



XPS and in-situ IR investigation of Ru/SiO₂ catalyst

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Abstract

Ru(NO)(NO₃)₃/SiO₂ catalyst precursors were characterized via XPS and in-situ reflectance IR spectroscopy before, during and after reduction by hydrogen over the temperature range 300–800 K. IR results indicated that the catalyst precursor lost NO₃ groups first, with subsequent loss of NO both in a reducing atmosphere and during thermal annealing. XPS was used to derive information on the oxidation state of Ru in the various steps of the annealing and/or reduction processes. © 1997 Elsevier Science B.V.

Keywords: Ru catalyst; XPS; In-situ IR

1. Introduction

Electron spectroscopic techniques along with IR and NMR have successfully been employed to characterize the chemical species formed in various steps of catalytic processes [1–3]. Pederson and Lunsford reported an XPS study of ruthenium in zeolite-Y under both oxidizing and reducing environments [4]. Bianchi et. al. studied various ruthenium compounds and catalysts via XPS [5]. They observed that thermal annealing was sufficient for reduction when the Ru compound was in its pure form. They further indicated that a reducing atmosphere was needed to bring Ru to its zero-valent state when an oxide phase was present as a catalyst support. Muhler et al. reported a study of an alkali-promoted ruthenium catalyst for ammonia synthesis [6]. Their XPS measurements indicated that the Ru 3d peak shifted

by 1 eV to a lower binding energy in the presence of Cs. Interaction of OH groups in silica with zero-valent Ru was followed via ¹H NMR spectroscopy in a previous study [7]. In this work, we will extend the NMR study to include XPS and IR studies while following the course of reduction of a Ru(NO)(NO₃)₃ compound to its zero-valent state.

2. Experimental

A 4 wt% Ru catalyst was used in this study, which is prepared via an incipient wetness technique using ruthenium nitrosyl–nitrate solution (Strem Chemicals, 1.5 wt% Ru) as described previously [8]. Ruthenium nitrosyl–nitrate powder obtained from Johnson–Matthey Chemicals was used to investigate the behavior in the absence of SiO₂. A pure silica sample with a specific surface area of 450 m² g⁻¹ from Riedel de Haen was also used as a reference.

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The IR spectra were obtained using an a Bomem MB 102 FT-IR spectrometer equipped with a Harrick DRA-B03 diffuse reflectance attachment and an MCT detector. An in-situ infrared cell, equipped with ZnSe windows and capable of operating in the range of $300 < T < 800$ K and $10^{-4} < P < 1000$ torr, was used for reduction studies.

Powdered samples were introduced into a copper sample holder, placed in the reactor cell and reduced by successive evacuation/hydrogen exposure cycles at 100, 200, 300 and 350°C and at a pressure of 1.5 atm for 1 h. IR data were collected at 4 cm^{-1} resolution and 1024 scans.

XPS measurements were performed on a Kratos ES300 spectrometer using Mg $K\alpha$ excitation ($h\nu = 1253.6 \text{ eV}$). The C 1s line (B.E. = 285.0 eV) from residual hydrocarbons deposited on the surface of the sample was used as a reference. Our XPS spectrometer is not suitable for in-situ analysis. Therefore, thermal treatments of the samples were carried out in the UHV chamber of the spectrometer by gradual heating of the sample to 170°C in situ. XPS data were recorded after each step. XPS data of samples after reduction in the reactor were taken after an unavoidable brief exposure to air during their transfer into the spectrometer.

3. Results and discussions

Fig. 1 displays the IR diffuse-reflectance spectra of the 4% Ru/SiO₂ powders at room temperature and after 60 min reduction under H₂ atmosphere at the corresponding temperatures. The bands at 1427 and 1925 cm⁻¹ are attributed to bent NO and terminal NO groups respectively, and the band at 1521 cm⁻¹ is attributed to NO₃ [9]. Loss of hydrogen bonded O–H bands and stepwise removal of NO₃ bands followed by those of NO are the general features, and complete removal is achieved only after heating to 350°C in hydrogen. In addition, the NO bands are red-shifted and broadened during this reduction process.

Fig. 2 shows the XPS spectra of the N 1s and Ru 3d regions before, during and after annealing of the unsupported Ru(NO)(NO₃)₃ compound. Owing to the small cross-section of the N 1s level in comparison with the Ru 3d level [10], only in the pure ruthenium nitrosyl–nitrate compound could a

