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Ferric ions doped 5A molecular sieves for the oxidation of HCHO with low concentration in the air at moderate temperatures

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Abstract

Zeolite 5A molecular sieve was doped with iron ions Fe^{3+} by ion exchange and the catalytic activity of the obtained solids for the formaldehyde oxidation was investigated. The catalysts are able to oxidize formaldehyde of a very low concentration at moderate temperatures. The light-off temperatures were about 70–100 °C and the temperatures for the complete oxidation were about 160–190 °C. The oxidation reaction product contains HCOOH, and its formation is associated with the silanol groups on the catalyst structure. The pH value of the suspension during the ion exchange and the temperatures at which the catalysts were calcined has profound influence on the amount of the silanols in the catalysts. Ferric species are also active sites on the zeolite, which are more active at higher temperatures than silanols and responsible for producing carbon dioxide.

Keywords: Ferric ions; Molecular sieves; Catalyst

1. Introduction

HCHO released to the air from many industrial and/or civil process such as painting, printing, pharmacy, shoes making and room decoration etc. can cause harmful problems to the human health [1,2]. Chronically being exposed to the air polluted by HCHO with low concentration can result in watery eyes, skin irritation, respiratory diseases, e.g. bronchitis, throat hurt and pneumonia etc., even more severe diseases such as nasopharyngeal or nasal cancers, leukemia etc. From 1980 to 2004, formaldehyde had been classified as definite human carcinogen three times by different international organizations including EPA (the U. S. Environmental Protection Agency) in 1987 and IARC (International Agency for Research on Cancer) in 1995 and 2004, respectively. Therefore, the techniques for the removal of the low concentration HCHO in the air have been extensively studied. In general, they can be classified into two major classes: recycling and combustion of the formaldehyde [3–9]. Although it is technically feasible for the recycling of the low concentration HCHO, it is not an economic approach. Accordingly, catalytic combustion at relatively low temperatures appears the potential solution for this environmental problem by virtue of its lowest energy cost. The catalysts reported for the oxidation of volatile organic compounds, can be classified into three categories: noble metals, such as Pt, Rh, Pd and nano-gold etc. [10–12]; Perovskites [13] and other transition metal catalysts [14,15]. Noble metals usually exhibit superior catalytic activity for the removal of VOCs, but their applications are impeded by their costs. On the other hand, the temperatures at which the VOCs are oxidized on perovskite catalysts are relatively high so that the reaction will consume substantial

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energy and thus limits the application of perovskites for this purpose. Consequently, developing new catalysts, which contain non noble metals and are able to catalyze the VOCs at moderate temperatures is vital for VOC combustion technique, as well as formaldehyde removal.

Zeolite 5A molecular sieves are widely used as desiccant and sorbent, nevertheless, they are not often used as catalysts possibly because their thermo-stability, resistance to acids and bases is not good enough [16,17]. If the catalytic reaction can proceed at relative low temperatures, this weakness can be avoided. However, the 5A molecular sieves are not active for the oxidation of HCHO at the temperatures below 280 °C. In the present study, iron ions Fe^{3+} were doped to 5A molecular sieves via ion exchange, and we found the obtained solids are active catalysts for the HCHO oxidation at moderate temperature and their catalytic performance was investigated in detail. The structural features of the catalysts were characterized by XRD, TPR and FT-IR techniques, in order to understand the catalytic performance.

2. Experimental

2.1. Catalyst preparation

Fe^{3+} ion doped 5A molecular sieves were obtained by ion exchange. Ten grams of 5A molecular sieve (Shanghai Chemicals Co. Ltd.) with a particle size below 80 mesh was dispersed in an aqueous solution of $Fe(NO_3)_3$ (0.1 M, 30 mL) under stirring. While 0.1 M HNO_3 solution was used to adjust the pH value of the mixture to about three, and the stirring was prolonged for two more hours. The mixture was then left over night at room temperature, and the solid was recovered and washed with deioned water until the pH value of the suspension of the sample and water approached seven. The washed sample was dried at 70 °C in the air. Portions of the dried samples were calcined at designed temperatures between 200 and 400 °C, respectively, prior to the activity test and characterization. The samples with grain size of 40–60 mesh were used for the catalytic test. A $Fe–SiO_2$ catalyst was obtained by mixing Fe_2O_3 and SiO_2 powder and subsequently calcined the mixture at 450 °C for 2.5 h. The H-MS catalyst was prepared by ion exchange of 5A zeolite with diluted HNO_3 solution. The catalysts used in the experiment were labeled as follows (Table 1).

