

# The synergy between Fe and Ru in N<sub>2</sub>O decomposition over FeRu-FER catalysts: A mechanistic explanation

Gerhard D. Pirngruber <sup>a,\*</sup>, Lukas Frunz <sup>a</sup>, Johannis A.Z. Pieterse <sup>b</sup>

<sup>a</sup> Institute for Chemical and Bioengineering, ETH Zurich, CH-8093 Zurich, Switzerland

<sup>b</sup> ECN Hydrogen & Clean Fossil Fuels, PO Box 1, Westerduinweg 3, 1755 ZG, Petten, The Netherlands

Received 10 May 2006; revised 8 August 2006; accepted 12 August 2006

## Abstract

Fe-FER is an active catalyst for the abatement of N<sub>2</sub>O in the tail gas of nitric acid plants. The activity of Fe-FER can be increased if Ru is added as a second active component. This is a surprising finding, because noble metals are usually strongly inhibited by NO, which is always present in tail gas. Yet the bimetallic FeRu-FER catalyst is more active than the sum of the components, Fe-FER and Ru-FER. A synergy between Fe and Ru can explain this phenomenon. This work discusses the role of Fe and Ru in the reaction mechanism as well as the interplay of these two components. In situ IR measurements show that the preferential adsorption of NO and its reaction products on Fe in the bimetallic catalyst reduces the inhibiting effect of NO on the Ru component; this effect largely contributes to the synergy between Fe and Ru. Moreover, in situ X-ray absorption data are presented, which allow for tracing the average oxidation state of the two active components Fe and Ru under reaction conditions.

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**Keywords:** In situ spectroscopy; NO adsorption; XANES; IR; Ferrierite

## 1. Introduction

Direct catalytic decomposition of N<sub>2</sub>O in the tail gases of nitric acid plants is a safe, cost-efficient method for N<sub>2</sub>O abatement. Consequently, much effort is invested in developing improved catalysts that convert N<sub>2</sub>O at moderate temperatures (below 773 K). Iron zeolites, especially Fe-ZSM-5, have been studied extensively for use as catalysts in N<sub>2</sub>O decomposition [1–5]. NO<sub>x</sub>, which is usually present in off-gases, promotes N<sub>2</sub>O decomposition over iron zeolites [6–9]. Fe-FER [4,10] and Fe-BEA [5] perform particularly well. However, a temperature of 773 K is still necessary to achieve 75% N<sub>2</sub>O conversion with Fe-FER in the presence of H<sub>2</sub>O and NO<sub>x</sub> [10]. Noble metal catalysts have a higher intrinsic activity for N<sub>2</sub>O decomposition compared with iron [11]. Unfortunately, N<sub>2</sub>O decomposition over noble metal catalysts is inhibited by NO, O<sub>2</sub>, and H<sub>2</sub>O

[12,13], precluding their use in the tail gas of nitric acid factories. Recently it was shown that using a bimetallic FER catalyst containing iron and ruthenium significantly enhances N<sub>2</sub>O decomposition if some NO is present [14,15]. This effect also manifests in the presence of O<sub>2</sub> and H<sub>2</sub>O. The bimetallic catalyst is more active than the sum of the single components, Fe and Ru; there is a synergy between Fe and Ru [16]. Possible explanations for this synergy have been offered [15], but the effect remains incompletely understood. The goal of the present contribution is to unravel the mechanism by which Fe and Ru cooperate, with the aid of in situ spectroscopy (IR and XANES).

## 2. Experimental

### 2.1. Catalyst preparation

NH<sub>4</sub>-FER was obtained from Na/K-FER (Tosoh HSZ-720KOA, Si/Al = 9.2) by threefold ion exchange with a NH<sub>4</sub>NO<sub>3</sub> solution for 1 h at room temperature. The sample was filtered and washed with a large amount of demineralized

\* Corresponding author.

E-mail address: [gerhard.pirngruber@ifp.fr](mailto:gerhard.pirngruber@ifp.fr) (G.D. Pirngruber).

<sup>1</sup> Present address: Catalysis and Separation Division, Institut Français du Pétrole, 69390 Vernaison, France.

Table 1  
Elemental composition of the samples and intensity of Brønsted OH band

Sample	Fe (wt%)	Ru (wt%)	Fe/Al	Ru/Al	(Na + K) <sup>a</sup> /Al	Exchange Brønsted OH (%)
Fe-FER	2.2	n.d. <sup>b</sup>	0.31	–	–	17
FeRu-FER	2.2	0.4	0.31	0.03	0.22	32
Ru-FER	n.d.	0.4	–	0.03	0.29	28
Fe-FER-2	0.6	n.d.	0.09	–	–	20
FeRu-FER-2	0.6	0.45	0.09	0.04	0.73	68
Ru-FER-2	n.d.	0.45	–	0.04	n.d.	68

<sup>a</sup> Mainly K, only traces of Na.

<sup>b</sup> n.d. = not determined.

water to remove nitrate. Fe-FER (2.2 wt% Fe) was prepared by impregnating NH<sub>4</sub>-FER with iron nitrate.

Ru-FER was obtained by exchanging Ru(NH<sub>4</sub>)<sub>3</sub>Cl<sub>6</sub> with 25 g Na/K-FER at 353 K for 16 h (nominal Ru loading, 0.5%; initial pH, 8; final pH, 6.5), followed by two exchanges with 0.05 M NH<sub>4</sub>NO<sub>3</sub> for 1 h. The purpose of the treatment with NH<sub>4</sub>NO<sub>3</sub> was to maximize the exchange capacity for the subsequent impregnation with iron nitrate (vide infra). The final Ru loading was determined by ICP to be 0.40 wt%.

