchanged. Catalytic oxidation of TCE over all modified zeolites was performed at atmospheric pressure in a fixed bed reactor. 0.60 g of the catalytic sample (35–50 mesh) was introduced in the reactor and pretreated at 200 °C for 2 h in flow of nitrogen. For reaction the temperature was increased from 200 to 650 °C at a constant ramp with conditions of lean TCE concentration in air (1000 ppmv), 500 $cm^3\ min^{-1}$ of air and space velocity of 15000 h^{-1}. The reactor outlet composition was analyzed using on-line gas chromatography. The catalyst samples were characterized using BET surface area analyzer (ASAP 2020), the amount and distribution of the acidity were determined from TPD of NH_3. Also TEM and XRD analysis were used for broader understanding of the catalyst nature.

3. Results and discussion

3.1. Catalyst characterization

The surface area of all the prepared samples and used in reaction was determined and the values are given in Table 1, in which the acidity in the parent and modified zeolites determined TPD of ammonia is also shown. Table 1 makes evident that the surface area of the Fe incorporated zeolites decreased considerably when compared with their protonic counterpart. This may be due to the Fe particles blocking the pores, thus reducing the internal surface area of the zeolite. Also, when the surface area of the modified zeolites were compared, the surface area was in the following order IE > IMP > SSIE, as expected, although big differences cannot be noted. Acidity of the protonic zeolites was found higher than that of the modified zeolites as during modification the Fe tends to occupy the acidic sites, thereby decreasing the total acidity. TEM images are shown in Fig. 1(a–c), where it can be observed that the iron in IE sample is better dispersed than compared with samples prepared by SSIE or IMP. The TEM images also show that particles are agglomerated in the IMP samples and stacked in the SSIE samples. XRD diffractograms of zeolites indicated no structural change after Fe incorporation. However, no peak corresponding to iron in any form was observed, probably because some XRD invisible form of Fe was located within the internal structure and also due to the fact that the concentration of XRD active Fe (Fe_2O_3) on the surface was low and significantly dispersed. The presence of Fe was confirmed with EDS.

Since no reference on the activity of Fe-zeolite on oxidation of CVOC's was found, work was carried out in order to deduce

Table 1
BET surface area and total acidity of all studied catalysts.

Catalysts	BET ($m^2\ g^{-1}$)	Total acidity (mmol $NH_3\ g^{-1}$)
H-beta	520	0.561
Fe-beta-4 h	464	0.312
H-ZSM5	394	0.415
Fe-ZSM5-4 h	368	0.357
Fe-ZSM5-24 h	356	0.292
Fe-ZSM5-imp	354	0.335
Fe-ZSM5-SSIE	340	0.331

