

# Synthesis and Characterization of Fe-based ZSM-5 Catalysts for Low Temperature Selective Catalytic Reduction (SCR) of NO by NH<sub>3</sub>

Sayeda Halima Begum<sup>1</sup>, Xiaoxiang Han (韓曉祥)<sup>1,2</sup>, Shing-Jong Huang (黃信炘)<sup>3</sup>,  
Chin-Te Hung (洪錦德)<sup>1</sup>, and Shang-Bin Liu (劉尚斌)<sup>1,4,\*</sup>

<sup>1</sup> Institute of Atomic and Molecular Sciences, Academic Sinica, Taipei 10617, Taiwan

<sup>2</sup> College of Food Science and Biotechnology, Zhejiang Gongshang University, Hangzhou 310035, China

<sup>3</sup> Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

<sup>4</sup> Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan

\*E-Mail: sbliu@sinica.edu.tw

## Abstract

The abatement of nitrogen oxides (NO, NO<sub>2</sub>, NO<sub>x</sub>) has received much attention due to increasing environmental concerns and strengthening regulations worldwide. Selective catalytic reduction (SCR) is considered to be an effective and cost-effective technology for the removal of NO<sub>x</sub> from mobile and stationary sources. Fe and Ce containing zeolites have attracted much interests due to their remarkable catalytic activity for SCR of NO<sub>x</sub> (NO + NO<sub>2</sub>) by NH<sub>3</sub>. We report herein the fabrications of FeZSM-5, CeZSM-5, and FeCeZSM-5 (Si/Al = 15) zeolite catalysts by various methods, namely incipient wetness impregnation, chemical vapor deposition (CVD), and by refluxing with organic solvents (such as acetonitrile) while controlling the proportion of metal ingredients under a wide range of operating temperature (200 ~ 500 °C). The Fe and Ce contents were varied to optimize the metal loadings as well as surface acidity of the catalysts. The resultant catalysts were characterized by a variety of different analytical/spectroscopic techniques, *viz.* XRD, TPD of H<sub>2</sub> and NH<sub>3</sub>, and multinuclear (<sup>27</sup>Al, <sup>1</sup>H, and <sup>31</sup>P) solid-state NMR spectroscopy. It was found that FeZSM-5-CVD and FeCeZSM-5-CVD catalysts prepared by CVD method showed only weak SCR catalytic activities over the whole range of temperature examined. On the other hand, catalyst prepared by impregnation method revealed pronounced SCR activity and efficiency over the desirable range of temperature. Among them, the bimetallic FeCeZSM-5-Imp catalyst was found to be more superior over the mono-metal FeZSM-5-Imp sample. On the bases of TPR, TPD, and multinuclear MAS NMR

spectroscopy results, it is indicative that the amount and strength of Brønsted and Lewis acid sites on the surface of FeCeZSM-5-reflux increase with increasing concentration of the incorporated Ce, which is favorable for the absorption of NH<sub>3</sub> to form active intermediates and to increase catalytic performance at lower temperature (200 ~ 500 °C).

Keywords: Fe-based zeolite catalyst, SCR, NO<sub>x</sub>, ZSM-5, acidity.

## 1. Introduction

Nitrogen oxides emitted from mobile and stationary sources, are the major source of harmful air pollutants, which tend to react with hydrocarbons leading to undesirable environmental concerns such as photochemical smoke, acid rain, greenhouse effect, and depletion of stratospheric O<sub>3</sub> layer etc. Thus, R&D of DeNO<sub>x</sub> catalysts has drawn much research attentions over the past few decades. At present, the most efficient technology to remove NO from stationary sources is the selective catalytic reduction (SCR) of NO by ammonia (4NO + 4NH<sub>3</sub> + O<sub>2</sub> = 4N<sub>2</sub> + 6H<sub>2</sub>O) [1].

Zeolites are crystalline aluminosilicates that possess periodic framework, well-defined pore structures, and high surface areas (ca. 500 ~ 800 m<sup>2</sup>/g). Owing to their unique properties, numerous applications *viz.* as substrates for adsorption and separation, ion-exchange and reversible hydration/dehydration capabilities, and as acidic catalysts and so on. Moreover, in terms of operation temperature, zeolitic catalysts are known to sustain a wide of upto ca.

800 °C, and hence are suitable for applications as SCR DeNO<sub>x</sub> catalysts [2].