FeRu-FER was obtained by incipient-wetness impregnation of Ru-FER with a solution of iron nitrate, to obtain 2.2 wt% Fe. The samples were calcined under flowing air at 793 K for 3 h (at a ramp of 3 K/min).

A second batch of Ru-FER (coded as Ru-FER-2) was prepared at a larger scale, in which 100 g of Na/K-FER was exchanged with Ru(NH<sub>4</sub>)<sub>3</sub>Cl<sub>6</sub> for 16 h at 353 K. The sample was washed and filtered, followed by a single exchange with 0.05 M NH<sub>4</sub>NO<sub>3</sub> for 1 h. The final loading was determined by ICP to be 0.45 wt% Ru. FeRu-FER-2 was obtained by incipient-wetness impregnation of Ru-FER-2 (0.45 wt% Ru) with a more diluted solution of iron nitrate to obtain 0.6 wt% Fe. Similarly, Fe-FER-2 was obtained by impregnation of NH<sub>4</sub>-FER with a diluted solution to obtain 0.6 wt% Fe (Table 1).

The samples were characterized by UV-vis, TPR, IR, and XANES/EXAFS spectroscopy. UV-vis spectra were recorded on a Cary 400 UV-vis spectrometer with a Praying Mantis sample stage from Harrick. H<sub>2</sub>-TPR spectra were recorded with an Altamira AMI-1 apparatus equipped with a thermal conductivity detector and a Balzers MS-detector, applying 30 ml/min flow of 10% H<sub>2</sub> in argon at a heating rate of 20 K/min. IR and XAS are explained in more detail below. The elemental composition of the samples was determined by ICP or AAS (for Na and K).

## 2.2. Activity measurements

The catalytic tests were conducted in a computer-controlled six-flow setup. First, 50 mg of catalyst (sieve fraction, 0.25–0.5 mm) was placed on a quartz grid, then the quartz reactors (4 mm i.d.) were placed in an oven. The total gas flow was 100 ml/min, corresponding to a GHSV of ~60,000 h<sup>-1</sup>. Quantitative analysis of the gas-phase components was performed using a micro-gas chromatograph and a NO<sub>x</sub> analyzer. Data were collected at ascending temperatures from 533 to 773 K (ramp 5 K/min). Preconditioning was set for 20 min at each

temperature. Pseudo-first-order rate constants were calculated using the formula

$$k = -\frac{F}{m_{\text{cat}} \cdot p} \cdot \ln(1 - X),$$

where  $F$  is total flow,  $m_{\text{cat}}$  mass of the catalyst,  $p$  is total pressure, and  $X$  is the conversion. The equilibrium between NO and NO<sub>2</sub> was calculated using HSC software.

## 2.3. In situ IR spectroscopy

A 6-mg catalyst sample was pressed into a self-supporting pellet, placed in a gold sample holder, and inserted in the in situ IR cell [17]. The sample was heated in a flow of 5% O<sub>2</sub> in He to 673 K and kept there for 30 min, to remove all impurities. Subsequently, the cell was purged for 30 min in He flow at 673 K to facilitate autoreduction of the catalyst. The cell was cooled to 573 K. A spectrum of the catalyst was recorded and used as a reference for the subsequent measurements. The reaction was started by switching from He to a mixture of ~3000 ppm N<sub>2</sub>O, ~800 ppm NO, and 0–2% O<sub>2</sub>. The concentration of NO and N<sub>2</sub>O was twice as great as in the catalytic tests described above. The range of the mass flow controllers imposed this choice. The gas flow was kept at 20 ml<sub>NTP</sub>/min, corresponding to a GHSV of ~100,000 h<sup>-1</sup>. After ~30 min (once steady state was reached), the gas inlet was switched back to He, the catalyst was regenerated at 673 K for 30 min, and the procedure was repeated at the next reaction temperatures (i.e., 623 and 673 K). The IR spectra were recorded on a Biorad FTS 3000 MX spectrometer equipped with a broadband MCT detector. The spectral resolution was 4 cm<sup>-1</sup>. A total of 16–128 scans were co-added. 16 scans correspond to a time resolution of ~10 s. The reactor effluent was analyzed by mass spectrometry [17]. To remove impurities of NO<sub>2</sub> in the feed, the NO/He mixture was passed through a cold trap at 173 K.

## 2.4. In situ XANES spectroscopy

The in situ XANES measurements were performed at beamline BM26 (DUBBLE) at ESRF, Grenoble. An EXAFS cell dedicated for in situ measurements in the fluorescence mode was used [18]. A 10-mg catalyst sample was gently pressed into the sample compartment through which the gas flow passes. An Al foil (99.999% purity, 15 μm thickness) was used to seal the sample and also served as the window for the EXAFS radiation. A double-crystal Si(111) monochromator selected the energy of the X-rays, and a nine-channel monolithic Ge detector was used to collect the fluorescence radiation. Measurements were performed at both the Fe  $K$ -edge and the Ru  $K$ -edge. The scan time was ~8 min.

In the standard procedure, the sample was heated in 3% O<sub>2</sub> in He to 673 K and kept at that temperature for 30 min. After the cell was flushed in He for 30 min, three different reactions were performed: (i) 3000 ppm N<sub>2</sub>O + 800 ppm NO, (ii) 3000 ppm N<sub>2</sub>O + 800 ppm NO + 2% O<sub>2</sub>, and (iii) 5000 ppm N<sub>2</sub>O and the balance He. Each reaction was performed in situ for 30 min, followed by purging in He for 30 min. The

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