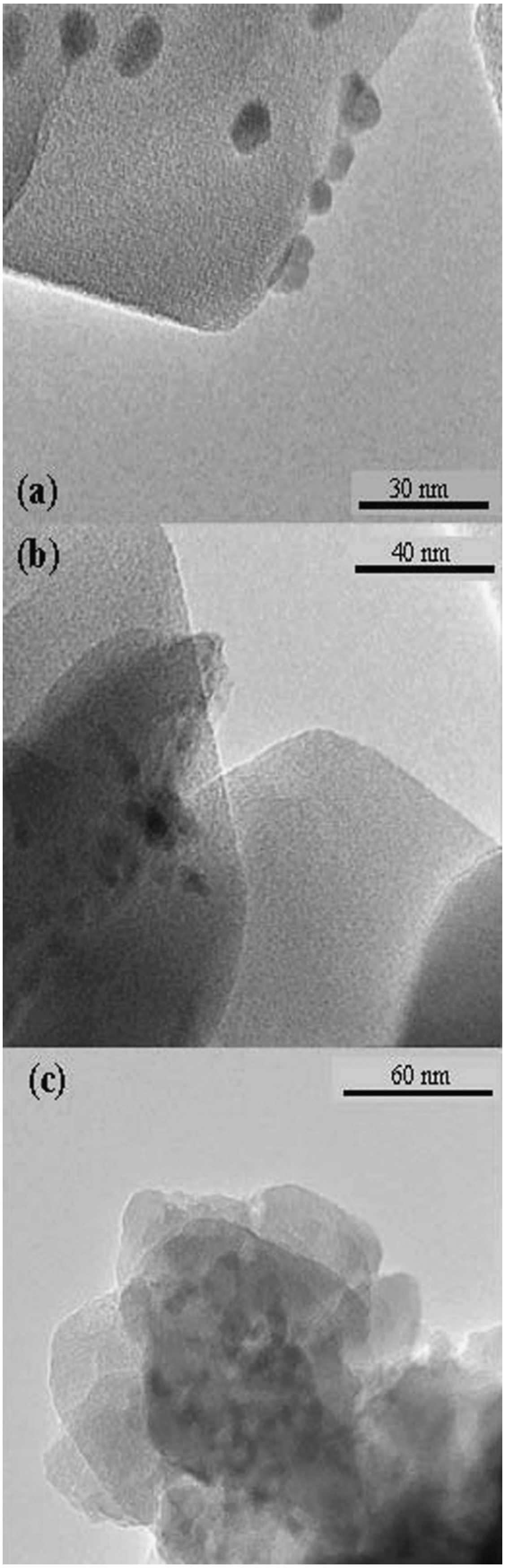

Fig. 1. TEM images of (a) 24 h ion exchanged Fe-ZSM-5, (b) impregnated Fe-ZSM-5 and (c) solid state ion exchanged Fe-ZSM-5.

a catalyst with the best activity towards TCE oxidation. Initially we checked the activity of two different zeolites followed by changing the preparation method maintaining Fe loading and base zeolite.

3.2. *Activity of Fe-ZSM-5 and Fe-beta*

The activity of ~2% Fe exchanged (4 h) ZSM-5 and beta was tested in the oxidation of TCE. Fig. 2(a) shows the light-off over both catalysts compared with H-beta and H-ZSM-5.The T_{50} values of protonic zeolites in the catalytic oxidation of TCE were very similar (515 °C for H-beta and 520 °C for H-ZSM-5), but when introducing Fe their activity improved significantly. The activity of Fe-beta was found to be less when compared Fe-ZSM-5. The exchange saturation reached in less than 4 h for both H-beta and H-ZSM-5. Since both samples had nearly the same amount of iron (1.46% in case of beta and 1.85% for ZSM-5) similar activity was expected, however, the T_{50} and T_{90} of Fe-ZSM-5 were about 25 and 40 °C less than Fe-beta counterpart. As the amount of Fe is not very different, only two possible reasons can be associated with the fact that incorporation of Fe improved activity: primarily the Si/Al ratio which is related with the inherent acidic nature of the zeolite, 50 in the case of ZSM-5 and 25 in the case of beta zeolite; the second reason may be due to the structural property of the zeolite which control the position and type of Fe binding, access to the reaction.

3.3. *Activity of Fe-ZSM-5 prepared by different methods*

Since the activity of Fe-ZSM-5 was better when compared with that of Fe-beta, different preparation procedures to incorporate Fe over ZSM-5 were followed, viz. ion exchange from solution, solid state ion exchange and impregnation. Fig. 2(b) shows the conversion of TCE with temperature over all the 3 forms of the catalyst. The Fe-ZSM-5 prepared by IE method showed better activity than the SSIE counterpart, although it had similar profile as the impregnated sample. The T_{50} and T_{90} values of IE sample were about 10 °C less than those of the IMP sample, (450, 510 °C for IE and 460, 520 °C IMP samples, respectively). T_{50} and T_{90} for the SSIE sample were about 485 and 565 °C. This is due to the fact that the percentage of iron present in inactive form is higher when the catalyst is synthesized by the SSIE method.

3.4. *Influence of exchange time on activity of ion exchanged Fe-ZSM-5*

Since the activity of Fe-ZSM-5 synthesized by IE was better among the various preparation procedures, two different exchange times, 4 h and 24 h, was compared for the synthesis. Again a significant difference in activity was observed: the 24 h-exchanged Fe-ZSM-5 had very high activity in the oxidation of TCE. Fig. 2(c) shows the light-off curve of the two samples under similar experimental conditions and it can be noticed that the T_{50} value was 390 °C when 24 h were used for exhange compared to 450 °C in the case of the 4 h exchanged Fe-ZSM-5. Likewise, the T_{90} value was 50 °C less. This shows that prolonged duration of exchange promotes the activity of the catalyst.