Among various zeolites, ZSM-5, which possesses interconnected 10-membered ring (10-MR) pore channels of ca. 0.6 nm, is known to be a favorable catalyst for NO decomposition. This has been attributed to the desirable acidity, higher activity for hydrocarbon conversion, suitable thermal stability, and resistance to water and SO<sub>2</sub> poisoning possessed by ZSM-5 over conventional metal oxide catalysts. Transition-metal incorporated zeolites, such as Cu-ZSM-5 was found to be a suitable catalyst for decomposition of NO owing to its high activity and stability [3]. However, Cu-ZSM-5 is also drawback by the narrow operation temperature range, lower activity under high space velocity; inhibition in presence of O<sub>2</sub>, sensitive to water vapor and SO<sub>2</sub>, and so on. In view of reducing NO<sub>x</sub> emission from automobile diesel engine, Fe-incorporated ZSM-5 is one of the desirable catalysts owing to its high activity and durability [4-6]. For example, Fe-ZSM-5 coated monolithic cordierite ceramics was found to exhibit a wide range of operating temperature and high selectivity during NH<sub>3</sub>-SCR reaction: more than 80% of NO<sub>x</sub> may be converted over 400 ~ 650 °C temperature range. It has been shown that while the denitrification activity during NH<sub>3</sub>-SCR over Fe-ZSM-5 may be jeopardized by selective catalytic oxidation (SCO) of NH<sub>3</sub> to N<sub>2</sub> and NO, a moderate decrease (ca. 5 ~ 15%) in SCR activity was observed [7]. While Fe-ZSM-5 may be prepared by a variety of different methods, leading to active sites in the form of Fe<sub>4</sub>O<sub>4</sub> nanoclusters and/or isolated Fe cations, but the nature, roles, and relative concentrations of Fe active sites remain uncertain [8]. It was hypothesized that the strengths and distribution of Brønsted and Lewis acid sites in ZSM-5 zeolite may be altered upon introducing Fe species onto the catalyst. This in turn promotes the formation of reactive intermediates in the presence of adsorbed NH<sub>3</sub>, which in turn improves low-temperature catalytic activity. By comparing the NH<sub>3</sub>-SCR reactivities of a series of Fe-Beta catalysts with varied Fe loading, Yang and co-workers [9] showed that catalyst with 2.5 wt% Fe exhibit the best activity with a NO conversion rate of 97% between the temperature range of 300 ~ 500 °C under a space velocity of 1.9 x 10<sup>5</sup> h<sup>-1</sup>. Fe-ZSM-5 catalyst may also be prepared by chemical

vapor deposition (CVD) of FeCl<sub>3</sub> [10-13], liquid ion-exchange [14-16], Fe<sup>2+</sup> ion generated by iron powder [4,17], hydrothermal synthesis [16] and conventional incipient wetness impregnation method [16,18]. Among them, CVD was found to be a facile route to prepare Fe-ZSM-5 catalyst with high Fe loading and highly active species. Three types of Fe species, namely α-Fe<sub>2</sub>O<sub>3</sub> aggregates, Fe<sub>x</sub>O<sub>y</sub> oligomeric material, and oxo-Fe<sup>3+</sup> were identified [19], the latter (oxo-Fe<sup>3+</sup>) was found to be the active site responsible for catalyzing the SCR. The authors also compared the catalytic performance of various Fe-based zeolite catalysts (e.g., MFI and MOR) during NH<sub>3</sub>-SCR. Regardless of the zeolite support used, a consistent increase in SCR activity with increasing silica-to-alumina (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, or likewise the Si/Al) ratio. The SCR activities over Fe oxides and nitrogen oxide loaded zeolite catalyst were found to independent of their loading and surface areas [20]. On the other hand, a high loading of active Fe species was found to be favorable for SCR reactivity.

The catalytic activity observed for NH<sub>3</sub>-SCR over various Fe-based catalysts was found to follow the following trend: Fe/MFI > Fe/MOR > Fe/FER > Fe/BEA > Fe/Y [21]. Obviously, zeolite with narrow pore channel structure is more favorable for NH<sub>3</sub>-SCR reasons. That the Fe/BEA catalyst prepared by impregnation method exhibited a better NH<sub>3</sub>-SCR activity over Fe/MFI catalyst was attributed to the higher surface area of the former catalyst [9]. On the other hand, for Fe-based zeolite catalysts prepared by CVD method, the activities observed during HC-SCR were found to obey the order: Fe/BEA > Fe/MFI >> Fe/FER > Fe/MOR ≈ Fe/Y [6]. As mentioned earlier, DeNO<sub>x</sub> process have drawn lots of R&D attention for decades, while catalyst for NH<sub>3</sub>-SCR have been extensively studies and in some cases applied in related industries, several crucial issues remain as major challenges, including catalyst abrasion and corrosion resistance, anti-toxicity, and thermal stability of the catalyst. Moreover, detailed mechanism involved during the SCR remains to be verified.

The objective of this study is to prepare Fe- and Fe/Ce-based zeolite catalyst with different metal contents and preparation methods for effective applications as the NH<sub>3</sub>-SCR catalysts. Moreover, by varying the type and amount

of the metal species during different preparation methods and parameters, the nature and oxidation state of the incorporated metal and their roles during SCR will be investigated. On the basis of the studies mentioned about, detailed mechanism invoked during denitrification reaction may be inferred, which, in turn should be favorable for practical industrial applications.

## 2. Experimental

### 2.1 Catalyst preparation

Fe-based mono- and bi-metal ZSM-5 catalysts were prepared by different methods, namely incipient wetness impregnation (Imp), chemical vapor deposition (CVD), and by refluxing with appropriate amount of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and/or  $\text{Ce}(\text{NO}_3)_3$  (Aldrich, 99.99%) precursors with H-ZSM-5 (Si/Al = 15; surface area ca.  $400 \text{ m}^2/\text{g}$ ).

For the impregnation method, appropriate known amount of aqueous  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and/or  $\text{Ce}(\text{NO}_3)_3$  solution was introduced onto H-ZSM-5 at room temperature. Upon evaporating the residual water at 353 K, the solid was first dried at 383 K, then calcined at 873 K in air for 5 h. Whilst for CVD deposition method [6], H-ZSM-5 was first calcined in  $\text{N}_2$  at 873 K to remove the residual water. Subsequently, the calcined H-ZSM-5 was transferred to a glove box under inert environment and mechanically mixed with an appropriate amount of  $\text{FeCl}_3$ , followed by transferring this mixture in a sealed reactor. Finally, the sample was subjected to a heat treatment under flowing  $\text{N}_2$  by gradually increasing the temperature with a rate of K/min till it reaches 873 K, then, maintained at this temperature for 5 h. At this point,  $\text{FeCl}_3$  is anticipated to sublime to diffuse into the pore channels of H-ZSM-5. The sample was then cooled down to room temperature, thoroughly washed by deionized water to replace chloride ions with hydroxide ions, then dried at 383 K. Finally, the sample was calcined at 873 K in air for 5 h.

