



## Acidity-activity correlation over bimetallic iron-based ZSM-5 catalysts during selective catalytic reduction of NO by NH<sub>3</sub>

Sayeda Halima Begum<sup>a,b,1</sup>, Chin-Te Hung<sup>a</sup>, Yit-Tsong Chen<sup>a,b</sup>, Shing-Jong Huang<sup>c</sup>,  
Pei-Hao Wu<sup>a</sup>, Xiaoxiang Han<sup>d,\*\*</sup>, Shang-Bin Liu<sup>a,e,\*</sup>

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

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

<sup>c</sup> Instrumentation Center, National Taiwan University, Taipei 10617, Taiwan

<sup>d</sup> Department of Applied Chemistry, Zhejiang Gongshang University, Hangzhou 310035, China

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

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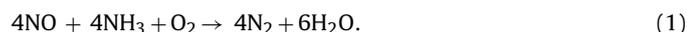
### ABSTRACT

The effect of acidic properties over a series of Lanthanide metal incorporated Fe-based H-ZSM-5 (Si/Al = 15) catalysts on catalytic activity during selective catalytic reduction (SCR) of NO by NH<sub>3</sub> was investigated. Various mono- (M<sub>1</sub>-ZSM-5; M<sub>1</sub> = Fe, Ce, Pr, Nd, and Sm) and bimetallic (M<sub>2</sub>Fe-ZSM-5; M<sub>2</sub> = Ce, Pr, Nd, and Sm) catalysts were prepared and their physicochemical properties were characterized by a variety of analytical and spectroscopic techniques. In particular, their acidic properties were studied by different molecular probe techniques, including the conventional ammonia-TPD and pyridine-IR methods, as well as solid-state <sup>31</sup>P MAS NMR of adsorbed trimethylphosphine oxide (TMPO). Among various catalysts examined, the CeFe-ZSM-5 catalyst was found to exhibit an optimal NO conversion exceeding 95% over a temperature range of 300–500 °C (WHSV = 68,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>). The superior SCR activity observed for the bimetallic Fe-based catalysts is attributed to the synergistic effect from the Brønsted acidity of the MFI zeolite and strong Lewis acidity induced by the incorporated active metal ion species, particularly when incorporated with a secondary Lanthanide metal ion.

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### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>; x = 1, 2), namely nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), are hazardous air pollutants, mostly emitting from both mobile and stationary sources. The state-of-the-art DeNO<sub>x</sub> process technology for efficient removal of NO invokes the standard selective catalytic reduction (SCR) of NO by ammonia [1,2]:



Microporous zeolites have been widely exploited as solid acid catalysts for the SCR DeNO<sub>x</sub> process owing to their unique prop-

erties such as well-defined pore structures, high surface areas (ca. 500–800 m<sup>2</sup> g<sup>-1</sup>), thermal stability (up to ca. 800 °C), and desirable acidity [3]. It has been revealed that the framework of microporous zeolites plays an important role during the SCR of NO and that the incorporation of non-reducible Al<sup>3+</sup> ions onto H-ZSM-5 zeolite tends to enhance the acidity of the catalyst desirable for the SCR reaction [4]. Moreover, in terms of reducing the NO<sub>x</sub> emission from mobile sources, such as automobile diesel engines, iron (Fe)-based zeolites are most desirable catalysts owing to their high activity and durability [5–11]. The advantage of employing metal-based zeolites for the SCR process is that NO must be first oxidized to form NO<sub>2</sub>, which is the rate-determining step of the reaction. For the Fe-based zeolite catalyst, the incorporated Fe metals act as the primary active centers for the formation of NO<sub>2</sub>, while the SCR reaction invokes acid sites located in pore channels of the zeolite. While NO<sub>2</sub> is anticipated to be consumed immediately after its formation during SCR processes, further reduction of NO<sub>x</sub> with NH<sub>3</sub> should be closely related to the incorporated Fe, whose presences greatly affect the detailed acid features (e.g., type, concentration, and strength of acid sites) of the acid catalyst.

\* Corresponding author at: Institute of Atomic and Molecular Sciences, Academic Sinica, Taipei 10617, Taiwan.

\*\* Corresponding author.