2.2. Characterization

X-ray powder diffraction (XRD) analysis of the samples was performed on a BRUKER D8 Advance diffractometer using a Cu Kα radiation. The samples were scanned at a rate of 4° (2θ)/min over a range of 5°–60°. Temperature-programmed reduction (TPR) experiments were conducted using 60 mg catalyst, which was heated in a gas flow of 5% H_2/95%N_2 mixture (30 $cm^3\,min^{-1}$) at a rate of 10° min^{-1}. A TCD detector was used for on-line monitoring of TPR effluent gas. Fourier transform infrared (FTIR) spectra of the samples were recorded by a Nicolet Nexus FT-IR 670 spectrometer. Specimens for the measurements were prepared by mixing 2 mg of the sample powder with 8 mg of KBr and pressing the mixture into pellets. The spectra were acquired in a wavenumber range between 410 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and averaged over 32 scans.

2.3. Catalytic reactions

The catalytic activity test was performed in a continuous-flow fixed-bed reactor of quartz tube. The inner diameter of the tube is 0.8 cm and 200 mg of the sample (40–60 mesh) was loaded together with silicon dioxide powder, which is used to dilute the sample to a volume of 0.8 cm^{-3} and inert to the reaction. The feed gas was 0.06 vol.% formaldehyde balanced with the air, which was obtained by passing an air flow through a 36 wt.% HCHO solution at 0 °C. The space velocity of the experiment was $5 \times 10^4\,h^{-1}$ ml g cat^{-1}. The effluent from the reactor was analyzed on-line by a Shimadzu DC-8A gas chromatograph (GC) equipped with a GDX-403 packed column and TCD detector. This GC-TCD system is capable of determining CO_2 in the minimum concentration of 10 ppm, which was calibrated by a FQ-W IR CO_2 analyzer, which can determine the CO_2 concentration as low as 2 ppm, the HCHO and HCOOH concentrations as low as 9 mg/m^3(air) with calibration using standard aqueous solutions of HCHO and HCOOH, respectively. The minimum CO concentration, which could be detected by the analyzer is 20 ppm.

Table 1
Label and composition of the samples

Serial number	Samples	Treatment	Composition
a	Fe(H)-MS	Exchanged with Fe^{3+}, modulated pH with HNO_3 and dried at 70 °C	Si:Al:Ca:Na:Fe/1:0.775:0.11:0.242:0.093
b	Fe(H)-MS(200)	Exchanged with Fe^{3+}, modulated pH with HNO_3 and calcined at 200 °C	Si:Al:Ca:Na:Fe/1:0.775:0.11:0.242:0.093
c	MS	The original 5A zeolite	Si:Al:Ca:Na/1:0.964:0.506:0.240
d	Fe(H)-MS(400)	Exchanged with Fe^{3+}, modulated pH with HNO_3 and calcined at 400 °C	Si:Al:Ca:Na:Fe/1:0.775:0.11:0.242:0.093
e	Fe-MS(200)	Exchanged with Fe^{3+} and calcined at 200 °C	Si:Al:Ca:Na:Fe/1:0.820:0.210:0.243:0.08
f	Fe-MS(400)	Exchanged with Fe^{3+} and calcined at 400 °C	Si:Al:Ca:Na:Fe/1:0.820:0.210:0.243:0.08
g	Fe-MS	Exchanged with Fe^{3+} and dried at 70 °C	Si:Al:Ca:Na:Fe/1:0.820:0.210:0.243:0.08
h	H-MS	Ion exchanged 5A zeolite with diluted HNO_3	Si:Al:Ca:Na/1:0.802:0.106:0.253
i	Fe-SiO_2	Fe_2O_3 mixed with SiO_2, calcined at 450 °C	Si:Fe/1:0.12

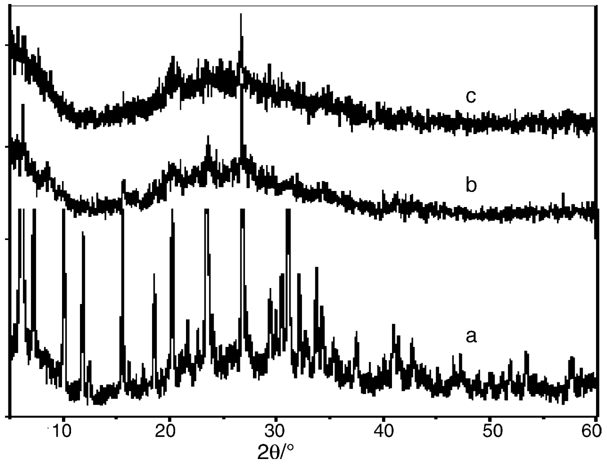

Fig. 1. XRD patterns of the samples: (a) 5A molecular sieves; (b) Fe(H)-MS (200 °C) and (c) Fe(H)-MS (400 °C).

