

Effect of water on cobalt speciation during solid-state synthesis of Co^{2+} /ZSM5 catalysts: Quantitative study by TPR and XAS

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Abstract

The effect of water on cobalt speciation in the synthesis of Co^{2+} /ZSM5 catalysts is quantitatively studied by the combined use of macroscopic and local characterization techniques, TPR and X-ray absorption spectroscopies, respectively. The addition of a small quantity of water to cobalt acetate and zeolite during the preparation of Co^{2+} /ZSM5 by solid-state reaction favors cobalt dispersion and migration into the zeolite. It also inhibits the formation of extraframework phases (Co_3O_4 particles, cobalt phyllosilicate). Dissociation of solid cobalt acetate upon contact with water is thought to be the driving force for enhanced cobalt migration into the zeolite.

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1. Introduction

Among the various processes used to introduce metal ions into zeolites, solid-state reactions between a protonic zeolite and a solid precursor salt have gained interest for two reasons: they avoid the handling of large quantities of solutions and there is no waste of precursor in contrast to the method of aqueous ion exchange at equilibrium [1,2]. However, a non-negligible fraction of metal ions deposited during solid-state reaction do not exchange with protons, especially when the amount of precursor salt exceeds the stoichiometry of exchange: they react instead with zeolite to form extraframework phases. It becomes thus important

to characterize such phases which have a different reactivity from that of exchanged ions, as shown for example in the cases of NO_x reduction [3–6] and hydrocarbon ammoxidation [7–9]. These phases are usually oxidic particles, but it has been shown recently that the use of solid cobalt acetate to prepare Co^{2+} /ZSM5 systems may lead to another type of phase, a well-crystallized phyllosilicate incorporating in its bulk the majority of cobalt ions, after dealumination of the zeolite by acetate anions during thermal treatment [10].

In order to modify this anion-support interaction leading to a result detrimental to catalysis [9], one can imagine to add another chemical partner, water, in a limited amount, as a way to change the type of contact between precursor salt and support before thermal treatments be involved. The purpose of this paper is to identify the phases formed during this “wet” solid-state procedure—hereafter

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referred to as “impregnation” by analogy with the classical catalyst preparation mode—and to compare them with the phases formed during a “dry” solid-state procedure. Quantification is attempted by the combined use of macroscopic and local characterization techniques, respectively, TPR and X-ray absorption spectroscopies, which are sensitive to all types of cobalt sites present in the system, unlike techniques such as X-ray diffraction, silent with respect to dispersed species and isolated ions.

2. Experimental

2.1. Catalysts preparation

Two series of three samples were prepared, one by solid-state reaction and the other one by impregnation (Table 1). For the sake of homogeneity regarding earlier results [11], samples prepared by solid-state reactions are referred to as Ax, following the nominal Co/Al atomic ratio, $x = 1/2$, 1 or 3/2 (i.e. corresponding to one, two or three times the exchange stoichiometry). Samples prepared by impregnation are referred to as Ix. It must be noted that the purpose of the synthesis of samples from series I is primarily characterization, while reaching the exact nominal ratio x is not sought for; consequently, x in the denomination Ix was chosen mostly by analogy with the A series with increasing Co/Al content.

Catalysts A were prepared by solid-state reaction between H-ZSM5 zeolite (Zeocat, Si/Al = 26, Al wt.% = 1.6, water content: 5 wt.%, pore volume: 0.54 mL g⁻¹) and cobalt(II) acetate [Co(CH₃COO)₂] · 4H₂O (Prolabo). Powders were finely ground and mixed in a mortar for 15 min in ambient conditions. The resulting mixture was heated in a helium flow (25 mL min⁻¹) up to 500 °C (heating rate: 2 °C min⁻¹) and kept at 500 °C overnight (12 h). After having been washed twice with deionized water and dried overnight at 110 °C in a static oven, the powder was submitted to a final activation treatment in O₂, up to 500 °C (25 mL min⁻¹, heating rate: 5 °C min⁻¹) and 1 h at that temperature.

In the preparation procedure of catalysts I, a volume of deionized water (1.5 mL g⁻¹ of zeolite) was added to the mixture of ground powders (zeolite and precursor). The whole system was pugged for 10 min and dried in air at

110 °C overnight. The resulting solid was heated in a helium flow (25 mL min⁻¹) up to 500 °C (heating rate: 2 °C min⁻¹) and kept at 500 °C overnight (12 h) before being submitted to the oxygen activation treatment described above.

It can be stressed here that during the preparation of catalysts I, the sample is contacted with water *before* the first thermal treatment, that is before reaction between zeolite and cobalt acetate; whereas the contact with water occurs *after* the first thermal treatment in series A, that is after the reaction between zeolite and cobalt acetate has taken place.

2.2. Characterization

Chemical analyses were performed by ICP at the Vernaison Center of Chemical Analysis of CNRS. Specific surface areas were determined by the BET method from nitrogen physisorption at -196 °C, using an automatic Micromeritics ASAP 2000 instrument. Micropore volumes were assessed by application of the Dubinin equation between 0.01 < P/P₀ < 0.1. Temperature-programmed reductions (TPR) were performed under 5% H₂ in argon (25 mL min⁻¹); the hydrogen consumption was measured using a thermal conductivity detector, from room temperature to 1000 °C with a heating rate of 7.5 °C min⁻¹.

UV–Vis–NIR spectra were recorded in the reflectance mode (1 nm resolution) on a Cary 5 spectrometer (Varian) equipped with an integration sphere, using Teflon as a reference. XANES and EXAFS spectra were recorded in the transmission mode at the Co K edge on the XAS 13 beamline of the DCI storage ring (LURE, Orsay, France). For XANES measurements, a double-crystal Si(311) monochromator was used and the energies were scanned in 0.3 eV steps from 7680 to 7830 eV. For EXAFS measurements, a channel-cut Si(111) monochromator was used, and the energies were scanned in 2 eV steps from 7600 to 8600 eV. The energy was calibrated using a Co metal foil reference. After background correction, the XANES spectra were normalized in the middle of the first EXAFS oscillation. EXAFS analyses were performed in the framework of single-scattering treatments with the package of programmes “EXAFS pour le Mac” [12]. The Fourier transforms (FT) were calculated on $w(k)k^3\chi(k)$, where $w(k)$ is a Kaiser–Bessel window with a smoothness parameter equal to 2.5. The k limits were 2 and 11.7 Å⁻¹. FT are presented without phase correction. A detailed discussion of the single-scattering fits referred to in this paper can be found in Refs. [10,11]. For the sake of clarity, values of N , R and σ are recalled in the text whenever necessary.

3. Results

3.1. UV–Visible spectroscopy

Before solid-state reaction in helium, solid mixtures A and I are investigated by UV–Visible spectroscopy at room temperature and exhibit different absorption spectra. In

Table 1
Cobalt content and physicochemical characteristics of Co²⁺/ZSM5 catalysts A and I

Samples	Co (wt.%)	BET surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)
H-ZSM5	–	356	0.15
A1/2	1.5	360	0.10
A1	3.5	350	0.10
A3/2	5.0	360	0.10
I1/2	1.3	341	0.10
I1	2.3	271	0.09
I3/2	5.3	299	0.09

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