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In situ FTIR spectroscopy of highly dispersed FeO*x* catalysts for NO reduction: Role of Na promoter

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ABSTRACT

The effect of Na on highly dispersed FeO*x* impregnated onto CeO_2 *via* the unique precursor Na/Fe-ethylenediaminetetraacetate (NaFeEDTA) was investigated by comparison to a series of well-defined catalysts synthesized by the traditional precursor $Fe(NO_3)_3$ both with and without Na addition. Catalysts were evaluated for steady-state NO reduction by CO and activities varied based on synthesis method and Fe:Na ratio. Na contributed a promoter effect when added at a stoichiometric ratio (Fe:Na = 1), providing an explanation for the higher activity of NaFeEDTA/CeO_2 for NO reduction by CO. Activity decreased when excess Na was present in $Fe(NO_3)_3$ catalysts, but the stoichiometric promoter effect persisted up to ~4.0 Fe/nm^2. *In situ* Fourier transform infrared (FTIR) spectroscopy during NO adsorption revealed the presence of unique NO adsorption species (1460 cm^{-1}) on the NaFeEDTA/CeO_2, suggesting enhanced NO adsorption due to Na. At reaction temperature, FTIR bands of bulk nitrates on CeO_2 were quantitatively shown to more rapidly undergo NO reduction catalytic transformations over NaFeEDTA/CeO_2. These results increase understanding of mechanistic effects of Na on NO reduction over FeO*x*/CeO_2 catalysts and serve to guide future design of oxide-based emission control catalysts that are free of Pt-group metals.

1. Introduction

The removal of NO*x* from automotive exhaust remains an important challenge for design of catalytic materials. While the three-way catalyst is a remarkable example of successful design, it remains dependent on scarce platinum group metals (PGM) such as Pt, Pd, and Rh [1]. It is, therefore, desirable to discover new NO removal catalysts utilizing earth-abundant materials. Over the past two decades, extensive research on Fe-exchanged zeolites has shown good activity for selective catalytic reduction (SCR) of NO [1–7], demonstrating the potential utility of earth-abundant base-metal oxides in NO reduction reactions. The active sites responsible for the NO reduction activity are generally accepted to be low-coordinated FeO*x* species [3–7].

This deeper understanding of the zeolite system suggests the possibility of creating similar surface metal oxide active sites on non-zeolitic oxide supports such as CeO_2, ZrO_2, and SiO_2, which can introduce a variety of support effects such as increased stability [8–10]. The traditional synthesis approach of incipient wetness impregnation (IWI) of metal nitrate precursors, however, is not conducive to the formation of homogeneous surface oxide structures [11,12], limiting the ability to design supported metal oxides with NO reduction catalytic active sites analogous to those in the zeolites. This issue is not new to supported metal oxide catalyst synthesis, and significant effort has been made to improve uniform nanostructuring of surface metal oxide active sites [13,14].

Recently, Prieto-Centurion et al. have improved on the ability of IWI to create a more homogeneous distribution of surface FeO*x* species on CeO_2 [15,16]. By utilizing a Na/Fe-ethylenediaminetetraacetate (NaFeEDTA) precursor, a higher density of redox cycling FeO*x* sites could be produced when compared to catalysts synthesized by the traditional $Fe(NO_3)_3$ precursor. The fraction of redox cycling Fe was directly correlated with activity for NO reduction by both H_2 and CO, and correspondingly, the activity of catalysts prepared *via* NaFeEDTA was higher than those prepared *via* $Fe(NO_3)_3$ [16,17]. It is notable, however, that use of the NaFeEDTA precursor necessarily deposits Na onto the CeO_2 surface at a Fe:Na ratio of 1:1 during IWI, which introduces ambiguity into the unique role of the organic ligand to improve catalysts synthesis and activity. While previous studies sought to account for

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this difference by synthesizing Na-modified CeO_2 prior to $Fe(NO_3)_3$ impregnation, the role of Na in the NO reduction reaction remained unaddressed as catalysts without Na were not compared.

The role of Na or other alkali atoms in deNO*x* catalysis has been found to vary. Reports of improved NO reduction activity in the presence of soot due to alkali promotion were attributed to improved NO adsorption properties [18,19]. This finding is similar to those made for alkali promotion of Pd supported on yttria-stabilized-zirconia and Rh on zeolite Y catalysts for NO reduction by CO, where the alkali introduced enhanced NO surface bonding or resulted in desirable bridge bonded NO [20,21]. Conversely, for NH_3-SCR, poisoning of Brønsted acid sites in VO*x* catalysts by alkali ions competes with the adsorption of NH_3 [22–24].

The current study seeks to determine the role of Na as a poison or promoter in supported FeO*x*/CeO_2 catalysts for NO reduction by CO by first replicating previous results utilizing the NaFeEDTA precursor and comparing activity to reference catalysts without Na and with various ratios of Fe:Na. Once the role of Na is established, deeper insight into its mechanistic effect on NO reduction is explored by *in situ* NO adsorption FTIR spectroscopy. This technique will facilitate understanding of the effect on NO adsorption; a process that is typically thought to be affected by Na addition. Finally, the reactivity of NO adsorption species is determined with time-resolved *in situ* FTIR spectroscopy under model NO reduction by H_2 reaction conditions. Understanding of the role of Na in NO reduction over FeO*x*/CeO_2 catalysts is expected to support future rational design of improved supported base-metal oxide catalysts.