For FeCeZSM-5 catalyst prepared by refluxing with organic solvent [1], first, iron acetylacetonate and cerium nitrate were dissolved in acetonitrile ( $\text{CH}_3\text{CN}$ ), then, mixed with H-ZSM-5. Being possesses a high dielectric constant and a higher dipole moment than water, acetonitrile serves as an interaction medium for the metal precursor inside the pore channels of H-ZSM-

5. To attain sample with a desired molar ratio of the incorporated metal, iron and/or cerium precursor solution was added slowly (typically over a period of 8 h) over 5 g of zeolite dispersed in 80 mL of acetonitrile at 430 K under vigorous stirring in a refluxing flask. The tri-phase solution at high temperature helps to facilitate specific interactions between the metal cations and the pore walls of zeolite. The mixture solution was hydrothermally treated at 393 K for 48 h. After evaporating the solvent, the resultant product was dried at 383 K overnight, followed by calcination treatment at 873 K in air for 5 h.

### 2.2 Characterization

All catalysts were characterized by powder X-ray diffraction (XRD) using a PANalytical (X' Pert PRO) diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) at 40 kV and 120 mA. The XRD spectrum was recorded in the range of  $20 < 2\theta < 80$  at a 0.02 interval.

$\text{H}_2$ -TPR was carried out with a Micromeritics AutoChem 2920 apparatus using TCD detection. The  $\text{H}_2$  consumption was determined after trapping  $\text{H}_2\text{O}$  at ca. 200 K. Prior to the measurement, ca. 100 mg sample was first calcined at  $600^\circ\text{C}$  in air for 2 h, then cooled to room temperature (RT).  $\text{H}_2$ -TPR profile was recorded under  $\text{H}_2/\text{Ar}$  (25/75, v/v) mixture gas flow ( $13 \text{ cm}^3/\text{min}$ ) from RT to  $900^\circ\text{C}$  (ramp rate  $10^\circ\text{C}/\text{min}$ ).

Likewise, for  $\text{NH}_3$ -TPD studies, ca. 100 mg of finely ground powder was loaded into a quartz tube reactor and pretreated by heating in the presence of He flow ( $50 \text{ mL}/\text{min}$ ) from ambient to  $600^\circ\text{C}$  (ramp rate  $15^\circ\text{C}/\text{min}$ ), then, kept at the final temperature for 2 h. While the sample was stabilized at a desirable temperature  $T_{\text{ads}}$  (for example, at  $100^\circ\text{C}$ ), the sample was dosed with  $50 \text{ mL}/\text{min}$  of 15%  $\text{NH}_3/\text{He}$  for 15 min. Next, the sample was flushed with  $50 \text{ mL}/\text{min}$  of He for 15 min to remove the weakly bound (physisorbed)  $\text{NH}_3$ , after which the sample temperature was reduced to  $50^\circ\text{C}$ . Once a stable baseline has been reached by TCD (thermal conductivity detector), The  $\text{NH}_3$ -TPD profile was recorded by ramping the temperature from  $50^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  to  $600^\circ\text{C}$ , then kept for 2 h [21].

All NMR experiments were carried out on a Bruker AVANCE III 500 spectrometer using a 4-mm double-resonance MAS probehead. The Larmor frequencies for

$^{31}\text{P}$  and  $^{27}\text{Al}$  are 202.46 and 130.32 MHz, respectively. Spectra were acquired using a single-pulse sequence under a sample spinning rate of 12 kHz. The excitation pulse for  $^{31}\text{P}$  and  $^{27}\text{Al}$  was 1.5 ( $\pi/6$ ) and 1.0 us ( $\pi/12$ ) and the recycle delay was 10.0 and 0.5 s, respectively. The chemical shifts of  $^{31}\text{P}$  and  $^{27}\text{Al}$  were referenced to 85% phosphoric acid and 1 M  $\text{Al}(\text{NO}_3)_3$  aqueous solutions, respectively.

The acid properties of various catalyst were characterized by solid-state  $^{31}\text{P}$  NMR of adsorbed trimethylphosphine oxide [22,23]. Prior to the adsorption of TMPO probe molecule, catalyst was first subjected to a thorough dehydration treatment at 350  $^\circ\text{C}$  for 48 h under vacuum ( $< 10^{-5}$  Torr). Subsequently, a known amount of TMPO dissolved in anhydrous  $\text{CH}_2\text{Cl}_2$  was introduced into a vessel containing the dehydrated solid sample in a  $\text{N}_2$  glove box, followed by removal of the  $\text{CH}_2\text{Cl}_2$  solvent by evacuation at 50  $^\circ\text{C}$ . To ensure a uniform adsorption of adsorbate probe molecules in the pores/channels of the porous adsorbents, the sealed sample vessel was further subjected to thermal treatment at ca. 150  $^\circ\text{C}$  (note that the melting point of TMPO is ca. 140  $^\circ\text{C}$ ) for at least 1 h. Finally, the sealed sample vessel was placed in a  $\text{N}_2$  glove box where the TMPO-loaded sample was transferred into a MAS rotor and then sealed by a gas-tight Kel-F cap.

