



Cr–ZSM-5 catalysts for ethylene ammoxidation: Effects of precursor nature and Cr/Al molar ratio on the physicochemical and catalytic properties

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ABSTRACT

Cr–ZSM-5 catalysts prepared by solid-state ion exchange with different Cr/Al molar ratios were characterized and tested in ethylene ammoxidation to acetonitrile in the temperature range 425–500 °C. Starting from Cr acetate like precursor and lower Cr load (Cr/Al = 0.5), small amount of chromate species, sited inside the zeolite matrix, exhibited lower catalytic activity in ammoxidation (12.5% of CH₃CN yield). Increasing the Cr amount (Cr/Al = 1) does not significantly improve the catalytic properties since agglomerates of amorphous Cr₂O₃ inhibited the accessibility of chromate species to the reactants. However, at higher Cr amount (Cr/Al = 1.5), crystalline Cr₂O₃ particles reduced the diffusion of reactants to the internal active sites. Starting from Cr chloride like precursor, the corresponding solids are low-exchanged since CrCl₃ evaporates. At Cr/Al molar ratios of 0.5 and 1, chromate species, sited in the exchange sites, exhibited interesting catalytic properties (18.5 and 25% of CH₃CN yield at 500 °C, respectively). Nevertheless, at higher metal load (Cr/Al = 1.5), the excess of Cr transforms into crystalline Cr₂O₃ which inhibits the diffusion of reactants to the active sites and enhances the hydrocarbon oxidation mainly at low temperatures. As ethylene ammoxidation required ammonia activation over (poly)chromate sites, a possible pathway of such a step has been proposed on the basis of NH₃-TPD results.

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1. Introduction

Acetonitrile is used as a basic feedstock in a wide range of industrial applications. It is typically obtained as a by-product (2–3%) during propylene ammoxidation to acrylonitrile [1]. Acetonitrile can also be produced by other methods, unfortunately, most of conventional processes, e.g., dehydration of acetamide, acetylene ammoxidation, are less-selective, expensive and hazardous [2]. As there is no appropriate commercial scale synthesis available for acetonitrile, and as a result of the global economic slowdown, there is a worldwide shortage of this chemical. Ethylene is a convenient feedstock to produce acetonitrile via ammoxidation. The quest of such a process and the associated scientific challenge has stimulated a large amount of research over the last decay on catalysts for direct synthesis of acetonitrile. For example, Co/ZSM-5 catalysts [3–5] have been evaluated in ethylene ammoxidation after varying several preparation parameters, e.g., nature of cobalt precursor, metal loading, temperature of solid-state ion exchange and the cobalt exchange level. On the other hand, the authors [3–5] used several efficient techniques in order to characterize their solids and correlate the speciation of cobalt with the

catalytic performances. Though Co/ZSM-5 system is known as suitable for ethylene ammoxidation, and as such is not definitely commercialized, it would be interesting, at least from the scientific viewpoint, to investigate further catalysts.

Lately, we reported the catalytic properties of sol–gel derived M/Al₂O₃ solids (M = Cr or Co) in ethylene ammoxidation [6]. The obtained results showed that the catalytic performances strongly depended on textural and structural properties of alumina support. In fact, aerogel and xerogel substrates led to efficient Cr/Al₂O₃ catalysts while Co phase dispersed over xerogel substrate is poorly active. More recently, we reported the catalytic performances of Cr-zeolite catalysts prepared by solid-state exchange of Cr acetate salt with zeolites of MFI, BEA, MOR and FAU structures [7]. Such a study showed that the zeolite topology played a key role in ammoxidation. On the other hand, the zeolite of MFI structure is suitable for higher catalytic activity. The characterization results showed that Cr with the higher oxidation state is required for ammoxidation while agglomerates of Cr oxide should be avoided during the catalyst preparation.

Generally, Cr–ZSM-5 catalysts issued from solid-state ion exchange are over-exchanged and exhibit on their surface a large fraction of Cr oxide. On the other hand, the characterization of Cr–ZSM-5 catalysts after varying the nature of metal precursor [8] showed that higher amounts of undesired Cr oxide were associated to the catalyst

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issued from Cr nitrate salt. In fact, nitrate ions decompose in the solid-state reaction into the strong oxidizing agent NO_2 which pronounced the agglomeration of Cr_2O_3 . In order to avoid such a problem, we investigated the effect of Cr exchange level on the catalytic properties of Cr-ZSM-5 catalysts in ammoxidation [9]. The results showed that catalysts issued from aqueous exchange are low-exchanged, while solid-state ion exchange afforded over-exchanged solids. At higher reaction temperatures, the low-exchanged catalysts exhibited the highest catalytic activity [9]. However, in the temperature range 425–450 °C, the solid-state exchange offered promising ammoxidation catalysts by choosing the appropriate Cr precursor [8,9]. The use of Cr sulfate like precursor caused several problems during the characterization and in catalysis, mainly because of residual sulfate groups which persist on the freshly prepared catalyst even after 12 h of thermal treatment at 500 °C in helium. On the other hand, the catalyst issued from ammonium dichromate like precursor exhibited bad exothermic reactions during the catalytic tests. Accordingly, if we discard Cr nitrate, Cr sulfate and ammonium dichromate precursors, Cr chloride and Cr acetate seem promising for further investigation.

The stoichiometry of exchange, i.e., the Cr/Al molar ratio, is a crucial parameter to be optimized in the solid-state reaction for improving the catalytic performances of Cr-ZSM-5 catalysts in the ethylene ammoxidation.