E-mail addresses: [hxx74@126.com](mailto:hxx74@126.com) (X. Han), [sbliu@sinica.edu.tw](mailto:sbliu@sinica.edu.tw),

[sbliu.iams@gmail.com](mailto:sbliu.iams@gmail.com) (S.-B. Liu).

<sup>1</sup> Present address: Department of Chemistry, University of Chittagong, Chittagong 4331, Bangladesh.

Nonetheless, regardless of the R&D attention drawn for Fe-based zeolite catalysts (particularly Fe-ZSM-5) in the activation of NO<sub>x</sub>, the active sites invoked for the superior catalytic performance during the SCR reaction and the role of acidity of the supported catalyst remain uncertain [12]. In addition, while the Fe-ZSM-5 catalyst may be prepared by a variety of facile methods, leading to the formations of Fe<sub>3</sub>O<sub>4</sub> nanoclusters and/or isolated Fe cations, the nature, concentration, and roles of these Fe active sites remain to be understood [13]. Boroń et al. [14] reported a series of Fe-containing zeolites prepared by different methods. The authors attributed the variations in catalytic activities during NO reduction due to the presence of pseudo-tetrahedral Fe<sup>3+</sup> species. It was hypothesized that the strength and distribution of Brønsted and Lewis acidic sites in H-ZSM-5 may be altered upon incorporation of the Fe metal species onto the zeolite catalyst, which would in turn shifting the overall catalytic activity towards lower temperatures [13]. However, the authors proposed that the influence of Brønsted acidity is less obvious during NH<sub>3</sub>-SCR. Brandenberger et al. [12] reported that the presence of Brønsted acidity in the zeolite catalyst (hereafter denoted by 'Z') is vital during the SCR of NO<sub>x</sub> in NH<sub>3</sub>; the formation of ammonium ions tends to further react with the surface NO<sub>x</sub> species to form active complex, such as [(NH<sub>4</sub>)<sub>x</sub>NO<sub>2</sub>]<sub>(x = 1, 2)</sub>, leading to the yields of N<sub>2</sub> and H<sub>2</sub>O [12,15–23]. On the other hand, Peña et al. [24] pointed out that the coexistence of Brønsted and Lewis acidic sites is essential for the SCR of NO. The existence of Brønsted–Lewis acid synergy during NH<sub>3</sub>-SCR has been proposed over the Mn/Al-SBA-15 catalyst by Liang and co-workers [25]. However, the effect of Brønsted and/or Lewis acidity during the DeNO<sub>x</sub> process is still lacking, mainly due to inadequate information on detailed acid features.

An alternative approach for promoting the SCR activity of the Fe-based catalyst is through the incorporation of a secondary metal species. Recently, a notable increase in relevant field was evident [5,26–30]. For example, Long and Yang [5] introduced cerium (Ce) as the secondary metal onto the Fe-ZSM-5 catalyst and found that the presence of Ce readily helped to improve the activity and stability of the catalyst while in the presence of H<sub>2</sub>O and SO<sub>2</sub>. As one of the key ingredients in automotive three-way catalysts, the redox cycle prevailing between the trivalent and tetravalent oxidation states of Ce metal ions readily helps to promote the oxygen storage capability of the catalyst during the reaction. However, unlike bimetallic CeFe-ZSM-5 catalyst, the monometallic Ce-ZSM-5 showed inferior SCR activity and stability owing to the demand for a higher reduction temperature (above 700 °C) and vulnerability for sintering [29].

In view of the existing debates on the nature of active sites and the role of acidity during NH<sub>3</sub>-SCR over the Fe-based mono- and bimetallic MFI zeolite catalysts, the objective of this study aims to resolve these crucial issues in a more inclusive manner. Herein, a series of Fe-based H-ZSM-5 zeolite catalysts incorporated with different secondary Lanthanide metals (Ce, Pr, Nd, and Sm) were prepared by using the reflux method. Their physico-chemical properties were characterized by a variety of analytical and spectroscopic techniques. In particular, their acidic properties were examined by different molecular probe techniques, namely NH<sub>3</sub>-TPD, pyridine-IR [31,32], and <sup>31</sup>P MAS NMR of the adsorbed trimethylphosphine oxide (TMPO) probe molecule [33–35]. As will be shown later that the latter <sup>31</sup>P TMPO NMR approach readily affords simultaneous quantitative determination of detailed acid features, viz. type, concentration, and strength of acid sites for various mono- and bimetallic Fe-based ZSM-5 catalysts before and after the NH<sub>3</sub>-SCR reaction. To the best of our knowledge, this is the first study to directly correlate the SCR activity of the Fe-based supported zeolites with detailed variations of acidic features possessed by the catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

