

FTIR characterization of Ru/SiO₂ catalyst for ammonia synthesis

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Abstract

Carbon monoxide adsorption on a Ru/SiO₂ catalyst was followed by IR spectroscopy to investigate the active sites. Using this catalyst, ammonia synthesis was achieved at 350°C in an N₂/H₂ gas mixture (N₂/H₂ ≈ 3 : 1) for different reaction times. In addition to NH₃ other NH_x (x = 1,2) species were also observed. CO adsorption after NH₃ production was also performed to investigate the change in nature of the active sites. Based on the experimental evidence participation of Ru⁰ sites in ammonia synthesis was confirmed and a partial oxidation of the reduced Ru sites during the synthesis was observed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ruthenium based catalysts are expected to be the second generation ammonia synthesis catalysts. The high activity of Ru-based catalysts at low temperatures coupled with their ease of reduction and good tolerance toward common reaction poisons make them potentially excellent catalysts for use in ammonia synthesis at thermodynamically favored low temperatures [1].

Aika et al. [2] prepared and characterized the chlorine-free ruthenium catalysts for ammonia synthesis. It was reported that Ru(NO)(NO₃)₃ and Ru₃(CO)₁₂ were effective precursors among four compounds, including Ru(acac)₃ and K₂RuO₄ (precursors) when they were supported on Al₂O₃. These authors also found MgO to be the most efficient support among several pure oxides under low pressure

conditions. They reported that the activity was correlated roughly with the basicity of the support. The reason for studying chlorine-free ruthenium catalysts is that the chlorine originated from the precursor is left on the catalyst after activation and chlorine retards ammonia synthesis [3]. It was also reported [3] that Ru/Al₂O₃ prepared from RuCl₃ gave a low dispersion and that the value depends on the reduction temperature. All the supports studied so far possess coordinatively unsaturated cations. In order to avoid the influence of the Lewis acidity of the support and to isolate the role of ruthenium, we studied silica-supported ruthenium catalyst. Earlier, we used XPS and in-situ FTIR methods to characterize the Ru/SiO₂ catalyst [4] and the mechanism of CO adsorption on it [5]. In this article we report FTIR spectroscopic investigation of ammonia synthesis using this catalyst.

2. Experimental

A 4 wt.% Ru/SiO₂ catalyst was used in this study

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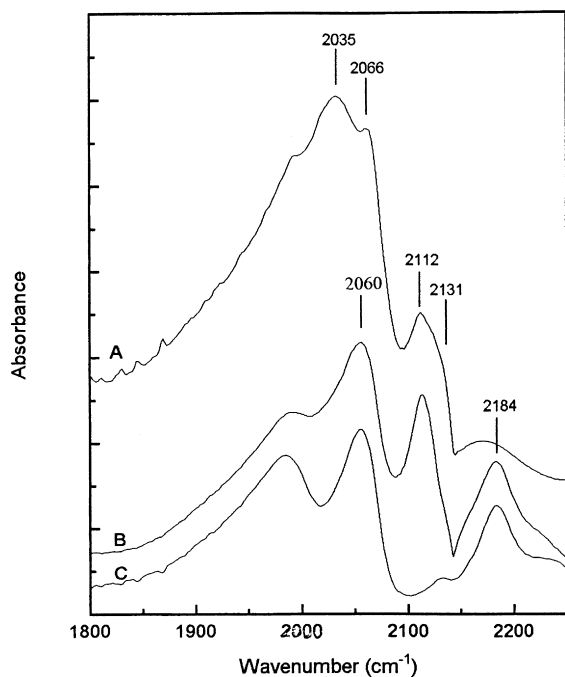


Fig. 1. 32 Torr of CO adsorption on reduced Ru/SiO₂ (A), after ammonia synthesis (B) and after evacuation (C).

which was previously prepared via an incipient wetness technique using ruthenium nitrosyl-nitrate solution (Strem Chemicals, 1.5 wt.% Ru) and SiO₂ (Degussa) [6]. IR spectra were obtained using a Bomem MB 102 FTIR spectrometer at 4 cm⁻¹ resolution. A specially designed cell allowed registration of the spectra at ambient temperature and catalyst activation at higher temperatures. The cell was connected to a vacuum/adsorption apparatus. The reduction of the catalyst was performed with successive hydrogen

Table 1
Infrared assignments for ¹²CO adsorbed on Ru/SiO₂

Frequency (cm ⁻¹)	Assignment	Adsorption site
1909	Bridged CO	
1957	Bridged CO	
1997	Bridged CO	
2035	Linear	Ru
2066	Tricarbonyl	Ru, Ru ^{δ+}
2112	Tricarbonyl	Ru ^{δ+}
2131	Tricarbonyl	Ru
2184	Linear	Ru ⁿ⁺
2226	Linear	Ru ⁿ⁺

exposure/evacuation cycles at 350°C for 2 h. Carbon monoxide adsorption was accomplished by admitting CO on the reduced catalyst and after ammonia synthesis in order to characterize the change in active sites. The ammonia synthesis is accomplished at 350°C in a N₂/H₂ gas mixture (N₂/H₂ ≈ 3 : 1) for 8 and 12 h.

