



An *operando* FT-IR study of the NO_x SCR over Co-HFER and Fe-HFER using acetylene as a reducing agent



Ingrit Castellanos, Olivier Marie*

Laboratoire Catalyse et Spectrochimie, ENSICAEN, 6 Bd. Maréchal Juin, 14000, Caen, France¹

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ABSTRACT

The selective catalytic reduction by hydrocarbons (HC-SCR) has shown relevant efficiencies in reducing the NO_x from the automobiles waste gases, thus emerging as a suitable alternative to urea as a reducing agent. Previous studies by Wang et al. showed that acetylene (C₂H₂) has a high activity at low temperatures and a satisfactory intracrystalline diffusion over zeolites. The present work investigates C₂H₂ as a reducing agent under NO, NO₂ conditions and a mixture of NO and NO₂. Ferrierite zeolites loaded with iron and cobalt ions were evaluated as catalysts by InfraRed (IR) *operando* and *in-situ* techniques. This latter technique allowed a clear identification of the vibration bands of the species formed on the surface in reaction conditions. Two different sites for the localization of cations in the Ferrierite were identified from the NO experiment, with only one common to both cations. Regarding C₂H₂, its interaction with both Lewis and Brønsted sites could be identified. Thanks to the *IR operando* methodology, it was possible to identify hydrocyanic acid as a relevant intermediate species for the SCR of NO_x by C₂H₂ over Co-HFER. Moreover, the NO oxidation to NO₂ was found to be a determining step for the SCR reaction when using the Co loaded catalyst.

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1. Introduction

Road transportation is now recognized as the main source of NO_x pollution: according to the European Environment Agency (EEA): 40.5% of the nitrogen oxides total emission arises from this sector [1]. The abatement of this pollutant has been recently considered mainly in Diesel powered engines, whose growth in the automotive market in Europe is important. Furthermore, when compared with gasoline engines, higher amounts of NO_x are produced due the operating conditions, which feature an excess of air. Indeed, in these conditions, the catalytic removal of NO_x is also challenging.

It is known that the selective catalytic reduction (SCR) of NO_x compounds by ammonia (from urea) reaches reduction efficiencies of more than 80%. However, this reducing agent presents some limitations, such as the rejection of some quantities of unreacted ammonia (NH₃ slip). Moreover, at relatively low temperatures (below about 170 °C), prolonged SCR operation results in the accu-

mulation of undesired solid deposits, such as ammonium nitrate or ammonium sulphate especially in presence of NO₂ rich conditions [2]. On the other hand, the HC-SCR has shown in the last 25 years, efficiencies of around 70% [3] similar to other processes such as the Lean NO_x-Trap (LNT). Nevertheless, the synergy between the catalyst and hydrocarbons as reducing agents has still to be improved. The application of HC-SCR in the NO_x reduction has gained interest thanks to the work of Iwamoto et al. [4] who introduced metal-ion exchanged zeolites as catalysts. In fact, zeolitic catalysts play a significant role in the NO_x removal thanks to their relatively high efficiencies in a wide temperature range but also for their noble metal free economic formulation. Regarding the zeolite structure, in general terms and in decreasing order of NO_x conversion, we found: FER > MOR > Y [5].

On the other hand, with respect to the hydrocarbons, many alkanes (as methane, ethane, propane, butane) and alkenes (as ethene, propene, butene and also alkenes with 5, 6, 7, 8, 9, 10 and 16 carbons) have been tested [6]. The most studied among those hydrocarbons has been the methane, showing an acceptable NO_x reduction using Co-Pd-zeolites [7–9]. However, methane is very little abundant at the outlet of a fuel based combustion engine and its corresponding deNO_x efficiency only initiates for temperature above 350 °C.

* Corresponding author.

E-mail addresses: ingrit.castellanos@hotmail.fr (I. Castellanos), olivier.marie@ensicaen.fr (O. Marie).

¹ 'Permanent address' for the second author and 'Present address' for the first author.

In 2005, Wang et al. [10] proposed the use of acetylene as a reducing agent for NO_x. This triple bonded small molecule, presents no limit concerning the intracrystalline diffusion over most of zeolites [11]. Furthermore, it can be easily produced using calcium carbide ($\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$) [10] rendering possible its application to automotive depollution via on boarding of solid CaC₂ and liquid water. It thus represents an interesting and safe alternative to on boarding ad-blue that is an aqueous solution of 37 wt% urea. Finally, NO_x SCR using C₂H₂ was also reported to present a high activity in the 250–450 °C temperature range [12].

To summarize, the development of a catalyst showing a high deNO_x efficiency will greatly depend on an appropriate combination of the zeolite, the transition metal ion (TMI) used and the used stoichiometric ratio NO_x/C_xH_y.

This work focuses on the comparison between Fe and Co ions as TMI introduced in the FER zeolite for the acetylene-based SCR by means of *operando* FT-IR spectroscopy. This methodology enables the simultaneous measurement of the activity/selectivity of the catalyst and of the nature of adsorbed species during the reaction [13]. The study of the adsorption at room temperature of C₂H₂ and NO on the active sites (Lewis and Brønsted) of the zeolite will be first performed and characterized by *in-situ* FT-IR. This preliminary step will allow the identification of the various adsorption modes of both reactants but also of the type of active sites that are involved. This will be especially interesting for C₂H₂ whose interaction with zeolites has not been yet described in the literature.

