Influence of the cobalt salt precursors on the cobalt speciation and catalytic properties of H-ZSM-5 modified with cobalt by solid-state ion exchange reaction

Mourad Mhamdi *, Sihem Khaddar-Zine, Abdelhamid Ghorbel

Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, 2092 Tunis, Tunisia

ABSTRACT

Co-ZSM-5 catalysts prepared by either aqueous or solid-state ion exchange using different cobalt precursors (acetate, chloride, nitrate or formate) were studied in the selective ammoxidation of ethylene and ethane to acetonitrile. Co^{2+} supported catalysts were characterized by chemical analysis, X-ray powder diffraction, N_2 adsorption (BET), TEM/EDX, FTIR, XANES and EXAFS spectroscopy, H_2 TPR and TPD of ammonia. It was found that all the preparations led to cobalt exchanged metal ion at the bridging oxygen of Si–OH–Al groups or to Co oxide or phyllosilicate. XRD, TEM and H_2 TPR indicated the presence of cobalt oxide when cobalt chloride, formate or nitrate was used. TPD of ammonia and FTIR of pyridine, used respectively as probe molecules showed that solid-state exchange catalysts exhibited new Lewis acid sites. The catalyst resulting from cobalt acetate, which contained mostly isolated Co^{2+} ions in cationic exchange position and cobalt phyllosilicate, showed high activity and selectivity toward acetonitrile.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

One of the typical features of zeolites is their ability to exchange cations which are retained in their channels at specific sites. Cations are brought via an external medium, most often an aqueous solution. One can take advantage of this property in catalysts preparation to introduce a catalytically active phase inside the zeolite. However, ion exchange in solution is ruled by equilibrium and the reaction is not total, resulting in the handling of large quantities of solution and in a waste of cations in the mother liquor when the solid catalyst is separated from the solution. It is then tempting to optimize other techniques of preparation in which the whole amount of cations is theoretically forced to get fixed on the zeolitic support without the barrier imposed by equilibrium.

Transition metal ions can be introduced into molecular sieves by different methods, the most common ones being incipient wetness impregnation, decomposition of metal organic complex, hydrothermal synthesis or ion exchange. Ion exchange can be carried out in liquid solution or by solid-state exchange reaction. 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. This method consists in heating a mixture of two powders, one being the zeolite and the other the active phase salt precursor, so as to induce thermally the diffusion of the salt into the zeolite [1,2]. The exchange process initially takes place at the solid–solid interface between the precursor salt and zeolite grains, and the success of the exchange depends on the type of interactions developed. Overstoichiometric exchanges can be expected by solid-state ion exchange while they cannot be obtained in solution. Nevertheless, the extent of the exchange in the narrowest sense can be higher or lower depending on the formation of extraframework phases at the expense of the migration of ions into the zeolite channels [3,4], resulting in different speciation. It becomes thus important to characterize such phases which have a different reactivity from that of exchanged ions and a detailed characterization of cobalt based materials may be helpful for developing new systems for the different catalytic applications.

In the case of Co–zeolites systems considerable efforts directed at characterizing cobalt species in Co-ZSM-5 catalysts [5–10], there is an ongoing debate on the nature and role of catalytic entities. Dedecek et al. showed that Co^{2+} cations could be located at α, β, and γ sites in ZSM-5 [11]. When all exchange sites are occupied by cobalt cations, formation of aggregates of cobalt [12–14], and of particles of oxides Co_2O_3, Co_3O_4, and CoO has been reported previously [15–17]. For the case of overexchanged material (e.g., Co/Al = 1.5) using cobalt acetate, the formation of well-crystallized

* Corresponding author. Tel.: +216 71 872 600; fax: +216 71 885 008.
E-mail address: mourad.mhamdi@gmail.com (M. Mhamdi).

cobalt phyllosilicate incorporating in its bulk the majority of cobalt ions, after dealumination of the zeolite by acetate anions during thermal treatment, has been reported [4].

Cobalt-containing zeolites have drawn a great deal of attention in recent years. They are reported to be the most promising catalysts for reducing NO with methane in oxidizing atmosphere [18–23]; another reason is their activity in several reactions of organic molecules such as Fisher–Tropsch synthesis [24], phenol acylation [25], benzylalcohol oxidation [26], regioselective oxidation of alkanes [27] and hydrocarbon ammoxidation [28–33].

The aim of this work is to compare the effect of four different precursor salts on cobalt speciation after a solid-state reaction in overstoichiometric conditions with H-ZSM5, focusing on the identification of extraframework phases and the catalytic performances of these solids in the ammoxidation reaction.

2. Experimental

2.1. Catalysts preparation

2.1.1. Solid-state ion exchange

The catalysts were prepared by solid-state reaction between H-ZSM-5 zeolite (Zeocat, Si/Al = 26) and solid: cobalt(II) nitrate hexahydrate (Aldrich), cobalt(II) formate dihydrate (Merck), cobalt(II) chloride hexahydrate (Prolabo) or cobalt(II) acetate tetrahydrate (Prolabo). The nominal atomic Co/Al ratio was fixed to be equal to 1, i.e., twice the stoichiometry of protonic exchange by Co^{2+}. Powders were finely ground and mixed in a mortar for 15 min in ambient conditions. The resulting mixture was then heated in a helium flow (25 mL min^{-1}) up to 500 °C (heating rate: 2 °C min^{-1}) and left at 500 °C overnight (12 h). Cooling was performed in helium. After washing the powder twice with deionized water, and drying it overnight in air at 110 °C in a static oven, a final activation treatment during 1 h in O$_2$ at 500 °C (25 mL min^{-1}, heating rate: 5 °C min^{-1}) was achieved. Herein, Co-ZSM-5 catalysts are identified as Co-Z-X, where X means cobalt precursor (acetate (A), formate (F), chloride (Cl) or nitrate (N)).