3. Results and discussion

The spectra of CO adsorbed at 298 K on reduced Ru/SiO₂ is shown in Fig. 1. CO band assignment and their behavior are previously reported [5] and are also in good agreement with those reported in other investigations [7–9] (Table 1).

Introduction of gas mixture (H₂ : N₂ ≈ 1 : 3) in the IR cell at 350°C causes the appearance of broad and strong absorption centered at about 3004–3020 cm⁻¹ for reaction times of 8 and 12 h, respectively (Fig. 2). The shift observed at different reaction times could be explained by different degrees of hydrogen bonding. At the same time, sharp and less intensive bands at 3324 and 3405 cm⁻¹ are observed. In the low-frequency region an asymmetric band with a maximum at 1624 cm⁻¹ (Fig. 2(b)) and a complex band in the region 1260–1300 cm⁻¹ (Fig. 2(a)) are detected. The bands in the 2800–3000 cm⁻¹ region present in the background spectrum (Fig. 2(c)) are because of hydrocarbon residue on the sample surface. The bands at 3405 and 3324 cm⁻¹ correspond to stretching ν_{as}(NH₃) mode whereas, the bands in the low-frequency region are because of δ_{as}(NH₃) (1624 cm⁻¹) and δ_s(NH₃) (the complex band in the region 1300–1260 cm⁻¹) vibrations of coordinated ammonia [10]. As the position of the latter band is sensitive to the strength of the coordination center [10], it could be assumed that there are two types of adsorption sites differing in their coordinative unsaturation. These sites are characterized by δ_s(NH₃) of coordinated NH₃ at 1267–1280 and 1278–1291 cm⁻¹, respectively (Fig. 2(a), Table 2).

It is known [11] that SiO₂ does not possess Lewis acidity, i.e. it cannot form coordination complexes with ammonia. On this oxide only NH₄⁺ ion is observed upon ammonia adsorption owing to the presence of Brønsted acid sites. For this reason it could be concluded that the ammonia produced on Ru/SiO₂ catalyst is located on Ru sites. The ν_s(NH₃)

