

Coordination chemistry of cobalt ions in ferrierite: An FTIR spectroscopic study

Kristina Chakarova^{*}, Konstantin Hadjiivanov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bld. 11, Sofia 1113, Bulgaria

ARTICLE INFO

Article history:

Received 3 February 2009

Received in revised form 25 March 2009

Accepted 27 March 2009

Available online 5 April 2009

Keywords:

Co-FER

Adsorption

Carbon monoxide

Nitrogen monoxide

FTIR spectroscopy

ABSTRACT

The state of the accessible cobalt ions in a Co-FER sample was studied by CO and NO as IR probe molecules. Both Co²⁺ and Co³⁺ sites were detected. With NO the Co³⁺ ions formed mononitrosyl species (band at 1934 cm⁻¹) and with CO, monocarbonyls (band at 2204 cm⁻¹). A part of the Co³⁺-CO species was converted into dicarbonyls (band at 2194.5 cm⁻¹) at low temperature and presence of CO in the gas phase. The respective cobalt ions were supposed to be located in the so-called β-positions where the two CO molecules can approach the cation from different zeolite cages. The remaining part of the Co³⁺ sites was not able to accommodate two CO molecules and were supposed to be located at α-positions. In addition, two kinds of Co²⁺ sites were detected. With CO they formed two kinds of monocarbonyl species (bands at 2199 and 2196 cm⁻¹). No dicarbonyls were detected in this case and one of the possible reasons is the very low adsorption energy of CO. NO was a less sensitive probe to the environments of Co²⁺: one kind of dinitrosyl species (ν_s at 1897 cm⁻¹ and ν_{as} at 1813 cm⁻¹) were distinguished after interaction of Co²⁺ ions with NO and only at low coverage the heterogeneity of the Co²⁺ sites is seen.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Metal-exchanged zeolites are a subject of steady interest due to their wide application as sorbents and catalysts. In particular, they are among the most promising catalysts for selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons [1–15]. Li and Armor [1] reported, in 1992, the successful reduction of NO_x by methane over Co-ZSM-5 in the presence of O₂. More recently, the same authors stressed that Co-H-FER (Co-H-ferrierite) was the best catalyst for this purpose [2–4]. Performing SCR with methane is of particular interest since CH₄ is naturally occurring (main component of natural gas), commonly available and safe fuel source. Thus, it could replace ammonia as a reducer in stationary NO_x sources.

The activity of the species greatly depends on their location inside the network of cavities or even on the external surface of zeolite crystallites. Therefore, it is very important for catalysis to know the state and properties of the cobalt cationic sites in order to achieve an appropriate balance of the suitable catalytic sites that will provide an active and stable catalyst. It is established that cobalt cations are relocated upon hydration/dehydration and are also able to redistribute within the zeolite matrix [7,15]. This is one of the reasons for catalyst deactivation in the presence of water. Studies on the location and coordination of cobalt in ferrierite have revealed existence of different extra-framework cobalt sites. In as

prepared (hydrated) samples one of the sites is located at the centre of the ferrierite cage and is six-coordinated to water molecules in a slightly distorted octahedral configuration [13,14]. Although this is the most populated site, in the cobalt-exchanged forms the centre of the ferrierite cage is only partially occupied by cobalt ions. A second cobalt site is detected near the centre of the 10-membered ring coordinated to four of the framework oxygens in tetrahedral symmetry. According to Ciambelli et al. [7] these cations are considered to be responsible for the SCR catalytic activity of Co-H-FER. The third site is situated not far from the centre of the eight-membered ring [13,14]. In the case of overexchange of cobalt ions, presence of cobalt oxides was suggested. According to Kaucy et al. [16], cobalt ions in dehydrated zeolite are located in three different positions. The most populated site denoted β is in the plane of a deformed six-membered ring of the eight-ring channel (see Fig. 1). A metal ion in this site is supposed to be coordinated to four oxygens. The second populated site is α, located in the main ferrierite channel. A cation in this site is coordinated to four oxygens creating a rectangle on the wall of the main channel. With increasing cobalt loading, the occupation of this site increases. The third site where the occupation is rather low, is the so-called γ-site. It is located in the eight-ring channels and is probably not accessible to adsorption.

Furthermore, recent findings of Capek et al. [17] and Montanari et al. [18] take notice of alervalent states of cobalt, namely the active sites are assumed to be small oxide-like clusters containing both Co³⁺ and Co²⁺. In addition, strong evidence was provided that Co³⁺ sites are located in the cavities of the zeolite, which suggests that exchanged cobalt ions are in a trivalent state [18,19].

^{*} Corresponding author. Tel.: +359 2 9792556; fax: +359 2 8705024.

E-mail addresses: kristina@svr.igic.bas.bg, kristina_chakarova@yahoo.com (K. Chakarova).

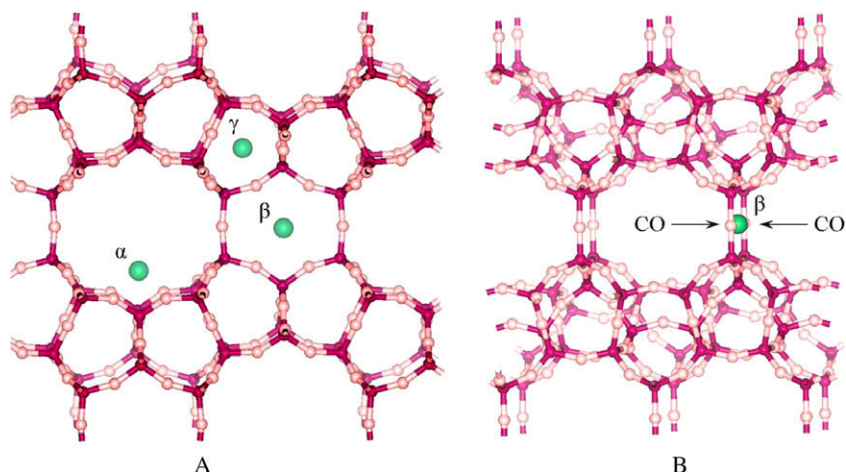


Fig. 1. Location of extra-framework α , β and γ Co ions in ferrierite: (A) looking along the 10-ring channels and (B) looking along the eight-ring channels. Panel B shows the possibility of formation of dicarbonyls.