2.1.2. Aqueous ion exchange (Co-ZSM-5,3)

H-ZSM-5 zeolite (Si/Al = 26) was used as starting material. A sample was prepared by stirring 2 g of zeolite in 200 ml of 0.1 M cobalt acetate solution for 24 H at 80 °C. After three identical consecutive exchanges, the zeolite slurry was filtered, washed with de-ionized water and dried at 110 °C. Finally, the catalyst was pretreated with flowing oxygen at 500 °C for 1 h.

A reference sample (LEN) containing only isolated cobalt ions for EXAFS analysis was prepared by three consecutive aqueous ion exchanges from a 0.01 M cobalt nitrate solution. After drying at 110 °C, the catalyst was treated in oxygen at 500 °C for 1 h (O$_2$ flow 25 mL/min, heating rate 5 °C/min). The final Co wt% was 0.5 (exchange ratio: 30%).

2.2. Catalyst characterization

Chemical analyses were performed by ICP at the Vernaison Center of Chemical Analysis of the CNRS. XRD patterns were obtained on a diffractometer with a copper anode. The K$_\alpha$ radiation was selected with a diffraction beam monochromator. Scan was taken at 2θ rate of 0.2°/min and structural data for reference compounds were taken from the ASTM X-ray powder data file.

N$_2$-BET analysis and porosity measurements were done on a Micrometrics ASAP 2000 apparatus at liquid nitrogen temperature. IR experiments were performed in an IR vacuum cell, with CaF$_2$ windows. The spectra were recorded on a PerkinElmer spectrometer. All the IR spectra were measured after activation of the

sample at 500 °C in vacuum. For the adsorption of pyridine, the sample was first evacuated then connected with pyridine vapour at room temperature for 1 h. Finally, desorption was performed under vacuum treatment at 150 °C for 1 h.

The temperature programmed desorption of ammonia was made as follows: the catalyst was first exposed to a helium flow at 500 °C for 1 h, then saturated with ammonia at 100 °C and flushed with helium at the same temperature. Finally, the temperature was ramped to 550 °C at a rate of 5 °C/min. Quantitative analysis was performed by means of a catharometer.

The H$_2$ TPR experiments were performed in U-shaped tubular quartz reactor, using H$_2$/Ar (5%) flow of 1.8 L/h, starting from room temperature to 950 °C, with a heating rate of 7.5 °C/min. The H$_2$ consumption was determined by a thermal conductivity detector.

TEM-EDX analyses of the final catalysts were obtained on a 200 kV JEOL JEM 2010 microscope equipped with a X-ray emission spectrometer (PGT Imix PC system). The ground powder was dispersed in pure ethanol, the suspension stirred in an ultrasonic bath and one drop placed on a carbon-coated copper grid for analysis.

XANES and EXAFS spectra were recorded in transmission at the Co K edge on the XAS 13 beamline of the DCI storage ring at LURE (Orsay, France). For XANES measurements, a double-crystal Si(3 1 1) 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(1 1 1) 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" [34]. The Fourier transforms (FT, presented without phase correction) 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 2.4 and 11.8 Å^{-1}. Single-scattering fits of experimental curves were performed with the Round Midnight programme [35]. Ab initio amplitude and phase functions for Co-O, Co-Si and Co-Co pairs were calculated using FEFF7 code [36].

2.3. Catalytic reactions

Ammoxidation of ethylene and ethane were studied between 450 and 500 °C using a dynamic micro reactor operating at atmospheric pressure. A total flow rate equal to 6 L/h and a catalyst weight between 0.05 and 0.1 g were used. In all cases, the inlet reagent composition was 6.5% O$_2$, 10% C$_2$H$_4$ or C$_2$H$_6$, 10% NH$_3$ and the rest helium. Preliminary tests were made in order to prove that the reaction rate was not affected by inter particles mass diffusion by studying the influence of catalyst weight and the flow velocity on the activity. The analysis of the reaction partners was recorded on line by two chromatography units, one operated with a flame ionization detector while the other was equipped with a thermal conductivity detector.

The conversion and selectivity are defined as follow:

$$\text{Conversion} \quad \text{TTG}\,(\%) = \frac{[\sum_i y_i n_i]}{[y_0 n_0 + \sum_i y_i n_i]}$$

$$\text{Selectivity of reaction product (carbon basis)} \quad S(\%) = \frac{y_i n_i}{\sum_i y_i n_i}$$

Where y_i and y_0 are the mole fractions of product and hydrocarbon (ethane or ethylene) respectively; n_i and n_0 are the number of carbon atoms in each molecule of reaction product and the hydrocarbon (ethane or ethylene), respectively.