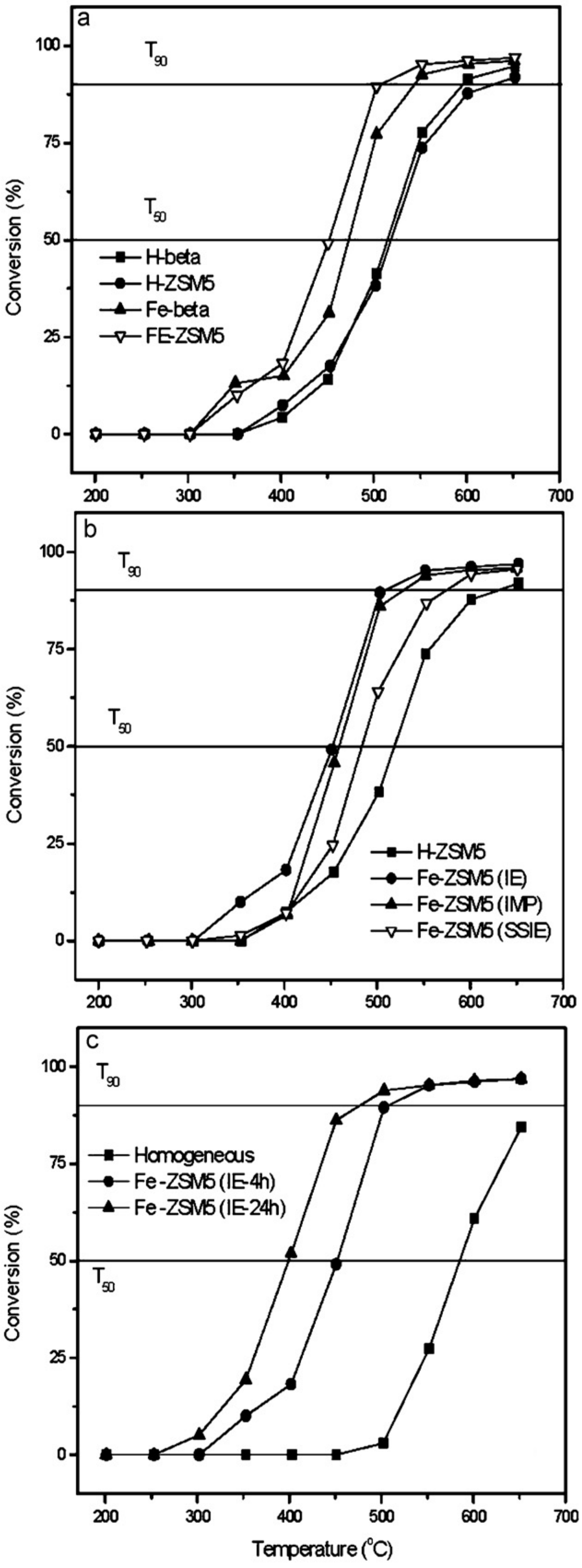

Fig. 2. TCE conversion with temperature for (a) influence of different zeolites H-form and Fe exchanged (4 h), (b) influence of different preparation method and (c) influence of duration of exchange.

3.5. *Stability studies*

In order to understand the stability of Fe-zeolite, the catalyst with best activity, Fe-ZSM 5 (24 h IE), was chosen and compared with H-ZSM-5 catalyst for stability. The stability was tested by following the activity in terms of TCE conversion as a function of time-on-stream under same reaction conditions as before, maintaining temperature at 500 °C for 14 h. The comparison plot is shown in Fig. 3. We can observe that the activity of Fe-ZSM-5 was higher than H-ZSM-5.Initial activity for Fe-ZSM-5 was 88% against 37% over H-ZSM-5, with similar intermediate trend, and

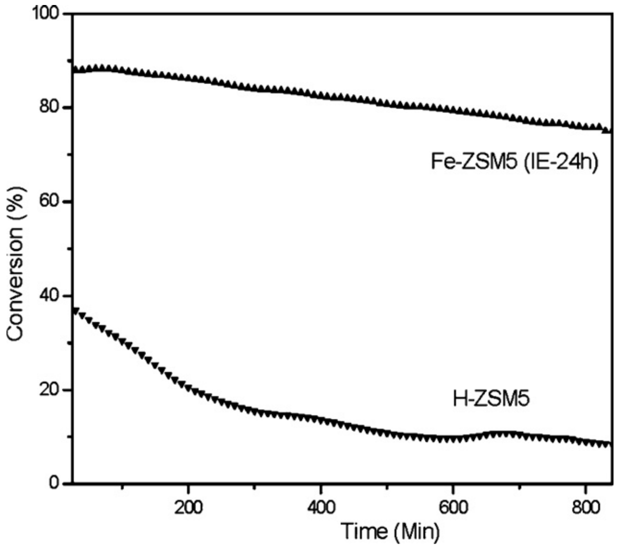

Fig. 3. Deactivation of Fe-ZSM5 and H-ZSM5 catalysts with time, studied with respect to conversion of 1000 ppmv TCE at 500 °C, with a space velocity of 15,000 h^{-1}.

