Applied Catalysis A: General 439–440 (2012) 88–100

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Influence of the parent zeolite structure on chromium speciation and catalytic properties of Cr-zeolite catalysts in the ethylene ammoxidation

F. Ayari [a,*], M. Mhamdi [a], T. Hammedi [a], J. Álvarez-Rodríguez [b], A.R. Guerrero-Ruiz [b], G. Delahay [c], A. Ghorbel [a]

[a] Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire Tunis ElManar, 2092 Tunis, Tunisia
[b] Unidad Asociada Group for Desig. and Appl. of Heter. Catal. UNED-ICP(CSIC), Dpto. Inorganic and Technical Chemistry, Faculty of Sciences, UNED, 28040 Madrid, Spain
[c] Institut Charles Gerhardt Montpellier, UMR 5253, CNRS-UM2-ENSCM-UM1, Eq. "Matériaux Avancés pour la Catalyse et la Santé", ENSCM (MACS-Site la Galéra), 8, rue Ecole Normale, 34296 Montpellier Cedex 5, France

ARTICLE INFO

Article history:
Received 17 February 2012
Received in revised form 22 June 2012
Accepted 24 June 2012
Available online 1 July 2012

Keywords:
Ammoxidation
Solid-state exchange
Zeolite structure
Thermal analysis
H_2-TPR

ABSTRACT

Cr-zeolites with MFI, BEA, MOR and FAU structures, prepared by solid-state ion exchange, were characterized and tested in C_2H_4 ammoxidation to acetonitrile in the temperature range 425–500 °C. Based on characterization results, chromate and/or polychromate species, oxo-cations and small Cr_2O_3 oxide clusters played a key role in the ammoxidation of ethylene, while agglomerated Cr_2O_3 and bare Cr cations should be avoided. Cr ions sited in the sodalite and hexagonal cages of NH_4^+–Y are not accessible to the reactants while available catalytic sites are poorly active. However, the mesopores of the ultra stable Y zeolite (USY) favor the diffusion of reactants to the clustered Cr oxide. The corresponding catalyst is therefore active, but the presence of octahedral Al species is crucial to the ammoxidation. Cr ions in zeolites beta and mordenite led to less active catalysts when compared to ZSM-5. In zeolite beta, the micropores are small; therefore, pronounced interactions between ethylamine intermediate molecules could discourage the acetonitrile formation. In mordenite, agglomerates of Cr_2O_3 oxide inhibited the accessibility of active sites to the reactants and enhanced the hydrocarbon oxidation. The catalytic performance of Cr ions in ZSM-5 provided from a synergy of different parameters: structural, textural and the acid strength (Si/Al ratio).

1. Introduction

Acetonitrile is used as a basic feedstock in a wide range of industrial applications [1]. The demand for acetonitrile remains strong, and consequently, various chemical processes were widely used to meet the demand [2]. Unfortunately, most of these conventional processes are hazardous, expensive and less-selective [2].

As an alternative, academic and patent literature has provided much information on the important aspects of light hydrocarbons ammoxidation to acetonitrile. For the direct ammoxidation of ethylene (Eq. (1)), a large number of catalytic systems have been developed using either microporous materials (zeolites) or transition metal oxides as supports.

$$C_2H_4 + O_2 + NH_3 \rightarrow CH_3CN + 2H_2O \quad (1)$$

Li and Armor [3,4], Mies et al. [5,6] and Mhamdi et al. [7–10] reported substantially higher activity of Co/zeolites catalysts with BEA and MFI topologies in ammoxidation of ethylene.

In our preliminary study [11] performed using sol–gel derived materials, aerogel Cr/Al_2O_3 and Co/Al_2O_3 catalysts (5 wt.% of metal) were not found to be highly active in ammoxidation of ethylene to acetonitrile. More recently, we reported that Cr–ZSM-5 catalysts (5 wt.% of Cr, Si/Al = 15 and 26) yielded mostly acetonitrile after varying the source of chromium [12] and the catalysts preparation method [13]. Consequently, we concluded that zeolites with Cr ions in the exchange sites seem to be the materials exhibiting higher activity, whereas, agglomerated Cr_2O_3 oxide enhances the hydrocarbon combustion.

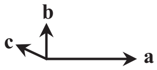
The nature of catalyst support is a crucial parameter which can affect the catalytic properties of Cr exchanged zeolites. Five zeolite supports of MFI, BEA, MOR and FAU structures were provided in this work. ZSM-5 [14] has a three-dimensional intersecting channel system. A straight channel of 0.56 nm × 0.53 nm runs parallel to the *a*-axis and a sinusoidal channel of 0.55 nm × 0.51 nm runs parallel to the *b*-axis (see Table 1 for axis). Zeolite beta [14] has a three-dimensional intersecting channel system. Two mutually perpendicular straight channels run in the *a*- and *b*-directions, each with a cross section of 0.66 nm × 0.67 nm. A sinusoidal channel of 0.56 nm × 0.56 nm runs parallel to the *c*-direction. Mordenite [14] has a semi-two-dimensional

---

[*] Corresponding author. Tel.: +216 50646504; fax: +216 71885008.
E-mail address: lcmc_fa@yahoo.fr (F. Ayari).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.06.037

Table 1
Chemical analysis results.