Fe-based mono- and bimetallic ZSM-5 catalysts incorporated with various Lanthanide metals (M = Ce, Pr, Nd, and Sm) were prepared by using the reflux method. The preparation of monometallic M<sub>1</sub>-Z (M<sub>1</sub> = Fe, Ce, Pr, Nd, and Sm; Z = ZSM-5 zeolite) catalysts were carried out by first dispersing a known amount of the respective metal precursor, namely iron acetylacetonate, cerium nitrate, praseodymium nitrate, neodymium nitrate, or samarium nitrate (Aldrich, 99.99%) in 80 mL acetonitrile, then mix with 5 g of H-ZSM-5 zeolite (Si/Al = 15; surface area ca. 375 m<sup>2</sup> g<sup>-1</sup>; Zeolyst) at 80 °C under vigorous stirring in a refluxing flask for 24 h [31]. The resultant mixture solutions were filtered, dried (at 110 °C overnight), then subjected to calcination treatment in air at 600 °C for 5 h. Similar method was exploited for the preparation of bimetallic Fe-based M<sub>2</sub>Fe-Z (M<sub>2</sub> = Ce, Pr, Nd, and Sm) catalysts, the only difference being the simultaneously dispersion of the primary (Fe) and the secondary (M<sub>2</sub>) metal acetylacetonate precursors in acetonitrile prior to mixing with the H-ZSM-5 zeolite. A typical metal content of ca. 5 wt% was used for both M<sub>1</sub> and M<sub>2</sub> during the preparation of various mono- (M<sub>1</sub>-Z) and bimetallic (M<sub>2</sub>Fe-Z) catalysts.

### 2.2. SCR performance

The SCR of NO by NH<sub>3</sub> were performed on a home-built fixed-bed quartz tube reactor (inner diameter 7 mm) under atmospheric pressure. The reaction temperature was manipulated and monitored by a programmable temperature controller. Prior to each run, ca. 0.1 g of the catalyst was first pretreated at 500 °C in air for 1 h. Reactions were carried out under the conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 2.9 vol%, balance N<sub>2</sub>, GHSV = 68,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>, and total flow rate 350 mL min<sup>-1</sup>. The concentrations of NO and NO<sub>2</sub> were simultaneously monitored by an on-line chemiluminescence NO<sub>x</sub> analyzer (Thermo Scientific, Model 42i-HL). Although the apparatus available was unable to monitor the N<sub>2</sub>O yield, it is anticipated that its concentration should be negligible over the temperature range (100–500 °C) examined [5]. Moreover, the NO<sub>2</sub> concentration detected during SCR was typically less than 1 ppm. In this context, the NO selectivity to N<sub>2</sub> observed for various catalysts examined herein should be in close resemblance to their corresponding NO conversion, which was obtained from the difference in NO<sub>x</sub> concentrations before and after the SCR reaction under steady-state condition (ca. 1 h) at each temperature.

### 2.3. Characterization methods

The chemical compositions of various catalysts were obtained by inductively coupled plasma mass/atomic emission spectrometry (ICP-MS/AES; PE/Sciex ELAN 6100 DRC and EVISA) as well as X-ray fluorescence (XRF; Horiba XGT-7000V) techniques. All catalysts were characterized by powdered X-ray diffraction (XRD) using a PANalytical (X' Pert PRO) diffractometer with CuKα radiation (λ = 0.15418 nm) at 45 kV and 40 mA. The XRD diffractograms were recorded over a 2θ range of 20–80° at a 0.02° interval and a counting time of 4.45 s. Physisorption of Ar and N<sub>2</sub> was performed at 77 K on a Quantachrome Autosorb-1 apparatus. Prior to each adsorption measurement, the sample was subjected to an evacuation treatment at 350 °C for 16 h. The microporous volumes of various samples were obtained from the *t*-plot analyses. The Brunauer-Emmett-Teller (BET) method was used to derive the total surface areas of the samples. Transmission electron microscopy (TEM) experiments were operated at 200 kV on a JEOL JEM-2100f apparatus, which was equipped with an Oxford INCA

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