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Ammoxidation of ethylene over low and over-exchanged Cr–ZSM-5 catalysts

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ABSTRACT

Catalytic performances of Cr–ZSM-5 catalysts (5 wt.% of Cr, Si/Al = 26), prepared by solid-state reaction and aqueous exchange, from Cr nitrate and Cr acetate precursors, were evaluated in the selective ammoxidation of ethylene into acetonitrile in the temperature range 425–500 °C. Catalysts were characterized by chemical and thermal analysis, XRD, N_2 physisorption, ^{27}Al MAS NMR, TEM, UV–vis DRS, Raman, DRIFTS and H_2-TPR. Characterization results shown that solid-state exchange was favorable for Cr_2O_3 formation, while exchanging chromium in aqueous phase led, essentially, to Cr(VI) species. Catalysts were actives and selectives in the studied reaction, and among them, those, prepared from aqueous exchange, exhibited the highest acetonitrile yields (23 ± 0.5%, at 500 °C). Improved catalytic properties can be correlated with the chromium species nature. In fact, mono/di-chromates and/or polychromate species, sited in the charge compensation positions, were definitively shown, as being, the active sites. Furthermore, during solid-state reaction, the agglomeration of Cr_2O_3 oxide should be avoided since these species inhibit the catalyst activity.

1. Introduction

In the past few decades, a large number of catalytic systems have been developed in our laboratory for light hydrocarbons ammoxidation into acetonitrile. In fact, numerous works have dealt with the shape-selective ammoxidation of ethylene using either microporous materials (zeolites) or transition metal oxides as catalyst supports.

For example, the catalytic performance of Co/ZSM-5 catalysts [1–4] has been evaluated in the ammoxidation of ethylene into acetonitrile. Sol–gel derived Co/Al_2O_3 and Cr/Al_2O_3 catalysts have also been used [5].

More recently, we have reported the performance of Cr–ZSM-5 catalysts, issued from solid-state exchange, in the ammoxidation of ethylene after varying the source of chromium [6]. The selectivity and the yield of acetonitrile largely depended on the nature of the applied catalysts. For example, 26% of C_2H_4 conversion and 95% of selectivity toward acetonitrile have been reached at 500 °C after choosing an appropriate chromium precursor.

The catalytic activity of Cr–ZSM-5 catalysts in the ammoxidation of ethylene lies in the variability of oxidation states of chromium, the degree of polymerization (mono/di-chromates or polychromates, etc.), the aggregation state of oxide species and their crystallographic structure (amorphous or crystalline). Thus, it has been accepted that the improved catalytic activity of Cr–ZSM-5 catalysts is due to the presence of (poly)-chromate species and Cr ions in charge compensation positions, while agglomerated Cr_2O_3 oxide should be avoided [6].

Cr_2O_3 oxide species provided essentially from the fact that, during solid-state exchange, a non-negligible fraction of Cr ions does not diffuse inside the zeolite channels but remains on the outer surface of the grain. In this way, an optimization of catalysts preparation method would thus consist in tuning the operating conditions and the nature of chromium salt to ensure the effective diffusion of Cr ions inside the zeolite.

In the case of zeolite based catalysts, fundamental studies [7–9] have provided a strong dependence of the exchange level, i.e. the preparation method, and the metal speciation in a wide range of catalytic reactions.

The aim of this work is the comparison between the catalytic behaviors of under- and over-exchanged Cr–ZSM-5 catalysts in the ammoxidation of ethylene into acetonitrile. It should be underlined that a large part of the work has been devoted to the physicochemical properties of the prepared materials.

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2. Experimental

2.1. Catalysts preparation

Solid-state exchange was performed as follows: 1.5 g of NH_4^+–ZSM-5 (Zeolyst, Si/Al = 26) was mixed in a mortar and pestle with Cr acetate (Strem Chemicals) or Cr nitrate (99%, Acros Organics) in the desired molar ratio Cr/Al = 1, which corresponds to 0.2 g of Cr acetate and 0.36 g of Cr nitrate. The finely ground powders obtained by mechanical mixture was heated for 12 h at 500 °C in helium (30 cm^3/min, heating rate 2 °C/min).

