

NH₃-TPD-MS study of Ce effect on the surface of Mn- or Fe-exchanged zeolites for selective catalytic reduction of NO_x by ammonia



M. Stanculescu*, P. Bulsink, G. Caravaggio, L. Nossova, R. Burich

Natural Resources Canada, CanmetENERGY, 1 Haanel Dr., Ottawa, ON, Canada K1A 1M1

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ABSTRACT

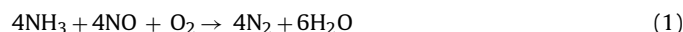
The selective catalytic reduction (SCR) of NO_x with NH₃ is considered to be a promising technique for the efficient reduction of highly detrimental NO_x emitted from diesel engine vehicles to N₂. This study was focused on a series of catalysts with ZSM-5 as support, prepared by Mn- or Fe-exchange followed by wet impregnation of Ce, or Fe or Mn. These catalysts were characterized by temperature-programmed desorption coupled with a mass spectrometer using ammonia (NH₃-TPD-MS). Specifically, NH₃-TPD-MS was used as a means of identifying the various strengths of acid sites and their relative abundance in an attempt to explain the effect of the catalyst surface acid sites on DeNO_x activity. Acid sites with adsorption energies ranging from 47.0 to 75.6 kJ/mol were detected for all of the catalysts. For the same concentration of exchanged metal it was found that the DeNO_x activity depends strongly on the type of metal. Furthermore, the acid site strength and distribution depend on the active metal and correlate with the observed DeNO_x catalyst activity. Additionally, SEM metal mapping images confirmed the presence of well dispersed active metal on the surface of all catalysts. The catalysts with bimetallic active phase were stable and demonstrated high NO_x conversion over a broad temperature range. Impregnation of metal-exchanged zeolites with Ce enhanced the low temperature NO_x conversion. Observed differences of activity between the various catalysts of this study may be due to the formation of new ammonia activation sites. The ammonia desorption profile during the elevation of temperature was correlated to the DeNO_x activity.

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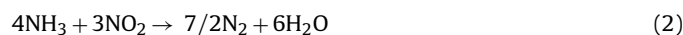
1. Introduction

During the last 30 years, great efforts have been made to limit the effect of pollutants such as SO_x, NO_x and VOCs from diesel engine emissions by application of various existing methods and/or new technologies to convert such pollutants to acceptable compounds [1–4]. The information regarding environmental catalysis became available and new approaches to develop and test novel catalysts have been investigated [5,6]. Most of these catalysts are based on transition metals ion-exchanged into zeolites. Novel catalysts were obtained by modifying the surface and creating Brønsted or Lewis acid sites. This approach was pursued due to the fact that activity of zeolitic catalysts is in some extent dependent on the concentration of acid sites [7,8]. The selective catalytic reduction (SCR) of NO_x by ammonia occurs through many possible mechanisms on the catalyst surface [9,10]. The standard SCR reactions for NO, involving

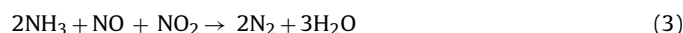
oxygen (which is plentiful in a lean burn exhaust stream) is shown in Eq. (1):



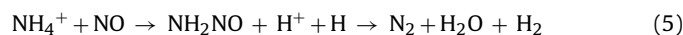
Similarly for NO₂:



If both NO and NO₂ are present in the stream, the “fast” SCR reaction may occur:



These reactions all take place on the active metal phase loaded into zeolites. NH₃ is adsorbed on Lewis acid metal sites and is subsequently transformed to NH₂ species, which participate in the formation of intermediates active for NO_x reduction, particularly at low temperatures [11,12]. Brønsted acid sites are present on the zeolite surface as well and these reduce NO and NO₂ by different mechanisms. The exact mechanism is still a matter of discussion, but one possibility was described by Yuan et al. [13]:



* Corresponding author. Tel.: +1 613 943 0103; fax: +1 613 996 9400.
E-mail address: mstanciu@nrcan.gc.ca (M. Stanculescu).

Table 1
Catalyst names, surface areas by BET and compositions by SEM-EDX.

Catalyst name	S_{BET} (m ² /g)	Composition (wt.%)				Si/Al (mol/mol)	
		Fe	Mn	Ce	Si	Al	
CBV-2314	415	–	–	–	43.4	3.6	11.6
3MnCBV	340	–	3.2	–	41.7	3.5	11.4
3Ce3MnCBV	327	–	2.7	2.9	40.5	3.4	11.4
3Fe3MnCBV	332	2.9	2.9	–	40.4	3.2	12.1
3CeCBV	336	–	–	3	42.2	3.4	11.9
3FeCBV	335	3.2	–	–	41.9	3.3	12.2
3Ce3FeCBV	340	3.4	–	3.4	39.7	3.2	11.9
3Mn3FeCBV	359	2.8	2.9	–	40.5	3.2	12.2

One of the methods applied for the estimation and characterization of acidic sites on the catalyst surface is temperature-programmed desorption (TPD) of ammonia in a carrier gas flow or in a dynamic vacuum [14–18]. However, the nature of the acid sites, (e.g., Brønsted or Lewis) cannot be differentiated by ammonia-TPD alone. For this reason other techniques have to be used for the above investigation, e.g. NH₃-TPD combined with *in situ* IR [19] and MS [20], or a combination of IRMS-TPD of ammonia, where the strength of Brønsted acid sites is correlated with IR band position of OH and bending vibration of NH₄⁺ [21].