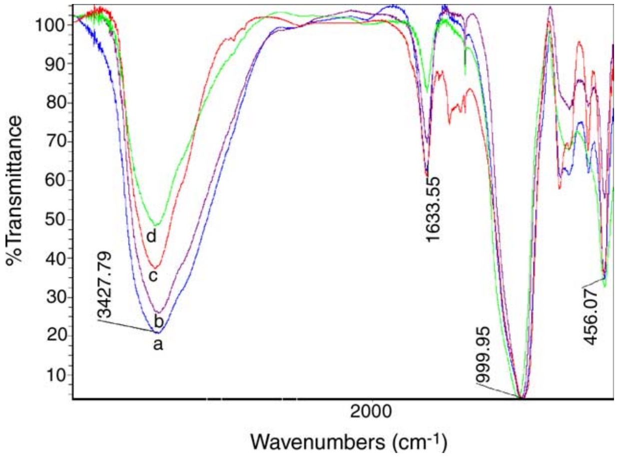

Fig. 2. FT-IR spectra of the samples obtained at pH 3: (a) dried at 70 °C; (b) calcined at 200 °C; (c) 5A molecular sieves and (d) calcined at 400 °C.

3. Results

3.1. Catalyst characterization

The XRD patterns of three samples are shown in Fig. 1, providing important information of structural characteristics of the catalyst samples. The XRD pattern of the original 5A molecular sieve (trace a) is in a good agreement with the patterns of the 5A zeolite [18]. However, most of the sharp characteristic diffraction peaks of the parent 5A zeolite disappeared in the patterns of Fe^{3+} ion exchanged samples, instead, broad humps are observed. This indicates that in the samples b and c the zeolite crystal structures have been seriously damaged, especially for sample c. The aluminum and the silicon in the frameworks of 5A molecular sieves can be leached out in an acidic or an alkaline environment [19], and the 5A zeolite underwent such acidic environment during the preparation of the ferric 5A molecular sieves in this study. Notwithstanding, it appears that the leaching causes defect in the frameworks but not collapse of the frameworks, as supported by the evidences from the spectra (Figs. 2 and 3) of the FT-IR.

One can deduce the effect of experimental parameters in the preparation by analyzing the FT-IR spectra of a series of samples. All samples were dried in vacuum prior to the FT-IR measurement. The spectra of the ferric 5A zeolite obtained by ion exchange and the precursor 5A zeolite are illustrated in Figs. 2 and 3. The ferric 5A samples were obtained from an acidic environment with a pH value about 3, which was achieved by adding diluted HNO_3 solution into the suspension in the ion exchange. Samples e and f in Fig. 3 were prepared without lowering the pH value of the ion exchange mixture. The absorption bands at about 1000 cm^{-1} in the spectra of Figs. 2 and 3 can be assigned to the diagnostic of the asymmetric stretching of the O–Si(Al)–O bonds, and the peaks at about 456 cm^{-1} should be attributed to the bending vibration of the O–Si(Al)–O bonds [20,21]. It is noticed that the intensity and broadness of these two peaks for Samples a, b, d, e and f are similar to those for Sample c, indicating that the most framework of the precursor 5A zeolite retains during the preparation, although the perfect crystal structure of the molecular sieve is lost as the XRD results in Fig. 1 show. Besides, the crystal defects caused by the acid leaching in the framework do not always lead to lose in catalytic activity of the catalysts.

The peaks at 3427 cm^{-1} in Fig. 2 and 3444 cm^{-1} in Fig. 3 are due to the vibrations of the internal silanols [22,23] and the adsorbed water molecules, respectively. The intensity of the peaks decreases as the calcination temperature increases. In Fig. 2, the intensity is in an order Trace a > Trace b > Trace d, while the calcination temperatures of the samples for Traces a, b and c are 70, 200 and 400 °C, respectively. In Fig. 3, the intensity is in an order Trace e > Trace f while the temperatures are 70 and 200 °C, respectively for the two samples. Considering the relations between the silanols on the structure and the calcinations temperature, it can be inferred that

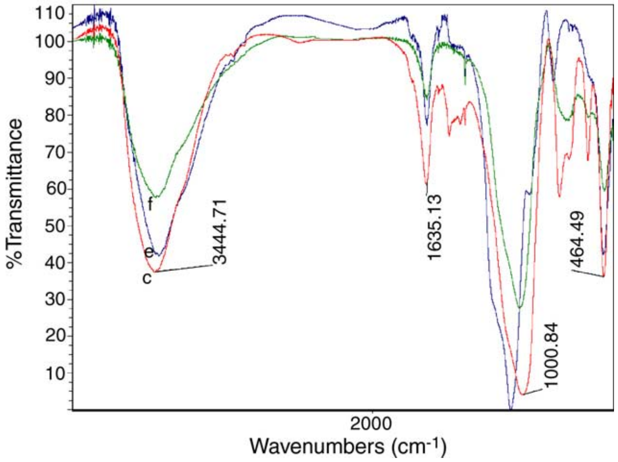

Fig. 3. FT-IR spectra of the samples obtained without lowering the pH value using HNO_3: (c) 5A molecular sieves; (e) dried at 70 °C and (f) calcined at 200 °C.