Infrared spectroscopy of probe-molecules is a valuable source of information on the catalytic surfaces and is one of the most frequently used techniques for investigations on the SCR mechanism [20]. The aim of this work is to characterise the accessible cobalt sites in Co-H-FER. The properties of the exchanged cobalt ions have been examined by using CO and NO as probe-molecules. To be able to detect all Co^{n+} sites, we have studied CO adsorption at low temperature. We have demonstrated the heterogeneity of the cobalt sites and the ability of some of them to coordinate simultaneously two CO molecules at low temperature. Additional information has been obtained by NO adsorption since NO is not only a molecular probe but also a reactant in the SCR processes.

2. Experimental

The parent NH_4 -FER zeolite ($\text{Si}/\text{Al} = 8.6$) used in this study was supplied by the Research Institute of Inorganic Chemistry, Ústí nad Labem (Czech Republic). The Co-H-FER sample was prepared by a conventional ion-exchange procedure. 0.2 g of NH_4 -FER were suspended in 20 ml 0.426 M solution of $\text{Co}(\text{NH}_3)_2 \cdot 6\text{H}_2\text{O}$ and stirred for 96 h at ambient temperature. Then the precipitate was thoroughly washed with distilled water and dried at 353 K for 12 h. The cobalt concentration in the sample thus obtained was 0.64 wt.%.

The IR spectra were recorded in a transmission mode on a Nicolet Avatar 360 spectrometer at a spectral resolution of 2 cm^{-1} and accumulation of 64 scans. Self-supporting pellets (ca. 10 – 20 mg cm^{-2}) were prepared from the sample powder and treated directly in the purpose-made IR cells. The latter were connected to a vacuum-adsorption apparatus with a residual pressure below 10^{-3} Pa . The low-temperature experiments were performed in a cell allowing IR measurements in the temperature range 100–300 K. Prior to the adsorption measurements, the samples were activated by heating in fresh oxygen at 673 K for 1 h followed by 1-h evacuation at the same temperature.

Carbon monoxide (>99.997) was supplied by Linde AG. Nitrogen monoxide (>99.0) was purchased from Messer Greisheim GmbH. Before use, carbon monoxide and oxygen were additionally purified by passing through a liquid nitrogen trap.

3. Results

3.1. Background IR spectra of the sample

The IR spectrum of the activated Co-H-FER sample displays, in the O–H stretching region, two bands with maxima at 3750 and

3606 cm^{-1} (see the inset in Fig. 2, spectrum a). These bands have also been recorded with the pure support and are attributed to terminal silanols (Si–OH) and acidic bridging hydroxyls (Si–OH–Al), respectively. In addition, bands arising from overtones and combinations of the skeletal modes are detected at 1978, 1876, 1637 and 1504 cm^{-1} . The so-called sample “cut-off” (the wavenumber below which the sample is practically opaque) was around 1300 cm^{-1} .

3.2. Adsorption of CO on activated Co-H-FER

Two experimental protocols were used to study the CO adsorption. Initially CO was admitted to the sample and spectra recorder as a function of time. Thus, information on the sequence of formation of different species can be obtained. After reaching saturation, the coverage was decreased by evacuation. In this way, information on the stability of the different species can be obtained.

Low-temperature adsorption of CO on the sample (267 Pa equilibrium pressure) leads to the appearance of a series of bands in the IR spectrum with maxima at 2204, 2194 and 2172 cm^{-1} (Fig. 2, spectrum b). Evolution of the spectra with time shows that the band at 2204 cm^{-1} somewhat decreases in intensity (Fig. 1, spectrum c) and afterwards reaches a stable level (Fig. 2, spectra d–h). This suggests that some of the species characterised by the band at 2204 cm^{-1} are converted to another species most probably

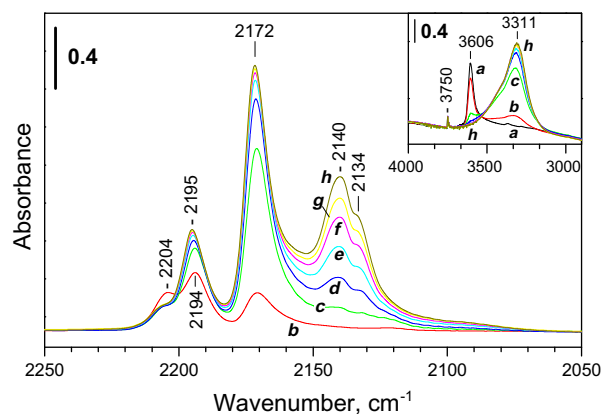


Fig. 2. FTIR spectra of CO adsorbed at 100 K on Co-H-FER: background spectrum after activation at 673 K (a), subsequent introduction of CO (267 Pa equilibrium pressure) (b) and evolution of the spectra with time (c–h) (spectrum h corresponds to 16 min in CO atmosphere). The spectra are background corrected except for those in the inset.

Download English Version:

<https://daneshyari.com/en/article/74873>

Download Persian Version:

<https://daneshyari.com/article/74873>

[Daneshyari.com](https://daneshyari.com)