Similar to our previous work [16], this study is an attempt to correlate the strength and distribution of the acid sites found by NH₃-TPD experiments with the DeNO_x activity of our catalysts used for NH₃-SCR. The TPD study is performed in order to analyze the effect of the number of acid sites as a function of amount and type of loaded active metals on the zeolite. These mono- and bimetallic active phase catalysts with DeNO_x activity were obtained by ion exchanging zeolite with one metal followed by impregnation of the second aqueous solution of metal precursor. The study is a combination of the TPD of ammonia with the MS technique, because it was expected to obtain information on the intermediates formed during the NH₃ adsorption/desorption from the catalyst surface. No H₂ or N₂ were detected by MS below 510 °C as an indication of NH₃ decomposition.

2. Experimental

2.1. Catalyst preparation

CBV-2314, a ZSM-5 type catalyst (Zeolyst International) was ion-exchanged with aqueous solutions of metal nitrates (Mn, Fe) (Fisher Scientific) to the desired metal loading concentrations. Additional metals were loaded by the incipient wetness impregnation (IWI) method, using the metal nitrates as precursors. 3CeCBV was prepared by IWI of the Ce (III) nitrate (Fisher Scientific) on a calcined sample of the CBV-2314. Catalysts were calcined between metal loadings at 500 °C for 6 h under air. Catalysts were named by their nominal weight percent metal loadings as shown in Table 1.

2.2. Catalyst characterization

2.2.1. BET surface area

Catalysts were analyzed to determine their surface area by the Brunauer, Emmett and Teller (BET) technique on a Micromeritics ASAP 2020 instrument. Samples were degassed at 250 °C for 16 h. The isotherms were then measured by standard nitrogen adsorption at 196.15 °C.

2.2.2. Composition

Catalyst samples were characterized using a Hitachi SEM with an Oxford INCA EDX system operating at 20 kV and 80 mA. Preparation of samples consisted of bonding a thin layer of catalyst to double sided carbon tape. Ten random points on each sample

were analyzed under vacuum to produce average composition and standard deviations.

2.2.3. SEM images

The samples were all imaged with a Hitachi S-3400 N Scanning Electron Microscope (SEM). It was operated at 5 kV with a working distance of approximately 5 mm. The probe current was approximately 30 μA. All samples were mounted on aluminum stubs with double sided carbon tape, and coated with 2 nm of Pd. All images were taken with the secondary electron detector.

2.3. Catalyst testing

Catalysts were tested for their NO_x reduction activity with ammonia as the reductant using a catalyst testing unit (CTU) described in greater detail in other papers [22–24]. A synthetic diesel exhaust stream and reductant composed of 5% O₂, 5% H₂O, 500 ppm NO_x, 500 ppm NH₃, with a He balance, was flowed through the catalyst bed at 1000 mL/min. The catalyst bed was formed in a quartz tube, with a 6 mm inner diameter. 500.0 ± 0.2 mg of catalyst, with 80–120 mesh particle size, was used, for a consistent weight time space velocity (WTSV) of 0.0300 g s cm⁻³, producing an approximate gas hourly space velocity (GHSV) of 80,000 h⁻¹. The products of NO_x reduction reaction were analyzed by an MKS FTIR multigas analyzer, and a ThermoElectric Chemiluminescence analyzer as the temperature was ramped from 75 to 600 °C at 3 °C/min. The catalyst activity was interpreted function of NO_x conversion and N₂ formation.

2.4. NH₃-TPD experiments

Approximately 150 mg of each tested catalyst was placed in a reaction tube in a Micromeritics ASAP 2920 instrument. After pre-treating at 600 °C for 2 h under a He flow of 50 mL/min, the sample was cooled to 170 °C and dosed for 30 min with a 15% NH₃ in He (balance), again at 50 mL/min. The dosing temperature was chosen to prevent physisorption of NH₃ on the catalyst surface. The dosing resulted in complete adsorption of NH₃ to all available acid sites. After dosing, the samples were cooled to 50 °C then heated to 600 °C at 5.0 °C/min, under He flow of 50 mL/min. Exhaust gases were analyzed by the onboard TCD detector and by an MKS Cirrus quadrupole mass spectrometer. The mass spectrometer followed the NH₃ desorption by *m/z* = 17. Other components were also identified such as *m/z* = 18 that came from the presence of water in the TPD exhaust stream.

3. Results and discussion

3.1. Characterization

3.1.1. BET surface area and catalyst composition by SEM-EDX

The catalyst surface areas, as measured by BET, decreased with the addition of metals loaded on the zeolite by ion exchange or IWI,

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