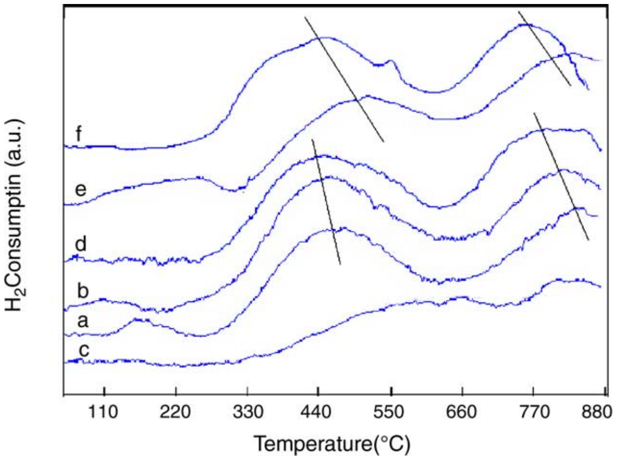

Fig. 4. TPR profiles of the samples: (a) Fe(H)-MS, dried at 70 °C; (b) Fe(H)-MS, calcined at 200 °C; (c) 5A molecular sieves; (d) Fe(H)-MS, calcined at 400 °C; (e) Fe-MS, dried at 70 °C and (f) Fe-MS, calcined at 200 °C.

higher calcination temperature causes greater loss of silanols on the structures. In addition, comparing the Fig. 2 with the Fig. 3, it can be found that the samples obtained at pH 3 (samples for Traces a and b) possess more silanols in their structures than the ones (sample e and f) prepared without lowering pH using HNO_3. This is because dealumination occurred during the preparation process of an acidic environment, which leads to the increase of silanols on the structure of the catalyst [23].

The temperature programmed reduction (H_2-TPR) profiles of the samples are shown in Fig. 4. There are two main peaks at about 450 °C (p1) and 800 °C (p2) for all iron ion exchanged samples. The first broad peak for 5A molecular sieves is at 330–770 °C (Curve c), which could be attributed to the reduction of the non-lattice oxygen, and the second peak at about 800 °C, is due to the reduction of the lattice oxygen. There is no reduction peak below 330 °C on the Curve c, which means that the 5A molecular sieves are thermostable below 330 °C in a reductive environment. It can also be observed that for the samples obtained from acidic medium, both the main peaks on other curves shift to the low temperature direction (from Sample a to Sample b and to Sample d), and the intensity of these peaks strengthens. It appears that the oxygen of the 5A molecular sieves becomes more easily to be reduced due to the introduction of iron ions. It can be explained, as the oxygen in the defective lattice formed in the preparation is more easily to be reduced. On the other hand, the reduction peak of the Fe_2O_3 to Fe_3O_4 (magnetite) in the structure of the 5A molecular sieves is around 390 °C [24,25], and the peak for the further transformation of magnetite to FeO occurs about 630 °C. These reasons could also contribute to the intensification and shift of the two peaks of the samples.

It can also be found that there are slight shifts to the low temperature direction of the peaks with the calcination temperature in the sample a, b and d, which were prepared at pH 3, and the sample e and f, which were prepared without lowering the pH value. This phenomenon can be interpreted as that higher calcination temperature causes more defects, and the oxygen on the structure with the more defects can be reduced more easily. The broad peaks below 220 °C in Curves a and b, and one below 280 °C in Curve e are ascribed to the reduction of the surface oxygen.

3.2. Catalytic activity

3.2.1. Effect of the PH value

The 5A molecular sieves are not active for the oxidation of HCHO at the temperatures below 280 °C. In contrast, its proton-exchanged derivative (H-MS sample obtained from HNO_3 solution) exhibits remarkable activity at relatively low temperatures (Fig. 5A). HCOOH is the unique product at the temperatures ranging from 100 to 140 °C and CO_2 is found at the temperatures above 140 °C. As the reaction temperature was raised further, HCOOH decreased and CO_2 increased in the products, and finally, HCHO was completely conversed to CO_2 at 190 °C and there was no HCOOH in the product.

It is also found that the pH value of the ion exchange process has substantial influence on the product. When Fe(H)-MS, the sample prepared at the pH 3, is the catalyst, the HCOOH content in the product (Fig. 5B) is much larger, compared to that in the product when the catalyst is Fe-MS (Fig. 5E), which was prepared at higher pH (without adding HNO_3 but the other conditions are the same). Similar situation can be observed in Fig. 5C and D. Obviously the use of HNO_3 during the preparation is beneficial to the selectivity to HCOOH. According to the FT-IR analysis results that the catalyst prepared at the pH 3 contains more silanol groups in its structure than the sample prepared without adding HNO_3. The silanols appear responsible for the selectivity of HCOOH. The Fe–SiO_2 sample is almost inactive below the temperatures of 210 °C as displayed in Fig. 5H.