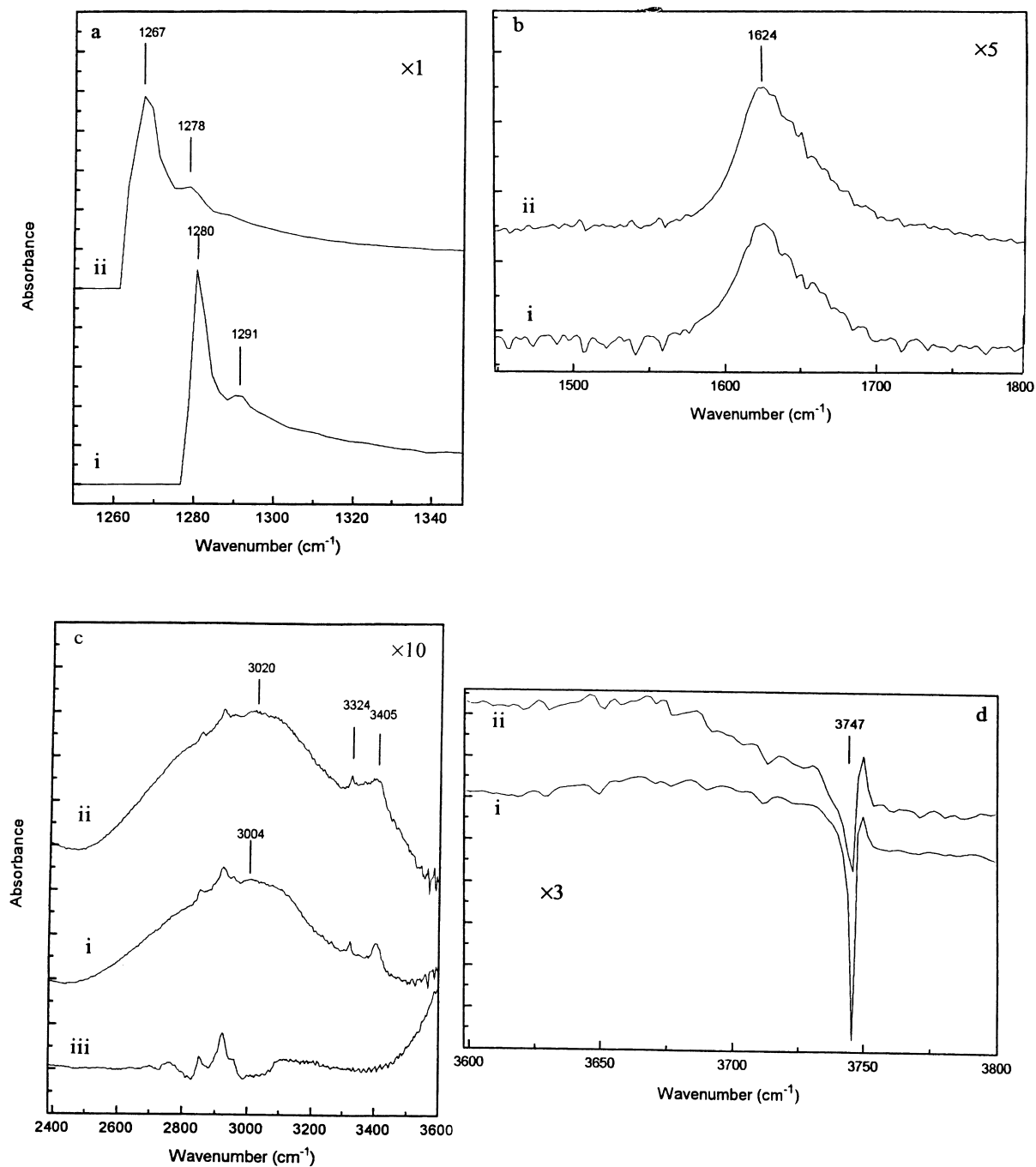


Fig. 2. Different regions of the IR spectra after ammonia synthesis after: (i) 8 h and (ii) 12 h.

Table 2
Assignment of IR bands observed after NH₃ synthesis

Absorption bands (cm ⁻¹)	Compound	Interpretation
1260–1300	NH ₃	δ_s (NH ₃)
1624	NH ₃	δ_{as} (NH ₃)
2800–3000	Hydrocarbon residue	
3004, 3020	NH _x ($x = 1-3$)	ν_{as} (NH _x), ν_s (NH _x)
3324	NH ₃	ν_{as} (NH ₃)
3405	NH ₃	ν_{as} (NH ₃)

stretching modes and ($\nu_s + 2\delta_{as}$) combination band of coordinated ammonia which are expected to be at about 3250 and 3150 cm⁻¹ respectively, are overlapped by the strong absorption at about 3000 cm⁻¹. This strong and broad band could reveal the presence of amide groups (NH). Indeed, the associated secondary organic amides manifests their stretching vibration in the region 3100–3070 cm⁻¹ [11,12]. These bands are intense and diffuse owing to hydrogen bonding. A decrease in the amount of isolated OH groups and appearance of OH hydrogen bonded groups may be because of interaction of NH_x species with surface single silanol groups (Fig. 2(d)).

When compared with the CO adsorption spectrum of the reduced sample, it was seen that the band originally at 2066 cm⁻¹ decreased significantly in intensity and shifted to 2060 cm⁻¹. The band at 2035 cm⁻¹ is not visible. The band at 2131 cm⁻¹ and a component of the band at 2066 cm⁻¹ were previously assigned to tricarbonyl species on metallic Ru centers whereas the band at 2035 cm⁻¹ corresponded to monocarbonyl of the type Ru–CO in accordance with the literature data [5,7]. The absence of the band corresponding to Ru–CO species (2035 cm⁻¹) and the decrease in intensity of the bands at 2057 and 2131 cm⁻¹ owing to Ru(CO)₃ on the reduced catalyst is an evidence about the participation of the Ru⁰ sites in the ammonia synthesis. The band at 2112 cm⁻¹ attributed to CO adsorbed on oxidized centers [5,7] is more intense suggesting an increase in the number of oxidized Ru sites. Here it should be noted that after evacuation of the reaction mixture at room temperature, no adsorbed NH_x ($x = 1-3$) was observed, i.e. that the active sites are liberated from the reaction product and intermediates and they were available for CO adsorption.

The origin of the bands at 2184 and 2226 cm⁻¹

observed upon CO adsorption on the catalyst used in ammonia synthesis (the reaction mixture was evacuated prior to CO adsorption) is not clear. However, it is possible to assign them to Ruⁿ⁺–CO where $n > 2$. They show stability upon evacuation suggesting the presence of strong Lewis acid sites. Based on the experimental observations it is concluded that during the ammonia synthesis partial oxidation of the reduced Ru sites takes place.

4. Conclusion

The Ru/SiO₂ catalyst studied is active for ammonia synthesis on which further kinetic studies should be accomplished for determination of its efficiency. The NH_x ($x = 1-2$) species represent intermediates in the ammonia synthesis reaction. The adsorption of CO on the catalyst surface after ammonia synthesis reveals that partial oxidation of the reduced Ru sites occurs which indicates that the active phase for ammonia production is metallic ruthenium.

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