2. Materials and methods

2.1. Catalyst synthesis, nitrogen physisorption, and elemental analysis

Incipient wetness impregnation (IWI) of non-porous CeO_2 (C.I. Kasei Co., Ltd., NanoTek powder, BET SSA = 101 m^2/g) was performed using various Fe-containing precursors. The precursor sodium Fe(III) ethylenediaminetetraacetate (NaFeEDTA) was prepared following the method of Prieto-Centurion et al. [15] which is based on that by Meier and Heinemann [25]. Due to solubility limits of the NaFeEDTA, multiple cycles of impregnation, drying overnight, and re-impregnation (1–3 cycles prior to calcination) were used to achieve the desired total Fe surface density. Calcination was performed in air at 550 °C for ∼1 h to remove the precursor ligand and form the highly dispersed Fe species. Using NaFeEDTA necessarily also impregnates Na onto the CeO_2 support in a 1:1 atomic ratio of Fe:Na. Other catalysts were synthesized using $Fe(NO_3)_3{\cdot}9H_2O$ as the source of Fe and $NaHCO_3$ as the source of Na. The CeO_2 support was first impregnated with $NaHCO_3$ and dried overnight to yield Na-modified CeO_2. The modified Na-CeO_2 support was then impregnated with $Fe(NO_3)_3{\cdot}9H_2O$. Catalysts were synthesized with up to 4 Fe/nm^2 or 4 Na/nm^2 and varying Fe:Na atomic ratios (Table 1). Characterization by X-ray diffraction, Raman spectroscopy, and Mössbauer spectroscopy was reported previously by several of the authors [17], and confirmed the nature of the catalysts as highly dispersed, non-crystalline, surface FeO*x* species on the CeO_2 support, regardless of preparation method.

Nitrogen physisorption isotherms were obtained using a Micromeritics ASAP 2010 instrument. Samples were degassed for 6 h at <5 mTorr and 120 °C to release absorbed water. Specific surface areas were calculated from the N_2 physisorption isotherms using the BET equation. Elemental analysis was performed using a Varian MPX ICP-OES instrument. Samples were prepared by dissolving 50 mg of solids in 1 mL of HF and subsequently diluting to 50 mL with H_2O. Metal contents were quantified by comparison against standards of known concentration. The resulting analyses of the catalyst samples used in this study are summarized in Table 1. The final catalysts prepared by NaFeEDTA, $Fe(NO_3)_3$ and $NaHCO_3$, and only $Fe(NO_3)_3$ are denoted as NaFeEDTA/CeO_2, $Fe(NO_3)_3$/Na-CeO_2, and $Fe(NO_3)_3$/CeO_2, respectively.

Table 1

Characteristics of catalysts in this study prepared using various precursors.

Fe precursor	Na precursor	Support	Fe loading[a] (Fe/nm^2)	Fe:Na ratio
–	–	CeO_2	0	0:0
$Fe(NO_3)_3$	–	CeO_2	1.11	1:0
NaFeEDTA		CeO_2	0.94	1:1
$Fe(NO_3)_3$	$NaHCO_3$	Na-CeO_2	0.98	1:1
			1.02	1:2
			1.02	1:3
			1.02	1:4
			2.04	1:1
			4.03	1:1
			2.05	2:1
			4.03	4:1

[a] Loadings confirmed by ICP-OES. Surface density calculated using the BET surface area of neat CeO_2, 101 m^2/g.

2.2. Steady-state catalytic activity

Steady-state catalytic activities were measured using a fixed bed quartz tubular reactor with temperature control and gas flow control. The reactor was loaded with ∼10–20 mg of catalyst powder that was mixed with quartz sand as a diluent in order to achieve a constant gas hourly space velocity (GHSV) of ∼15,000 h^{-1}. The catalyst was first pretreated in 30 sccm of 10% O_2/He at 500 °C for 30 min, and then cooled in flowing UHP He. The reduction of NO by CO was monitored at 250 °C and 450 °C for 45 min each and a total flowrate of 100 sccm with a stoichiometric composition of 4000 ppm NO, 4000 ppm CO, 8000 ppm Ar, and He balance. Mass spectrometry of the gas phase product stream was obtained continuously using a quadrupole mass spectrometer (MKS Instruments, Inc., Cirrus-2). The Ar present in the reactant stream acted as a tracer of constant concentration and the Ar signal at $m/z = 40$ was used to normalize each of the mass spectrum traces.

The 100% and 0% conversion of NO was defined as the normalized mass spectrum intensity at $m/z = 30$ under inert flow only, and in the presence of the NO + CO reaction mixture bypassing the reactor, respectively. Linear interpolation determined the resulting NO conversions at steady state temperatures. No significant amount of NO_2 was produced, based on the absence of fragments observed at $m/z = 46$. Rates at 250 °C are at differential NO conversions (<15%). The steady state NO conversion percentage for each of the catalysts is reported in Table S1. The reported activity is normalized by total mass of catalyst.

2.3. *In situ* transmission FTIR spectroscopy

The Harrick High Temperature Cell with environmental (gas flow) and temperature control was used for *in situ* transmission FTIR spectroscopy. Spectra were recorded using a Thermo Scientific Nicolet 8700 Research FT-IR Spectrometer equipped with a liquid N_2 cooled MCT detector. Spectra were obtained with a resolution of 2 cm^{-1} and by averaging 16 scans. The optical scan velocity was set to 3.1647 cm/s, which resulted in a collection time of 4.55 s per spectrum. Catalyst pellets were prepared by first diluting the catalyst with spectroscopy grade KBr at a ratio of 1:5 catalyst:KBr. Then ∼50 mg of catalyst were pressed at ∼1 tonnes for 1 min using a Specac 13 mm Pellet Die and Manual Hydraulic Press.

In situ transmission FTIR spectra were collected during NO adsorption in the presence of O_2 at 50 °C. Prior to NO + O_2 adsorption, the sample was first pretreated at 375 °C in 20 sccm of 10% O_2/He. The background spectrum (64 scans) was of the catalyst