Sample	Cr (wt.%)	Al (wt.%)	Si/Al (mol/mol)	Cr/Al (mol/mol)	Ion exchange degree (%)[a]	Pore size (Å), channel system [14] 
NH_4^+–Y	–	8.38	2.42	–	–	12-ring 7.4 × 7.4 (3D)[b]
Cr–Y	5.06	7.63	2.57	0.33	100	–
H^+–USY	–	2.17	15.00	–	–	–
Cr–USY	4.45	2.09	15.01	1.10	330	–
H^+–beta	–	2.71	11.88	–	–	12-ring 6.6 × 6.7 (3D) 12-ring 5.6 × 5.6
Cr–beta	4.05	2.44	12.46	0.86	198	–
H^+–ZSM-5	–	2.57	14.05	–	–	10-ring 5.3 × 5.6 (2D)[c] 10-ring 5.1 × 5.5
Cr–ZSM-5	5.13	2.19	15.12	1.21	363	–
NH_4^+–Mor	–	4.01	6.61	–	–	12-ring 6.5 × 7.0 (1D)[d] 8-ring 2.6 × 5.7
Cr–Mor	4.51	3.24	9.26	0.72	216	–

[a] Defined by 300 × Cr/Al (mol/mol) if we consider that Cr^{3+} ions are only the possible exchange species.
[b] Three-dimensional.
[c] Two-dimensional.
[d] One-dimensional.

channel system. Parallel straight channels of 0.70 nm × 0.65 nm perpendicularly intersect smaller channels of 0.57 nm × 0.26 nm. Zeolite Y [14] has a three-dimensional pore system which is constructed from large supercages with diameters of 1.20 nm that are connected via apertures of 0.74 nm diameter. Ultra stable zeolite Y (USY) results from the steaming treatment of H^+–Y or NH_4^+–Y at high temperatures. This treatment process extracts Al atoms from the tetrahedral positions in the zeolite framework and converts them to octahedral, amorphous aluminum oxide.

The aim of this work is to study the effect of the support structure on the catalytic properties of Cr-zeolite catalysts. It should be underlined that a large part of this work has been devoted to study the physicochemical properties of prepared materials.

2. Experimental

2.1. Catalyst preparation

Parent zeolites: H^+–ZSM-5 (Si/Al = 15), H^+–beta (Si/Al = 12.5), NH_4^+–mordenite (Si/Al = 10), H^+–USY (Si/Al = 15) and NH_4^+–Y (Si/Al = 2.55), furnished by Zeolyst, Zeocat and Rhodia, were used as starting materials. Solid-state ion exchange was performed by mixing 2 g of zeolite in a mortar and pestle with Cr acetate precursor (Strem Chemicals) in the desired Cr loading (5 wt.%, 0.44 g of Cr acetate). The finely ground powders were heated for 12 h at 500 °C in helium (30 cm^3/min, heating rate 2 °C/min). Catalysts were labeled Cr–S, where S refers to the zeolite support (S = ZSM-5, beta, Mor, USY and Y).

CrO_3–ZSM-5 and Cr_2O_3–ZSM-5 (5 wt.% of Cr) solids were prepared by mixing in a mortar 0.5 g of H^+–ZSM-5 (Si/Al = 15) and, either 0.048 g of CrO_3 (Merck 99%) or 0.036 g of Cr_2O_3 (Aldrich 99.9%), followed by an helium treatment at 500 °C for 1 h (30 cm^3/min, heating rate 2 °C/min). CrO_3–ZSM-5 and Cr_2O_3–ZSM-5 solids serve as references in catalysis.

2.2. Catalyst characterization

Elemental analysis (Cr, Si, Al) content of different solids was determined by ICP.

DTA/TGA–MS experiments were performed using a SDT Q600 apparatus with ~30 mg of precursor/zeolite mixture (5 wt.% of Cr) and a precursor mass which also corresponds to 5 wt.% of Cr. The thermal treatment was performed under helium (30 cm^3/min) between 30 and 700 °C at a heating rate of 5 °C/min. The chemical composition of gaseous products was determined using a mass spectrometer piloted with Quadstar 32 Bits software.

N_2 adsorption–desorption isotherms were determined at 77 K with an automatic ASAP 2000 apparatus from Micromeritics after a pretreatment under vacuum at 200 °C for 5 h. Specific surface area was determined by BET method, microporous volume by *t*-plot method and porous volume is the volume adsorbed at $P/P^{\circ} = 0.98$.

XRD measurements were performed on an X'Pert Pro X-ray diffractometer from PANalytical with CuKα radiation ($\lambda = 1.54060$ Å), generator setting of 40 kV and 40 mA, a scanning speed of 0.05°/min, and a scanning region of 2–70°. The diffractometer was operated at 1.0° diverging and 0.1° receiving slits and a continuous intensity trace was recorded as function of 2θ. The identification of structural data was performed using EVA software.

TEM study was performed with a JEOL JEM-2000 FX microscope at 200 kV. The samples were prepared by grinding and ultrasonic dispersal into an acetone solution, placed on the copper TEM grid, and evaporated.

^{27}Al MAS NMR spectra were recorded at 78.20609 MHz on a Bruker WB spectrometer using $AlClO_3 \cdot 6H_2O$ as reference. An overall 4096 free induction decays were accumulated. The excitation pulse and recycle time were 6 μs and 0.06 s, respectively.

NH_3-TPD analysis was performed with a Micromeritics Autochem 2910 analyzer. As the automatic NH_3-TPD program included a pretreatment in air, the sample (40 mg) was first exposed to an air flow (10 cm^3/min) at 500 °C for 1 h, then saturated with flowing ammonia at 100 °C and flushed with helium at the same temperature. Finally, the temperature was ramped to 700 °C at a rate of 10 °C/min. Quantitative analysis was performed by the means of a thermal conductivity detector.

UV–vis DRS spectra were recorded at room temperature in the wavelength range 900–200 nm on a Perkin Elmer Lambda 45 spectrophotometer equipped with a diffuse reflectance attachment. Parent zeolites were the reference materials.