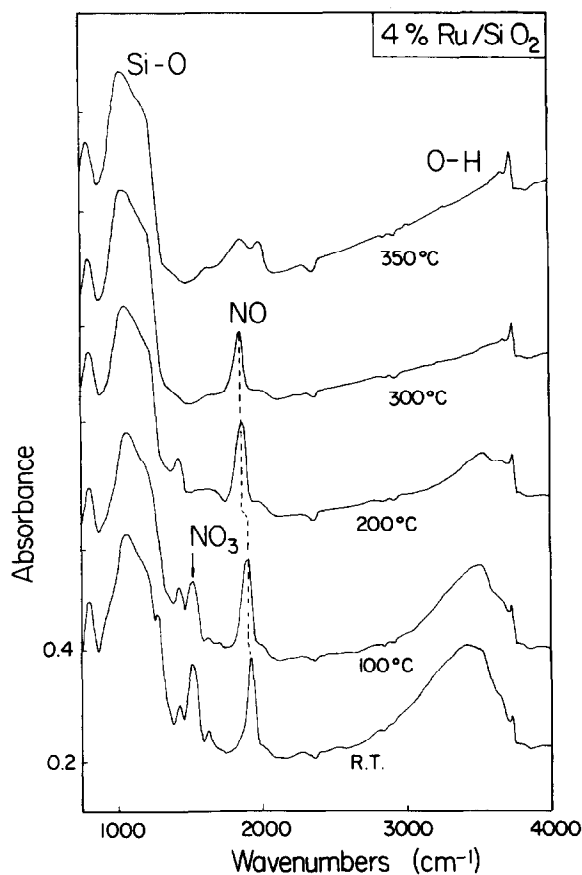


Fig. 1. Mid-IR diffuse-reflectance spectra of 4% Ru catalyst precursor dispersed in silica and after reduction in hydrogen for 1 h at the indicated temperatures.

reasonable signal-to-noise ratio be achieved in both the N 1s and Ru 3d regions. Before annealing, two N1s peaks at 405.6 eV and 401.8 eV, corresponding to NO₃ and NO nitrogens and with the correct stoichiometry of 3:1, are present. There is only one Ru 3d spin-orbit doublet with the 5/2 component at 283.1 eV which can be assigned to the +4 state [11]. During annealing, a stepwise removal of NO₃ followed by NO can again be observed. In spite of the gradual decrease in the intensity of the N 1s peaks, the binding energies remain constant in contrast with the case of Ru 3d. Starting with the initial loss of NO₃, a Ru 3d_{5/2} peak at 282.3 eV assigned to the +3 oxidation state appears, followed by another one at 281.3 (+2) all the way to metallic Ru at 279.4 eV. When the supported ruthenium compound was studied, the Ru 3d doublet was found to be broad, with a binding energy of

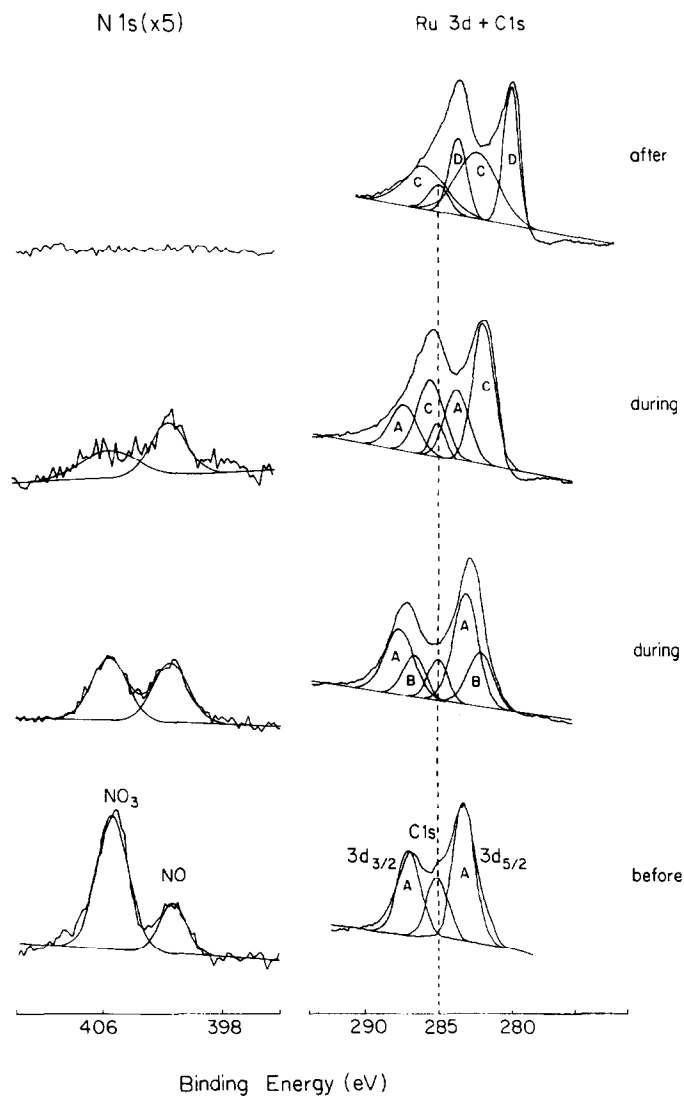


Fig. 2. N 1s and Ru 3d regions of the XPS spectra of Ru(NO)(NO₃)₃, before, during and after annealing up to 170°C in the UHV chamber of the spectrometer. A, B, C and D refer to the +4, +3, +2 and 0 oxidation states of Ru respectively.

282.3 eV corresponding to the +3 state (not shown here). Broadening can be attributed to dispersion of the metal particles on the support, and the reduction of Ru from +4 of the precursor compound to +3 of the supported one can either be attributed to a partial loss of NO₃⁻ groups and/or to electron transfer from the support and/or NO groups. XPS spectra of the same compound after reduction with hydrogen again revealed a single, broad Ru 3d doublet at a binding energy of 281.3 eV corresponding to Ru²⁺. The failure

to observe the zero-valent state is most probably due to exposure to air during transfer.

Acknowledgements

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