The NMR spectra were analyzed quantitatively by using external reference materials such as  $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  for  $^{27}\text{Al}$ , adamantane for  $^1\text{H}$  and  $(\text{NH}_4)_2\text{HPO}_4$  for  $^{31}\text{P}$ .

### 2.3 Catalytic tests

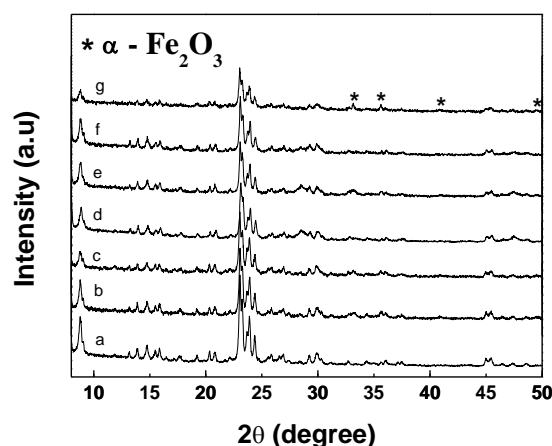
The SCR of NO by  $\text{NH}_3$  was operated in a fixed-bed flow reactor at atmospheric pressure. The reaction temperature was monitored using a programmable temperature controller. Reactant gases were a mixture consisting 500 ppm NO, 500 ppm  $\text{NH}_3$ , 2.9%  $\text{O}_2$ , and the balance of  $\text{N}_2$ . The catalyst weight was 0.1 g and the total flow rate was 350 mL/min.  $\text{NO}_x$  conversion was obtained from the difference in the  $\text{NO}_x$  concentrations before and after the SCR reaction under steady-state conditions.

## 3. Results and Discussions

### 3.1 XRD studies

The XRD patterns of FeZSM-5, CeZSM-5 and FeCeZSM-5 prepared by different methods are display in Fig. 1. All

Fe-based mono- and bi-metal catalysts showed the characteristics peaks of MFI skeleton, signifying that the composition of MFI remain unchanged even after introducing Fe and Ce and subsequent calcination treatment. Moreover, some small diffraction peaks at  $2\theta = 33.8^\circ$ ,  $36.5^\circ$ ,  $40.9^\circ$ , and  $49.5^\circ$  may be attributed to the presence of  $\alpha\text{-Fe}_2\text{O}_3$  phase [17]. The intensities of these peaks are more pronounced for FeZSM-5(Imp) and FeZSM-5(CVD) samples. For the bimetallic samples, the observed peak intensities follow the trends: FeCeZSM-5(CVD) > FeCeZSM-5(Imp) > FeCeZsm-5(Reflux), which is opposite to the observed NO activity (see below).

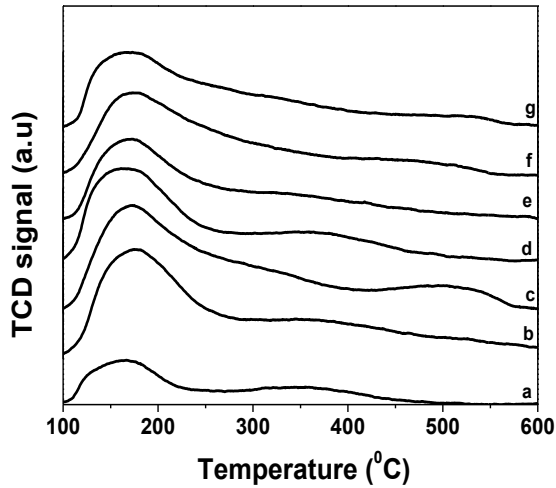


**Fig. 1.** XRD patterns over (a) HZSM-5, (b) Fe-ZSM-5(Imp), (c) FeZSM-5(CVD), (d) CeZSM-5(Imp) (e) FeCeZSM-5(Imp) (f) FeCeZSM-5(Reflux), and (g) FeCeZSM-5(CVD).

### 3.2 $\text{NH}_3$ -TPD

Figure 2 presents the  $\text{NH}_3$ -TPD profiles of FeZSM-5, CeZSM-5 and FeCeZSM-5 prepared by different methods. Two broad peaks located at about 170  $^\circ\text{C}$  and 350  $^\circ\text{C}$  were observed for H-ZSM-5, the former peak may be assigned to physisorbed  $\text{NH}_3$ , while the latter peak at higher temperature may be attributed to  $\text{NH}_3$  strongly adsorbed on the Brønsted acid sites [6,8,10]. Weaker desorption peak intensities were observed for FeZSM-5(Imp), CeZSM-5(Imp), and FeZSM-5(CVD) compared to that of pristine H-ZSM-5, due to substitution of Brønsted acid protons by  $\text{Fe}^{3+}$ . Whereas the low-temperature (at 170  $^\circ\text{C}$ ) peak intensity observed for FeZSM-5(CVD) is weaker than that of H-ZSM-5 is due to  $\text{Fe}^{3+}$  ion exchange. Likewise, much weaker high-temperature peak intensity was observed for FeCeZSM-5(CVD) than H-ZSM-5. In terms of the high-T peak intensity, the following trend

may be inferred: Imp > Reflux > CVD. It is intriguing to find desorption peaks for FeZSM-5(CVD) at ca. 175 °C, 325 °C, and 525 °C, which indicate NH<sub>3</sub> desorption from binuclear Fe (Fe-O-Fe) species.