Aqueous exchange was performed as follows: 1 g of NH_4^+–ZSM-5 (Si/Al = 26) was exchanged with 100 ml of 0.01 M Cr acetate solution (pH = 4.6) or Cr nitrate (pH = 3.5) for 24 h at 70–80 °C. After three identical exchanges, the resulting zeolite slurry was filtered, washed with 500 ml of de-ionized water and then filtered again. Finally, the zeolite was dried at 110 °C overnight and then treated in helium at 500 °C for 3 h (30 cm^3/min, heating rate 2 °C/min)

Catalysts were labelled Cr–P-PM, where P refers to the Cr precursor nature (A: Cr acetate and N: Cr nitrate), while PM refers to the preparation method: AE (aqueous ion exchange) and SE (solid-state exchange).

2.2. Catalysts characterization

The elemental analysis (Cr, Si, Al) content of different solids was determined by ICP at the Vernaison Center of the CNRS (France).

DTA/TGA–MS analyses were performed using a SDT Q600 apparatus with ∼30 mg of zeolite/precursor 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 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 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.

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

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

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 zeolite was the 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.

DRIFTS spectra were recorded on a Bruker IFS 55 spectrophotometer equipped with a Thermo Spectra Tech reacting cell at a spectral resolution of 4 cm^{-1} and accumulating 200 scans. Samples were treated in situ at 500 °C with helium (5 °C/min, flow: 30 cm^3/min).

H_2-TPR analysis was performed with a Micromeritics Autochem 2910 analyzer, in a Pyrex U-tube reactor and an on-line thermal conductivity detector. The catalyst (70 mg) was dried at 500 °C for 1 h and reduced from 50 to 1000 °C (15 °C/min) with H_2 (3%)/Ar flow.

Ammoxidation of ethylene was studied with 100 mg of catalyst between 425 and 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, one operated with a flame ionization detector, while the other was equipped with a thermal conductivity detector.

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),

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

Yield of product P_i (carbon basis), $Y_i = XS_i$where y_i and y_E are the mole fractions of product P_i and C_2H_4, respectively; n_i and n_E are the number of carbon atoms in each molecule of product P_i and C_2H_4, respectively.

3. Results

3.1. Chemical analysis

Table 1 gives the elemental analysis of the parent zeolite and Cr–P-PM catalysts. The Si/Al molar ratio values, determined by ICP, corresponded to the data provided by the zeolite manufacturer.

Cr–P-SE solids exhibit high Cr/Al molar ratios, which indicate that the metal was retained after solid-state exchange. On the other hand, Cr–P-AE solids exhibit the lowest Cr contents (thus the lowest Cr/Al molar ratios) because of diffusional limitation which occurs during the exchange in aqueous phase.

Besides elemental analysis, the resulting ion exchange degrees are presented in Table 1. Considering that Cr^{3+} ions are only the possible exchange species, the exchange degree is defined by 300 × Cr/Al (mol/mol). The data shows that the catalysts issued from solid-state exchange contain much more chromium than required for 100% total ion-exchange. These samples are regarded as 'over-exchanged' materials contrary to Cr–P-AE catalysts, which exhibit very low exchange degrees. Kouwenhoven [10] reported that in ZSM-5 zeolite type, the positions of tetrahedrally coordinated Al^{3+} ions are spatially much separated and therefore,

Table 1
Chemical analysis results.

Sample	Cr (wt.%)	Al (wt.%)	Si/Al (mol/mol)	Cr/Al (mol/mol)	Ion exchange degree (%)
NH_4^+–ZSM-5	–	1.40	27.38	–	–
Cr–A-SE	3.06	1.30	27.02	1.22	366
Cr–N-SE	2.16	1.33	27.53	0.84	252
Cr–A-AE	0.65	1.62	23.23	0.21	63
Cr–N-AE	0.09	1.41	26.23	0.03	10