Table 2
BET surface area and total acidity of the catalysts before (fresh) and after TCE oxidation carried out 500 °C, with 1000 ppmv TCE and space velocity of 15,000 h^{-1}.

	BET ($m^2 g^{-1}$)	Total acidity (mmol $NH_3 g^{-1}$)	Coke (%)
H-ZSM-5 (fresh)	394	0.415	–
H-ZSM-5 (used)	305	0.329	0.6
Fe-ZSM-5 (fresh)	356	0.292	–
Fe-ZSM-5(used)	329	0.158	0.3

after 14 h conversion over Fe-ZSM-5 was 75% but only 10% over H-ZSM-5.At the end of experiment, the amount of coke deposited was determined by TG analysis and resulted a loss of 0.3% for Fe-ZSM5 which was much less than the 0.6% of coke which was formed during reaction over H-ZSM5. The coke had a dominant role on the stability of the catalyst, as blocking the pores and thus preventing the access of the reactant to the active sites. Only small amount of deactivation was observed over Fe catalyst while a huge drop in stability was observed over H-ZSM-5 at the end of 14 h. This study showed that the Fe-ZSM-5 catalyst can be considered stable and active for much longer duration (Table 2).

The marked influence of the Fe incorporated zeolites is due to the fact that metal may exist in many forms and different sites. The forms include monomeric iron, extra framework or grafted species, binuclear or oligomeric clusters and iron oxide; all species can coexist simultaneously. The different Brönsted acid sites in ZSM-5 include α-sites present in the straight channel walls, β-sites at the intersection of straight and sinusoidal channels, and finally γ-sites at the sinusoidal channel wall. Though most of the species present at different positions are highly active, the activity of a particular type of species and its position can dominate depending on experimental conditions. The formation of these species depends on the zeolite structure, acidity, preparation procedure and concentration of iron or the Fe/Al ratio. The Fe/Al ratio has been 0.27 in all the procedures followed in this work. According to Brandenberger et al. [13], when the Fe/Al ratio is around 0.3 the percentage of monomeric species is 46% while clustered species is 54% (16% of dimeric species and 38% of ologomeric species). However, these values correspond when catalysts are synthesized by ion exchange method. According to Guo et al. [14] when Fe is ion exchanged from $Fe(NO_3)\cdot 9H_2O$ source the Fe is located predominantly in the β- and γ-sites. During impregnation and solid state ion exchange, the percentage of clustered species is expected to be high as also evidenced from TEM pictures where agglomeration is seen. The preparation method also controls the position of the Fe on the various sites present in ZSM-5. With IE method micro pore diffusion is higher which also result in a more homogenous distribution of the metal and does influence the activity of the catalyst. Increasing the ion exchange duration may facilitate this micropore diffusion to a greater extent as it can be seen in Table 1 that the surface area was slightly reduced for 24 h-exchanged samples when compared with 4 h-exchanged sample. This micropore diffused Fe has the possibility to be exchanged at a particular site (either β or γ) as we have observed that exchange saturation was well established for both samples within 4 h. Though the amount of Fe, which was determined by ICP AES indicated similar amount in both the 4 h and 24 h exchanged samples, their activity differ notably. Thus, the increased performance of Fe exchanged zeolites can be correlated with the above explained factors, namely presence of more monomeric form of Fe which is believed to be more active than the other forms and the influence of exchange time which facilitate the formation of more dispersed Fe predominantly in the internal surface of the zeolites and/or on a particular acidic site.

4. Conclusions

Fe-zeolites have been for the first time used for the oxidation of CVOC's and their activity was found to be appreciable. Fe incorporated beta and ZSM-5 catalysts were prepared and tested for TCE oxidation and compared with the protonic form of the base zeolite. The addition of Fe increased the activity of zeolite, especially in the case of ZSM-5, decreasing T_{50} by 125 °C. Also the influence of preparation methodology on the activity was studied. Ion exchanged zeolites showed better oxidation capability when compared with SSIE and impregnated samples, and the duration of ion exchange had also significant influence on the oxidation of TCE. Though the exact reason behind the increased activity is not yet well understood, one possible reason may be due to increased micropore filling of iron leading to better distribution of monomeric iron species which are expected to be the more active species in the oxidation of TCE. Also the stability of the Fe exchanged catalyst was found to be good as the catalyst resulted very active for long duration.

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