3.2.2. Effect of the calcined temperatures

The effect of the calcined temperatures to the catalytic activity is also remarkable. First of all, the light-off temperature and 100% conversion temperature increase with increasing calcined temperature. As demonstrated in Fig. 5E–G and Fig. 5C and D, the light-off temperature and 100% conversion temperature of the uncalcined catalysts were lower than that of the calcined counterparts and these temperatures go higher for the catalysts calcined at higher temperatures. In addition, the fraction of HCOOH in the product decreased with increasing the calcined temperature. For the catalysts calcined at 400 °C (Fig. 5D and G), there was little HCOOH produced even at the light-off temperature and CO_2 was almost the sole product in the reaction. According to these facts and the analysis of FT-IR spectra, we believe that the HCOOH formation is ascribed to the silanols on the structure of the catalyst.

3.2.3. Stability of the catalysts

To test the operation stability of the catalysts, the catalysts calcined at 200 and 400 °C were used repeatedly, and

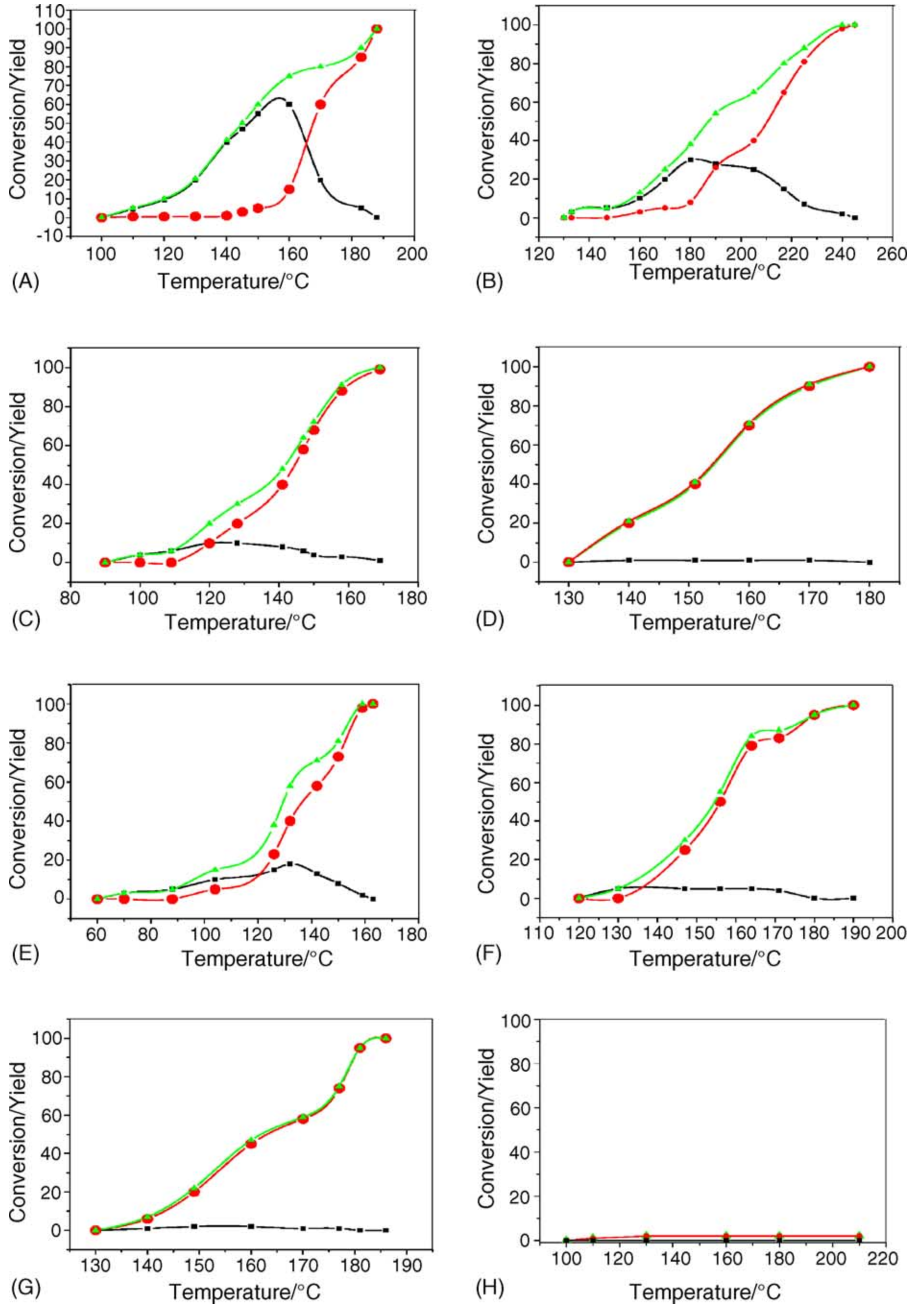

Fig. 5. (A) The activity of the H-MS sample: (▲) HCHO; (■) HCOOH; (●) CO_2. (B) The activity of the Fe(H)-MS sample: (▲) HCHO; (■) HCOOH; (●) CO_2. (C) The activity of the Fe (H)-MS (200 °C) sample: (▲) HCHO; (■) HCOOH; (●) CO_2. (D) The activity of the Fe (H)-MS(400 °C) sample: (▲) HCHO; (■) HCOOH; (●) CO_2. (E) The activity of the Fe-MS sample: (▲) HCHO; (■) HCOOH; (●) CO_2. (F) The activity of the Fe-MS (200 °C) sample: (▲) HCHO; (■) HCOOH; (●) CO_2, (G). The activity of the Fe-MS (400 °C) sample: (▲) HCHO; (■) HCOOH; (●) CO_2. (H) The activity of the Fe-SiO_2 (450 °C) sample: (▲) HCHO; (■) HCOOH; (●) CO_2.