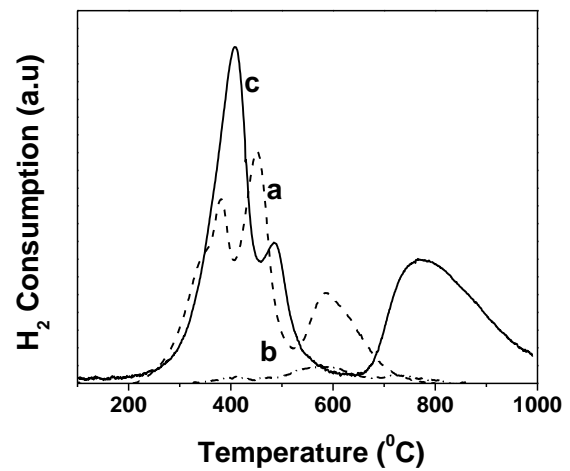
**Fig. 2.** NH<sub>3</sub>-TPD profiles (a) HZSM-5, (b) FeZSM-5(Imp), (c) FeZSM-5(CVD), (d) CeZSM-5(Imp) (e) FeCeZSM-5(Imp) (f) FeCeZSM-5(Reflux), and (g) FeCeZSM-5(CVD).

### 3.3 H<sub>2</sub>-TPR

H<sub>2</sub>-TPR curves of FeZSM-5, CeZSM-5, and FeCeZSM-5 prepared by CVD method are presented in Fig. 3. The TPR profile of FeZSM-5(CVD) shows three zones of hydrogen consumption: 380-400 °C, 400-480 °C, and 580-650 °C; in good agreement with previous studies [6,10]. The first peak should be corresponding to the reduction of Fe<sup>3+</sup> (bare Fe<sup>3+</sup> cations, oxo- or species such as FeO<sup>+</sup>, Fe(OH)<sup>2+</sup> or [(OH)FeO-Fe(OH)]<sup>2+</sup>) to Fe<sup>2+</sup>. Presumably, reduction of Fe<sup>2+</sup> to Fe<sup>0</sup> should occur at much higher temperature (> 800 °C), which is close to the collapse temperature of the zeolite network [15]. The reduction peak at ca. 600 °C may be attributed to reduction of Fe<sub>3</sub>O<sub>4</sub> nanoclusters to FeO, whereas reduction of FeO to Fe is anticipated to occur at ca. 580 °C. Species such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoclusters was found to reduce at ca. 350 °C [15]. On the other hand, the H<sub>2</sub>-TPR curves observed for CeZSM-5 (Figs. 3 and 4) show a broad peak with maximum at ca. 580 °C, which may be ascribed due to reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> [1]. Apparently, the Ce species are more difficult to reduce in zeolite than Fe. As for FeCeZSM-5, their H<sub>2</sub>-TPR profiles reveal that both Fe and Ce species are reduced at similar temperature due to strong mutual interactions, although Fe reduces must faster than Ce. The

maxima H<sub>2</sub> consumption peaks observed at 380 °C and 800 °C, which are more intense than that observe for FeZSM-5, corresponding to reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> and Ce<sup>4+</sup> to Ce<sup>3+</sup>, respectively.

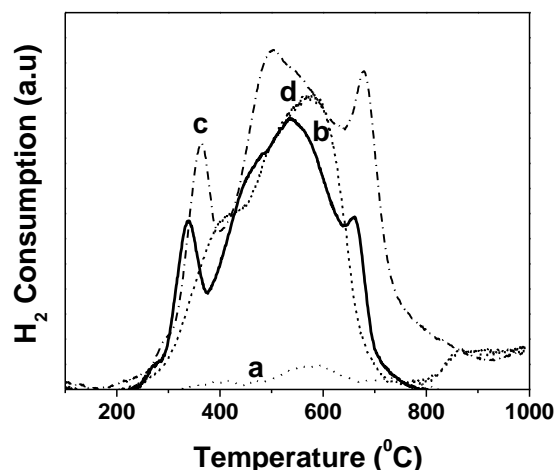
Moreover, the widths of the reduction peaks provide additional information. For example, the widths account for catalysts prepared by CVD method (Fig. 3) is obviously narrower than those by Imp method (Fig. 4), reflecting that the latter contain more variety of Fe species. For catalysts prepared by sublimation method by using FeCl<sub>3</sub>, additional weak H<sub>2</sub> consumption peak at ca. 580 °C (FeZSM-5) and 800 °C (FeCeZSM-5), which may be attributed to the reduction of iron oxide aggregates.



**Fig. 3.** H<sub>2</sub>-TPR curves of (a) FeZSM-5(CVD), (b) CeZSM-5(Imp), and (c) FeCeZSM-5(CVD).

The H<sub>2</sub>-TPR profiles of Fe-based catalysts prepared by Reflux and Impregnation methods are shown in Fig. 4. Two distinct reduction peaks may be identified for FeZSM-5(Imp) at ca. 310-340 °C and 410-580 °C. Again, the former corresponds to reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> [6], whereas the latter may be attributed to reduction of Fe<sub>3</sub>O<sub>4</sub> nanoclusters to FeO. On the other hand, FeCeZSM-5(Imp) shows three zones for H<sub>2</sub> consumption: 320-380, 420-580, and 700-750 °C. That these peaks exhibit much narrower peak widths compared to those in FeZSM-5(Imp) is ascribed due to simultaneous reduction of Fe and Ce species, indicating a strong interactions between them. The reduction peak arises at ca. 700 °C has been a matter of debate. Krishna *et al.* [10] attributed this peak to the reduction of Fe<sub>x</sub>O<sub>y</sub> nanoparticles. Likewise, for

FeCeZSM-5(Reflux), the broad reduction peak around 420-630 °C with a maximum at ca. 520 °C should be arising from reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>. Unfortunately, it is difficult to quantitatively identify all Fe (or Ce) species at present; additional studies by Mössbauer spectroscopy may provide further information.