The aim of this work is studying the effect of Cr/Al molar ratio on the catalytic properties of Cr-ZSM-5 catalysts prepared by solid-state ion exchange using Cr acetate and Cr chloride like precursors. Different characterization techniques have been adopted in order to study the physicochemical properties of the prepared solids. The chemical composition of different solids has been determined by inductively coupled plasma (ICP). The solid-state exchange of Cr salts with zeolite has been studied by thermal analysis coupled with mass spectrometry (TA/MS). Textural, morphological and structural studies have been performed by N_2 physisorption at -196 °C, transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively. Information about the metal oxidation states was obtained by UV-vis diffuse reflectance spectroscopy (DRS), Raman and X-ray photoelectron spectroscopy (XPS). The redox features and the interaction of ammonia molecule with the different solids were investigated by temperature-programmed methods. Temperature-programmed reduction was carried out under hydrogen flow (H_2 -TPR), while acidity measurements were performed by temperature-programmed desorption of ammonia (NH_3 -TPD).

2. Experimental

2.1. Catalysts preparation

Parent zeolite H^+ -ZSM-5 (Si/Al = 15), furnished by Zeolyst, was used as starting material. Solid-state ion exchange was performed by mixing the zeolite in a mortar and pestle with Cr acetate (Strem Chemicals) or Cr chloride (Prolabo) precursors in the desired Cr/Al molar ratios (Cr/Al = 0.5, 1 and 1.5). The finely ground powders were heated for 12 h at 500 °C in helium (30 cm^3/min , heating rate 2 K/min). Catalysts issued from Cr acetate and Cr chloride were labeled as Cr(Ac)- x and Cr(Ch)- x , respectively, where “ x ” stands to Cr/Al molar ratio. CrO_3 -ZSM-5 and Cr_2O_3 -ZSM-5 solids (Cr/Al = 1) were prepared by mixing in a mortar H^+ -ZSM-5 (Si/Al = 15) and, either CrO_3 (Merck 99%) or Cr_2O_3 (Aldrich 99.9%), followed by a helium treatment at 500 °C for 1 h (30 cm^3/min , heating rate 2 K/min). CrO_3 -ZSM-5 and Cr_2O_3 -ZSM-5 solids serve as references in catalysis.

2.2. Catalysts characterization

The elemental analysis of Cr, Si and Al was determined by ICP at the Vernaison Center of the CNRS (France). TA/MS analysis was

performed using a SDT Q600 apparatus with ~ 30 mg of precursor/zeolite mixture (Cr/Al = 1). A thermal treatment in helium (30 cm^3/min) between 30 and 700 °C (30–900 °C in the case of CrCl_3) was applied at a heating rate of 5 K/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 with an automatic ASAP 2000 apparatus from Micromeritics. Specific surface area was determined by BET method, microporous volume by t -plot method and porous volume is the volume adsorbed at $P/P^\circ = 0.98$. Information about the metal particles in the catalysts was obtained by TEM. The measurements were performed in a JEOL JEM-2000 FX Electron Microscope (200 kV) provided with an X-ray energy dispersive spectroscopy system (XEDS). The catalyst samples were suspended and dispersed by ultrasonic treatment in acetone. A drop of the fine suspension was placed on a copper TEM grid, which was then loaded into the microscope. XRD measurements were performed on an X'Pert Pro X-ray diffractometer from PANalytical with $\text{CuK}\alpha$ radiation ($\lambda = 1.54060$ Å), generator setting of 40 kV and 40 mA, a scanning speed of $0.05^\circ/\text{min}$, 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 . Structural data identification was performed using EVA software. UV-vis DRS analysis was performed on a Perkin Elmer Lambda 45 spectrophotometer equipped with a diffuse reflectance attachment. Spectra were recorded at room temperature in the wavelength range 900–200 nm using the parent zeolite as reference material. Raman measurements were carried out on a confocal Thermo Scientific DXR Raman Microscopy system using the visible line at 532 nm and an incident power of 10 mW. XPS spectra were recorded on a SSX 100/206 photoelectron spectrometer equipped with a monochromatized micro focused Al X-ray source (1486.6 eV, powered at 20 mA and 10 kV). H_2 -TPR profiles were obtained on a Micromeritics Autochem 2910 analyzer, in a Pyrex U-tube reactor and an on-line thermal conductivity detector (TCD). The catalyst (70 mg) was dried in air at 500 °C for 1 h and reduced from 50 to 1000 °C (heating rate: 15 K/min) with H_2 (3%)/Ar flow. NH_3 -TPD analysis was performed with the same H_2 -TPR 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 K/min. The outlet H_2O was trapped at low temperature (-40 °C) in a mixture of liquid N_2 /propan-2-ol before reaching the TCD. Ammoxidation of ethylene was studied with 100 mg of catalyst in the temperature range 425–500 °C using a down flow tubular glass reactor. In all cases, the inlet reactants composition was 10% O_2 (Air Liquide 99.995%), 10% C_2H_4 (Air Liquide 99.995%) and 10% NH_3 (Air Liquide 99.96%). The total flow rate was maintained at 100 cm^3/min by balancing with helium (Air Liquide 99.998%). The analysis of the outlet flow was recorded on-line by two chromatographic units (Intersmat, Delsi), one operated with a Porapak Q column (100–120 mesh) and a flame ionization detector while the other was equipped with a Molecular Sieve 13X column and a TCD.

The conversion, selectivity and yield are defined as follows:

Conversion of C_2H_4 ,

$$X = \frac{\sum_i y_i n_i}{y_E n_E + \sum_i y_i n_i}$$

Selectivity of product P_i (carbon basis),

$$S_i = \frac{y_i n_i}{\sum_i y_i n_i}$$

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