exhibited very good stability. There is no obvious deactivation observed after the operation with stream in the reactants. In contrast, the catalytic performance of the Fe(H)-MS catalyst dried at 70 °C altered distinctly with stream in the reaction. The HCHO conversion, the contents of HCOOH and CO_2 in product as functions of operation time in the stream presence are presented in Fig. 6. It can be seen that at a lower operation temperature of 140 °C the catalytic performance of the catalyst dried at 70 °C is poor but the activity remains stable over the period of the measurement. At higher temperatures (170 and 200 °C) the activity (and thus the catalyst) is unstable. Presumably, the calcined catalysts have relatively stable active sites in the catalyst structures, but the active sites such as silanols on the structure of the uncalcined catalysts were not thermally stable and they could be lost at higher temperatures at which the catalyst was operated. The

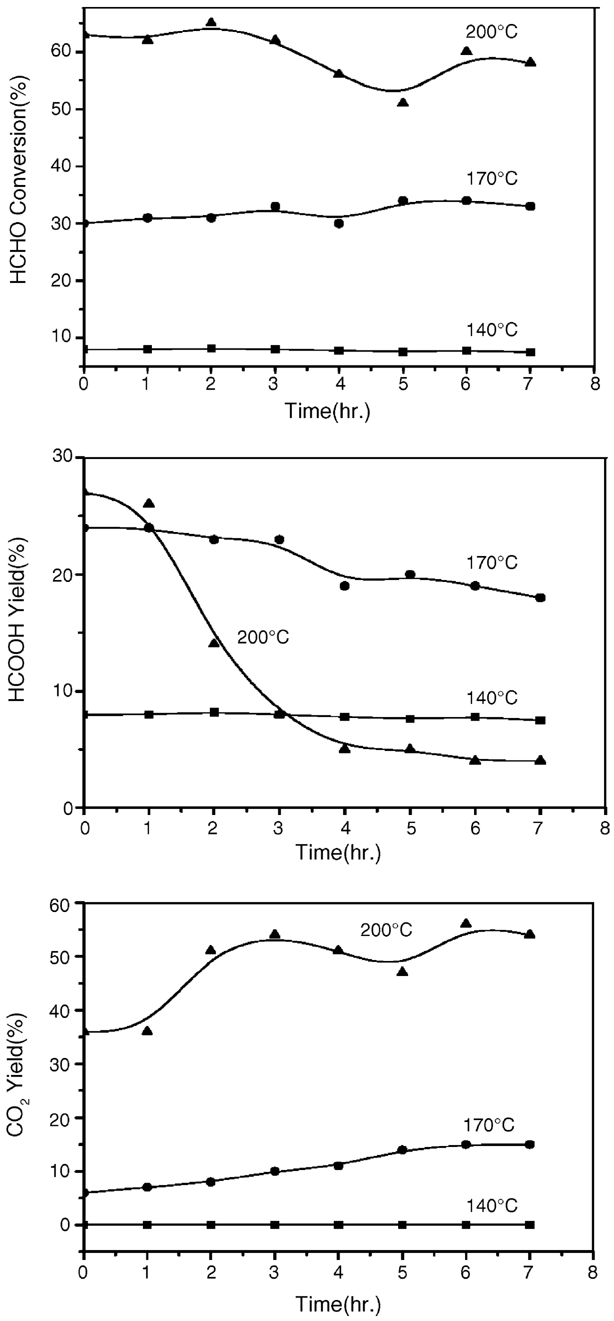

Fig. 6. The stability test of the Fe(H)-MS(70 °C) sample: (▲) 200 °C; (●) 170 °C; (■) 140 °C.

4. Discussion

The 5A molecular sieves itself is not active for the oxidation of HCHO below 280 °C and it becomes active for the HCHO oxidation when it was ion-exchanged with Fe^{3+} ions. Besides, silanols are found to be the active sites, which were related to the production of HCOOH on the catalysts. On the other hand, the ferric species in the catalysts contribute mainly to the production of CO_2. According to the loss of silanols leads to the decrease in the HCOOH fraction in the product and increase in CO_2. The higher the operating temperature is, the greater the HCOOH decrease and CO_2 increase are, as shown in Fig. 6. It can be observed from Fig. 5B and E that the difference between the light-off temperature and the 100% conversion temperature of the uncalcined catalysts is about 100 °C and it is about 60 °C for the other calcined catalysts. This fact also confirms that the silanol active sites are gradually losed when the reaction temperature rises.