**Fig. 4.** H<sub>2</sub>-TPR curves for (a) CeZSM-5(Imp), (b) FeZSM-5(Imp), (c) FeCeZSM-5(Imp), and (d) FeCeZSM-5(Reflux).

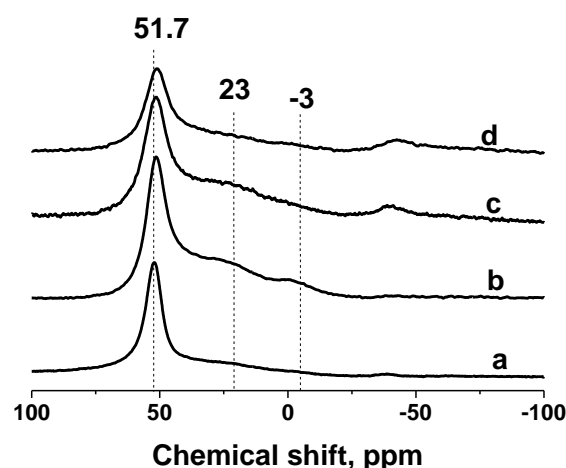
### 3.4 Solid-state NMR studies

#### 3.4.1 <sup>27</sup>Al MAS NMR

Figure 5 shows <sup>27</sup>Al MAS NMR spectra of TMPO loaded samples. For the Fe-based catalysts examined, three <sup>27</sup>Al resonances at ca. 51.7, 23.0 and -3.0 ppm were observed. The main peak at ca. 51.7 ppm only appeared for the parent H-ZSM-5, and may be unambiguously ascribed to tetrahedral Al species in the zeolite framework. The signals observed at ca. 23.0 ppm for metal-containing samples are due to distorted framework Al or penta-coordinated Al species, and the peak at ca. -3.0 ppm should be arising from extra-framework octahedral Al species. These spectra suggest that the chemical and thermal treatments used herein for incorporation of metal species into ZSM-5 inevitably lead to partial distortion and collapse of the zeolitic framework.

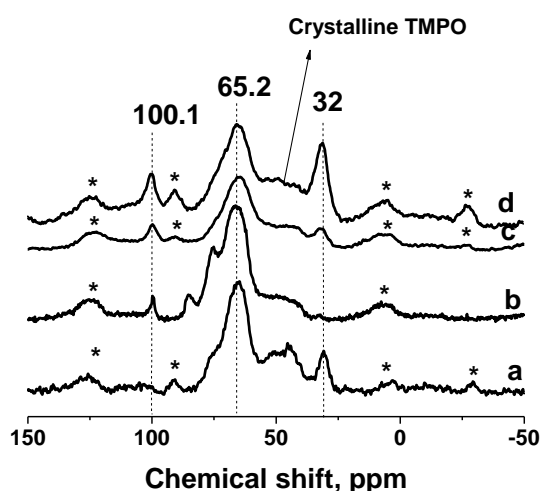
#### 3.4.2 <sup>31</sup>P MAS NMR

Figure 6 shows <sup>31</sup>P MAS NMR spectra of all TMPO loaded samples. In all cases, <sup>31</sup>P resonances appeared in the range from 32 to 100 ppm. It is well-known that the <sup>31</sup>P NMR chemical shift ( $\delta^{31}\text{P}$ ) of adsorbed TMPO should



**Fig. 5.** <sup>27</sup>Al MAS NMR spectra of TMPO adsorbed on various catalysts: (a) HZSM-5, (b) Fe FeZSM-5(Imp), (c) FeCeZSM-5(Imp), and (d) FeCe(Reflux).

increase with increasing acid strength of Brønsted acid site [22,23]. Typically, <sup>31</sup>P resonances with  $\delta^{31}\text{P} < 50$  ppm are due to physisorbed TMPO or bulk TMPO (at ca. 39 ppm) and hence are not related to the catalytic properties of the acid catalysts. For the parent H-ZSM-5 (Fig. 6a), broad <sup>31</sup>P signal with overlapped resonance peaks spanning from  $\delta^{31}\text{P} \sim 50$ -80 ppm with a main and a shoulder peak at ca. 65.2 and 75.7 ppm, respectively, in agreement with earlier reports [22]. Incorporation of Fe by Imp method further led to a more intense peak at 75.0 ppm and an additional peak at ca. 84.5 ppm (Fig. 6b), indicating that incorporation of Fe tends to promote enhancement of Brønsted acid sites with stronger acid strengths. However, in the case of bimetallic FeCeZSM-5(Imp) and FeCeZSM-5(Reflux), only acid sites with moderate acid strength with main peak at  $\delta^{31}\text{P} \sim 65.2$  ppm was observed. It is indicative that the introduction of a second metal (Ce) is unfavorable for enhancing the strength of Brønsted sites. Nevertheless, it is intriguing to observe an additional peak at ca. 100 ppm for all Fe-based catalyst samples. This peak with  $\delta^{31}\text{P}$  corresponding to acid strength far beyond the threshold of superacidity (86 ppm) [23], has never being observed for zeolitic materials. While its nature remains unclear, it may be arising from TMPO adsorbed on Lewis acid sites induced in the presence of promoted metals (Fe, Ce). More experiments have been undertaken to clarify related issues.