2. Material and methods

2.1. Catalyst preparation

The zeolite catalyst in the alkaline form was obtained from TOSOH Company (HSZ-700 series, FERRIERITE). It showed a Si/Al=9 ratio (measured by ICP-AES), a S_{BET} = 170 m²/g and was converted to the ammonium form with a 0.1 M solution of NH₄Cl. The ammonium exchange procedure was repeated 3 times during 3 h at 80 °C under strong agitation. The catalyst was centrifuged two times during 10 min after each exchange and 3 times for the last exchange. The catalyst recovered in a paste form was then dried at 100 °C overnight. For the introduction of TMI, aqueous solutions of FeSO₄ and of Co(CH₃COO)₂·4H₂O were prepared with a 10⁻³ M concentration (both reagent from Sigma-Aldrich). The ion exchange procedure was repeated 2 times during 4 h at 80 °C under strong agitation. The catalyst was then centrifuged in a similar procedure than that explained above and finally dried at 100 °C during overnight. The calcination of the catalyst in a pellet shape (d = 16 mm et ε ≈ 30 μm) was performed prior to each experiment at a temperature of 450 °C for 2 h (raising temperature speed of 2 K min⁻¹) either under vacuum, oxygen or hydrogen for the IR *in-situ* adsorption tests and under 10% of oxygen for the *operando* test. The final metal/aluminium atomic ratio (iron or cobalt metal) was measured to be lower than 0.1 (ICP-AES) with values for the two main samples of 0.09 for Fe-HFER (0.73 wt% and named 1%) and of 0.09 for Co-HFER (0.76 wt% and named 1%). For clarification purpose during the C₂H₂ adsorption, a third sample with higher amount of iron was prepared by increasing the number of ion exchange with the ferrous sulphate solution until a 2.7 Fe wt% was reached.

2.2. IR in-situ adsorption tests

In order to study the interaction with the redox sites during the adsorption of nitric oxide (99.908% NO, AIR-LIQUID), three different pretreatments were achieved before each NO adsorption on one single sample. In the first pretreatment, the sample

Table 1
Experimental conditions for NO_x SCR with acetylene.

Catalyst Mass (mg)	≈15
[O ₂] (%)	2.5
[C ₂ H ₂] (ppm)	200
[NO and/or NO ₂] (ppm)	400
Total flow rate (mL/min)	25

was placed under vacuum (<10⁻⁴ Pa) during the whole calcination period before the adsorption procedure (at room temperature).

In the second pretreatment, the sample was first heated under a vacuum at 450 °C during 2 h. Then, the vacuum was removed and 1.33 10⁴ Pa of oxygen (100% O₂—ALPHAGAZ 1 Oxygen, AIR-LIQUIDE) were introduced in the *in-situ* IR cell kept at 450 °C during 30 min. The O₂ removal was finally made under dynamic vacuum at lower temperature, i.e 200 °C to avoid/limit a possible reduction of the sample.

The third pretreatment under hydrogen (99.999% H₂—ALPHAGAZ 2Hydrogen, AIR-LIQUIDE) was similar to the oxygen pretreatment in terms of temperature, pressure and residence time of the gas. However, the evacuation was in that case performed at 450 °C under dynamic vacuum.

For the acetylene adsorption (99.6998% C₂H₂, AIR LIQUIDE), a fresh catalyst was always used and always preliminary heated under vacuum. Small doses of NO or C₂H₂ (between 25–230 μmol/g_{catalyst}) were then put in contact with each sample, further submitted to contact with relatively high equilibrium pressures (133, 266, 532, 666, 1064 and 1333 Pa). The IR spectra were recorded with a Nicolet 6700 FTIR spectrometer equipped with a DTG detector at a spectral resolution of 4 cm⁻¹ by accumulating 128 scans.

2.3. IR operando tests

For the *operando* experiments, a 'sandwich like' IR cell-reactor was used (described in Ref. [14]). Fig. 1 shows the used experimental set-up in which the central 6 ways valve allows to submit the catalyst (shaped as a pellet) to an activation procedure while simultaneously preparing and stabilizing the reaction flow.

In a first step, the catalyst is thus calcined at 450 °C during 2 h with a raising temperature speed of 2 K min⁻¹ under a flow made of 10% of O₂ in Ar (named here Activation Flow). Then, the temperature is decreased down to the chosen initial reaction temperature and the 6-ways valve is switched to send the reaction flow to the catalyst (second step). The Thermo Programmed Reaction analysis of the catalyst activity is achieved between 100 and 450 °C using a 2 K min⁻¹ heating rate. The experimental conditions are detailed in Table 1. All the reactants of the Reaction Flow are analysed by Mass Spectrometry (Quadrupole Pfeiffer Omnistar GSD 301) and stabilised before being sent to the cell. Finally, the composition of the output gas from the IR reactor cell is analysed simultaneously as follows: NO and NO₂ by Chemiluminescence (Thermo-Scientific, model 42 i-HL); C₂H₂, N₂O and CO by an IR spectrometer (Thermo Nicolet NEXUS 670 FTIR) equipped with a MCT detector with a spectral resolution of 4 cm⁻¹ and accumulating 64 scans.

3. Results and discussion

3.1. NO adsorption

3.1.1. Fe-HFER

Keeping the Fe-HFER sample under a 666 Pa NO equilibrium pressure leads, whatever the pre-treatment, to a predominant band at 1877 cm⁻¹ (Fig. 2A). This band indeed represents the mononitrosyls linked to the Fe²⁺ cations [15–17] that are majority after all the performed pre-treatments (under vacuum, oxygen or hydrogen).

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