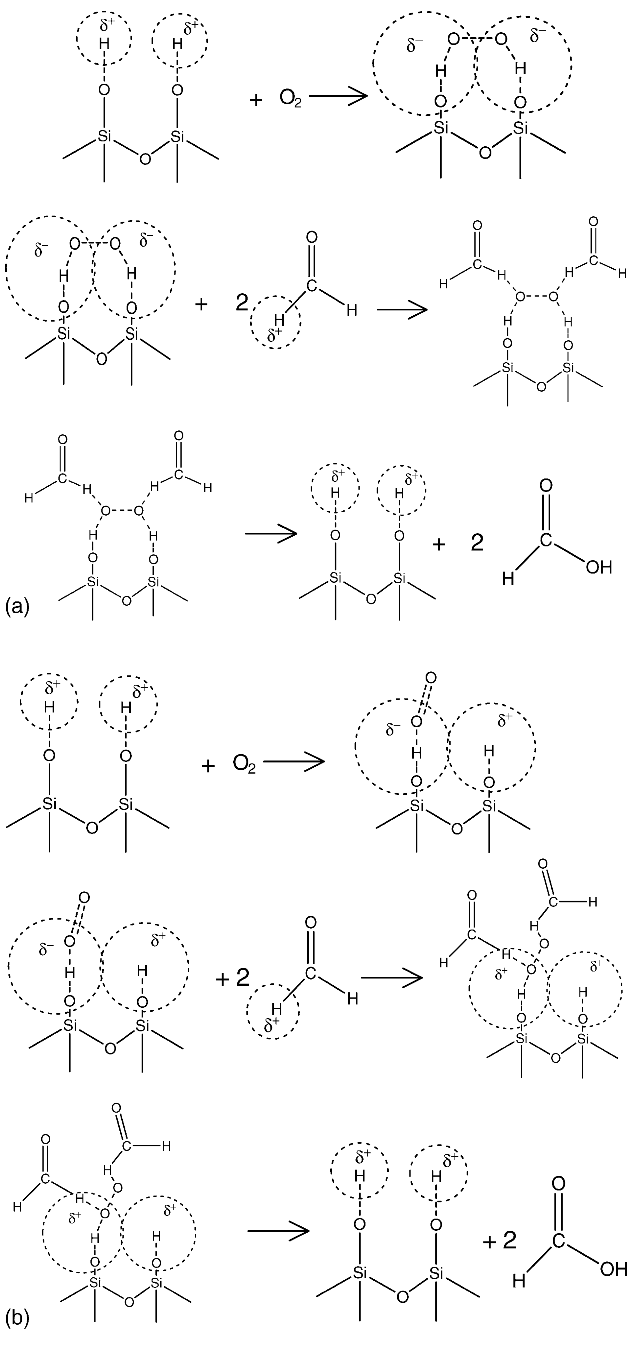

Fig. 7. (a) Mechanism of HCHO oxidation to HCOOH on silanols of zeolite 5A and (b) mechanism of HCHO oxidation to HCOOH on silanols of zeolite 5A.

results in Fig. 5A–G, and the FTIR analysis, there is close relation between the presence of silanols and the production of HCOOH. With the rise of the calcined temperature, the amount of silanols on the catalysts decreased substantially, but the activity for the oxidation of HCHO does not changed obviously. As the content of HCOOH in the product decreases, more CO_2 is produced instead by the reaction. It also reveals that there must be other active sites on the catalysts except for silanols. Ferric species are the most probable active sites in the catalysts. The characteristic peaks of ferric oxides were not observed in the XRD patterns in Fig. 1. On the other hand, the activity of $Fe–SiO_2$ catalyst is poor, compared with ferric 5A molecular sieve, according to the results in Fig. 5H. Thus, iron oxide crystals dispersing among silica are not the active sites for the CO_2 production. Fe^{3+} ions loaded by the ion exchange could be embedded in the frameworks of the zeolite 5A, and formed the Lewis acid sites on the catalysts [26]. Such sites are stable and active for the oxidation of HCHO and HCOOH to CO_2. Furthermore, the light-off temperature of the catalysts with more silanols was lower than that of the catalysts with less silanols. It means that the silanols on the catalysts are active at relatively low temperatures but the Lewis acidic sites formed by Fe^{3+} on the structure of the catalysts are active at relatively high temperatures.

According to the aforementioned analysis, the most probable mechanism of the reaction for the HCHO combustion on the ferric 5A zeolite might be as follows.

4.1. *The first reaction mechanism of HCHO oxidation at lower temperatures on silanols*

The first probable mechanism of the reaction is that two adjacent silanols absorbed one oxygen molecule through bridge connection by weak hydrogen bonds, subsequently; the protons on HCHO molecules and the absorbed oxygen on the silanols formed hydrogen bonds further. As a result, the proton on HCHO molecule and the absorbed oxygen formed hydroxyl, and eventually, HCOOH was formed and separated from the silanols, see (Fig. 7a).