**Fig. 6.**  $^{31}\text{P}$  MAS NMR spectra of TMPO adsorbed on various catalysts: (a) HZSM-5, (b) FeZSM-5(Imp), (c) FeCeZSM-5(Imp), and (d) FeCeZSM-5(Reflux).

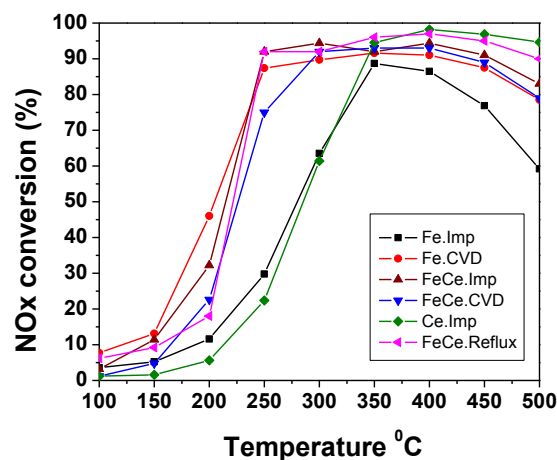
### 3.5 Catalytic activity

Figure 7 shows correlations of  $\text{NO}_x$  conversion during  $\text{NH}_3$ -SCR reaction as a function of reaction temperature over various FeZSM-5, CeZSM-5 and FeCeZSM-5 catalysts prepared by different methods. It is clear that FeZSM-5(Imp) sample does not exhibit the anticipated catalytic activity of  $\text{NO}_x$  over the temperature range than bimetallic FeCeZSM-5(Imp) having the same Fe and Ce content. On the other hand, CeZSM-5(Imp) shows more than 90% conversion of  $\text{NO}_x$  only over 350  $^\circ\text{C}$ . Catalyst samples (FeZSM-5 and FeCeZSM-5) prepared by CVD exhibit similar trends for NO conversion over 300-400  $^\circ\text{C}$  (with 90% conversion). On the other hand, FeCeZSM-5(Reflux) catalyst with the same content of Fe and Ce prepared by reflux method reveals better superior performances with > 90% conversion of NO over a wide range (250-500  $^\circ\text{C}$ ) of temperature. These results indicate that the collaborative effect of bimetallic (Fe and Ce) facilitates enhancement of catalytic activity during SCR of NO by  $\text{NH}_3$ .

## 4 Conclusions

In conclusion, Fe-based mono- and bimetal catalysts prepared by different methods with the same metal content were tested for SCR of NO by  $\text{NH}_3$  over the temperature range of 100- 500  $^\circ\text{C}$ . The activities observed

during SCR of NO by  $\text{NH}_3$  over various catalysts prepared



**Fig. 7.** SCR of NO by  $\text{NH}_3$  over various catalysts.

by different methods were found to follow the trend: Reflux > Imp > CVD. On the basis of  $\text{H}_2$ -TPR results, three types of Fe species were identified in these Fe-based catalysts, namely  $\alpha\text{-Fe}_2\text{O}_3$  particles,  $\text{Fe}_x\text{O}_y$  oligomer in the extra-framework of zeolite, and Fe-O-Fe and Fe-O-Ce species. The distribution of these Fe species in the catalysts depends strongly on the preparation method. Although  $\text{NH}_3$ -TPD data provided useful qualitative information regarding to acidity of the Fe-based catalysts, they fail to provide quantitative information of the Brønsted acid sites. On the other hand,  $^{31}\text{P}$  MAS NMR of adsorbed TMPO provides valuable information on relevant acid features of the catalysts. The observed  $\text{DeNO}_x$  conversions were above 90% for FeCeZSM-5(Reflux) and FeCeZSM-5(Imp) samples in a wide temperature window 250-500  $^\circ\text{C}$  and 250-450  $^\circ\text{C}$ , respectively, under a total flow rate of 350 mL/min. It is conclusive that these Fe-based (mono- and bimetallic) SCR catalysts which show satisfactory catalytic performances over a relative low operating temperature range may be useful for practical industrial applications.

### Acknowledgments

This support of this work by the National Science Council (NSC98-2113-M-001-017-MY3), Taiwan. SHB thanks Taiwan International Graduate Program (TIGP), Academia Sinica, for the student scholarship.