4.2. *The second reaction mechanism of HCHO oxidation at lower temperatures on silanols (Fig. 7b)*

The second probable mechanism of the reaction for the production of HCOOH is that one silanol absorbed one oxygen ion in the form of hydrogen bond. The absorbed oxygen ions and the two protons from different HCHO molecules formed hydrogen bonds further. And finally, HCOOH was formed and broke away from the silanol, see Fig. 7b.

4.3. *The reaction mechanisms of HCHO and HCOOH oxidation at higher temperatures on Lewis acid site formed by Fe^{3+} ions*

The Fe^{3+} on the structure of the 5A zeolite can form Lewis acid sites. The Lewis acid sites on zeolite 5A had strong

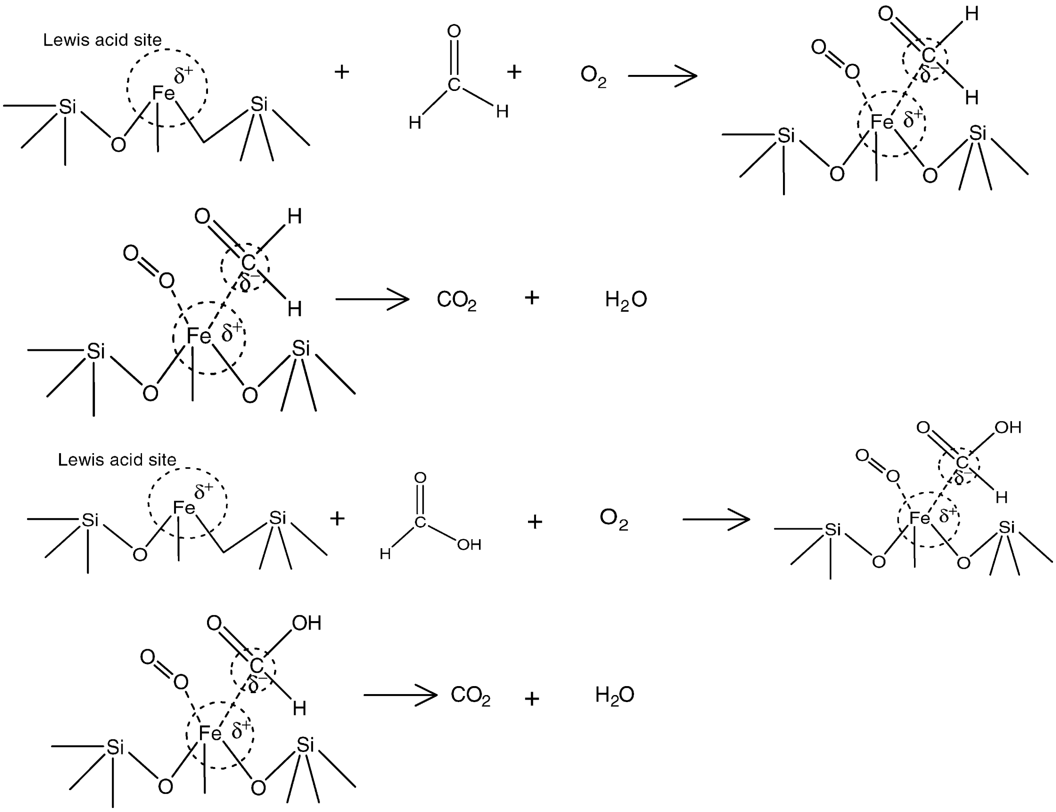

Fig. 8. Mechanism of HCHO and HCOOH oxidation to CO_2 and H_2O on Lewis acid site formed by Fe^{3+} ions on zeolite 5A.

capacity of absorbing negative ions. The oxygen molecule and the carbonyl of HCHO and HCOOH molecule might be absorbed on one Lewis acid site simultaneously. Accordingly, CO_2 and H_2O were formed, see Fig. 8.

5. Conclusions

Doping iron ions to 5A molecular sieves yields active catalysts for the oxidation of HCHO. The catalytic performance of the Fe(H)-5A molecular sieves for the oxidation of HCHO is investigated and we found that the acidity in preparation of the molecular sieves by an ion exchange using $Fe(NO_3)_3$ solution is crucial. It has important influence on the amount of silanols in the structure of the catalysts. From a process at low pH (∼3, adjusted by dilute HNO_3), the catalysts with large amount of silanols are obtained. The silanols on the structure of the Fe(H)-5A and Fe-5A molecular sieves are related to the production of HCOOH. The catalysts with large amount of silanols exhibit a high selectivity to HCOOH in the product. The active sites of silanols in the structure of the catalyst decrease as the calcined temperature is raised, but at high calcination temperatures the framework of the catalysts can be damaged. The appropriate temperatures for calcinations range from 200 to 400 °C. Ferric species on the structure of the catalysts form Lewis acid active sites on the catalysts, which are contributed to the production of CO_2. Therefore, we can manipulate the synthesis conditions to select the product.

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