## References

- [1] G. Carja, G. Delahay, C. Signorile, B. Coq, "Fe-Ce-ZSM-5 a new catalyst of outstanding properties in the selective catalytic reduction of NO with NH<sub>3</sub>", *Chem. Commun.*, **12**, 1404, 2004.
- [2] L. Olsson, H. Sjövall, R. J. Blint, "A kinetic model for ammonia selective catalytic reduction over Cu-ZSM-5", *Applied Catalysis B: Environ.*, **81**, 203, 2008.
- [3] M. Iwamoto, H. Fucrukawa, Y. Mine, F. Uemura, S. I. Mikuriya, S. Kagaw, "Copper (II) ion-exchanged ZSM-5 zeolites as highly active catalysts for direct and continuous decomposition of nitrogen monoxide", *Chem. Commun.*, **16**, 1272, 1986.
- [4] R. Q. Long, R. T. Yang, "Superior Fe-ZSM-5 Catalyst for Selective Catalytic Reduction of Nitric Oxide by Ammonia", *J. Am. Chem. Soc.*, **121**, 5595, 1999.
- [5] A. Z. Ma, W. Grunert, "Selective catalytic reduction of NO by ammonia over Fe-ZSM-5 catalysts", *Chem. Commun.*, **1**, 71, 1999.
- [6] H. Y. Chen, W. M. H. Sachtler, "Activity and durability of Fe/ZSM-5 catalysts for lean burn NO<sub>x</sub> reduction in the presence of water vapor", *Catal. Today*, **42**, 73, 1998.
- [7] K. Oliver, D. Mukundan, E. Martin, A. Wokaun, N. Söger, M. Pfeifer, Y. Demel, L. Mussmann, "Investigation of the selective catalytic reduction of NO by NH<sub>3</sub> on Fe-ZSM5 monolith catalysts", *Appl. Catal. B: Environ.*, **66**, 208, 2006.
- [8] R. Joyner, M. Stockenhuber, "Preparation, Characterization, and Performance of Fe-ZSM-5 Catalysts", *J. Phys. Chem. B*, **103**, 5963, 1999.
- [9] C. H. He, Y. H. Wang, Y. S. Cheng, C. K. Lambert, R. T. Yang, "Activity, stability and hydrocarbon deactivation of Fe/Beta catalyst for SCR of NO with ammonia", *Appl. Catal. A: Gen.*, **368**, 121, 2009.
- [10] K. Krishna, G. B. F. Seijer, C. M. van den Bleek, M. Makkee, G. Mul, H. P. A. Calis, "Selective Catalytic Reduction of NO with NH<sub>3</sub> over Fe-ZSM-5 Catalysts Prepared by Sublimation of FeCl<sub>3</sub> at Different Temperatures", *Catal. Lett.*, **86**, 121, 2003.
- [11] F. Heinrich, C. Schmidt, E. Löffler, M. Menzel, W. Grunert, "Fe-ZSM-5 Catalysts for the Selective Reduction of NO by Isobutane—The Problem of the Active Sites", *J. Catal.*, **212**, 157, 2002.
- [12] L. J. Lobree, I. C. Hwang, J. A. Reimer, A. T. Bell, "Investigations of the State of Fe in H-ZSM-5", *J. Catal.*, **186**, 242, 1999.
- [13] V. G. Komvokis, E. F. Iliopoulou, I. A. Vasalos, K. S. Triantafyllidis, C. L. Marshall, "Development of optimized Cu-ZSM-5 deNO<sub>x</sub> catalytic materials both for HC-SCR applications and as FCC catalytic additives", *Appl. Catal. A: Gen.*, **325**, 345, 2007.
- [14] G. Delahay, D. Valade, A. Guzman-Vargas, B. Coq, "Selective catalytic reduction of nitric oxide with ammonia on Fe-ZSM-5 catalysts prepared by different methods", *Appl. Catal. B: Environ.*, **55**, 149, 2005.
- [15] M. Schwidder, M. S. Kumar, K. Klementiev, M. M. Pohl, A. Bruckner, W. Grunert, "Selective reduction of NO with Fe-ZSM-5 catalysts of low Fe content: I. Relations between active site structure and catalytic performance", *J. Catal.*, **231**, 314, 2005.
- [16] R. Q. Long, R. T. Yang, "Fe-ZSM-5 for Selective Catalytic Reduction of NO with NH<sub>3</sub>: A Comparative Study of Different Preparation Techniques", *Catal. Lett.*, **74**, 201, 2001.
- [17] K. A. Dubkov, N. S. Ovanesyan, A. A. Shteinman, E. V. Starokon, G. I. Panov, "Evolution of Iron States and Formation of  $\alpha$ -Sites upon Activation of FeZSM-5 Zeolites", *J. Catal.*, **207**, 341, 2002.
- [18] A. Ribera, I. W. C. E. Arends, S. de Vries, J. Perez-Ramirez, R. A. Sheldon, "Preparation, Characterization, and Performance of FeZSM-5 for the Selective Oxidation of Benzene to Phenol with N<sub>2</sub>O", *J. Catal.*, **195**, 287, 2000.
- [19] M. Iwasaki, K. Yamazaki, K. Banno, H. Shinjoh, "Characterization of Fe/ZSM-5 DeNO<sub>x</sub> catalysts prepared by different methods: Relationships between active Fe sites and NH<sub>3</sub>-SCR performance", *J. Catal.*, **260**, 205, 2008.
- [20] M. Iwasaki, K. Yamazaki, H. Shinjoh, "Ethanol dehydration to ethylene on acid carbon catalysts", *Appl. Catal. B: Environ.*, **103**, 302, 2011.
- [21] B. Greenhalgh, M. Fee, A. Dobri, J. Moir, R. Burich, J. P. Charland, M. Stanculescu, "DeNO<sub>x</sub> activity-TPD correlations of NH<sub>3</sub>-SCR catalysts", *J. Mol. Catal. A: Chem.*, **333**, 121, 2010.
- [22] Q. Zhao, W. H. Chen, S. J. Huang, Y. C. Wu, H. K. Lee, S. B. Liu, "Discernment and Quantification of Internal and External Acid Sites on Zeolites", *J. Phys. Chem. B*, **106**, 4462, 2002.
- [23] A. Zheng, S. J. Huang, S. B. Liu, F. Deng, "Acid Properties of Solid Acid Catalysts Characterized by Solid-State <sup>31</sup>P NMR of Adsorbed Phosphorous Probe Molecules", *Phys. Chem. Chem. Phys.*, **13**, 14889, 2011.