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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, N₂ physisorption, ²⁷Al MAS NMR, TEM, UV–vis DRS, Raman, DRIFTS and H₂–TPR. Characterization results shown that solid-state exchange was favorable for Cr₂O₃ 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 ($23 \pm 0.5\%$, 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 Cr₂O₃ oxide should be avoided since these species inhibit the catalyst activity.

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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/Al₂O₃ and Cr/Al₂O₃ 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.

* Corresponding author. Tel.: +21650646504; fax: +216 71885008. *E-mail address:* lcmc_fa@yahoo.fr (F. Ayari). 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.

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 cm³/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 cm³/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 \sim 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 cm³/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° = 0.98.

XRD measurements were performed on an X'Pert Pro X-ray diffractometer from PANalytical with CuK α 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 2 θ . 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 AlClO₃·6H₂O as reference. An overall 4096 free induction decays were accumulated. The excitation pulse and recycle time were 6 μ s 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: $30 \text{ cm}^3/\text{min}$). $\rm H_2$ -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 H₂ (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% O₂ (Air Liquide 99.995%), 10% C₂H₄ (Air Liquide 99.995%) and 10% NH₃ (Air Liquide 99.96%). The total flow rate was maintained at 100 cm³/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 ,

$$X = \frac{\sum_{i} y_{i} n_{i}}{y_{\rm E} n_{\rm E} + \sum_{i} y_{i} n_{i}}$$

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 $300 \times Cr/Al$ (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 Al³⁺ 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 (%)
NH4 ⁺ -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



Fig. 1. DTA/TGA curves of (a) Cr₃(OH)₂(CH₃COO)₇ and (b) Cr(NO₃)₃·9H₂O.

bare Cr^{6+} and/or Cr^{3+} cations cannot exist since it would be necessary to have 3 or 6 aluminum neighbors. Similarly to Fe/ZSM-5 system [11], it is possible to have the presence of chromium (hydr)oxo-cation species like [OH–Cr–O–Cr–OH]²⁺ species, for example.

3.2. Thermal analysis

Fig. 1(a and b) illustrates DTA/TGA curves of chromium acetate and chromium nitrate, respectively. TG curve of Cr acetate shows different steps of weight losses: the first one, situated at relatively low temperatures (30–250 °C), corresponds to the elimination of adsorbed water, while the second one starts at ~300 °C and corresponds to the salt decomposition. TG curve of Cr nitrate displays three weight losses at relatively low temperatures (<200 °C) and another one at ~450 °C.

Fig. 2(a and b) illustrates DTA/TGA curves of chromium salts/zeolite mixtures. Fig. 2a and b indicates that the solid-state reaction is achieved before 500 °C. On the other hand, there is a similarity between DTA/TGA curves of precursors and those of mixtures, evidencing that the exchange process might involve the intermediate compounds of Cr precursors decomposition.

After dehydration, (weight loss of 8.62%, endothermic peak at 68 °C), Cr acetate begins to decompose (Fig. 1a), leading to the loss of various molecules such as acetic acid and water (weight loss of 53.61%, DTA peaks at 347, 383, 407 and 444 °C). This phenomenon is accompanied by the evolution of MS fragments such as: m/z = 14, 15 and 16 (CH₄⁺), 17 and 18 (H₂O⁺), 28 (CO⁺), 30 (CH₂O⁺), 43 (CH₃CO⁺), 44 (CO₂⁺), 45 (COOH⁺) and 60 (CH₃COOH⁺) and a change

of the residue color, from dark green to green, which reflect the decomposition of Cr acetate into Cr_2O_3 .

TG curve of Cr acetate/zeolite mixture (Fig. 2a) displays three weight losses of 2.79, 0.44 and 6.92%. The first one $(30-182 \degree C)$, endothermic peak at 65 °C) corresponds to the dehydration of both zeolite and precursor as confirmed by MS signal profile characterizing the evolution of water. The second weight loss, situated between 182 and 237 °C, corresponds to the loss of ammonia molecules, while the last one evidencing the solid-state reaction between Cr acetate and zeolite between 250 and 500 °C. The evolution of MS fragment profiles of CH₄⁺, CO₂⁺ and CH₃COOH⁺ (results not shown) reflect the solid-state exchange, which can be simplified as follows:

$$2(\mathrm{NH}_{4}^{+}, {}^{-}\mathrm{O} - \mathrm{Zeo} + \mathrm{Cr}(\mathrm{CH}_{3}\mathrm{COO})_{3} \cdot x\mathrm{H}_{2}\mathrm{O}$$

$$\xrightarrow{30-250^{\circ}\mathrm{C}}2\mathrm{CH}_{3}\mathrm{COOH} + 2\mathrm{NH}_{3} + x\mathrm{H}_{2}\mathrm{O} + (\mathrm{Cr}\mathrm{CH}_{3}\mathrm{COO})^{2+}(-\mathrm{O}-\mathrm{Zeo})_{2}$$

$$(CrCH_3COO)^{2+}(-O-Zeo)_2 + H_2O$$

 $\xrightarrow{250-500^{\circ}C}Cr(OH)^{2+} + (-O-Zeo)_2 + CH_4 + CO_2$

The thermal decomposition of Cr nitrate (Fig. 1b) occurs according to two principal steps: the first one (below $250 \,^{\circ}$ C) corresponds to the elimination of water molecules and the degradation of NO₃⁻ groups (weight loss of ~74%), while the second step, above $350 \,^{\circ}$ C, corresponds to the oxygen removal from Cr—O system (weight loss of 5.15%) [12,13].

TG curve of Cr nitrate/zeolite mixture (Fig. 2b) displays two weight losses of 14.75% (30–212 $^\circ C)$ and 0.49% (400–480 $^\circ C)$. On



Fig. 2. DTA/TGA curves of (a) Cr acetate and (b) Cr nitrate-zeolite mixtures.



Fig. 3. TEM images of (a) Cr-N-SE and (b) Cr-A-SE catalysts.

the other hand, MS study reveals the presence of the following fragments: NH_3^+ (m/z=15), O^+ (m/z=16), HO^+ (m/z=17), H_2O^+ (m/z=18), N_2^+ (m/z=28), NO^+ (m/z=30), O_2^+ (m/z=32), N_2O^+ (m/z=44), NO_2^+ (m/z=46) and HNO_3^+ (m/z=63). From both thermal analysis and mass spectrometry results, Cr nitrate decomposes according to the mechanism previously described [12,13]. Moreover, such mechanism is also suitable for Cr nitrate/zeolite mixture. Firstly, the precursor melts into Cr_2O_3 ($3O-212 \circ C$) then, at relatively high temperatures ($400-480 \circ C$), the desorption of oxygen atoms leads to Cr(III) ions, which may reach the exchange sites after diffusion.

3.3. Textural properties

Cr–P-AE catalysts as well as the zeolite support exhibit a type I isotherm evidencing a microporous texture, while Cr–P-SE catalysts exhibit a type IV isotherm, indicative of the mesoporous character of such solids. Textural properties are summarized in Table 2.

After aqueous exchange, the zeolite support exhibits a slightly decrease of its specific surface area and (micro)porous volumes. This effect can be induced by the presence of oxide aggregates and/or extra-framework aluminum species dispersed in the channels or deposited on the outer surface of the zeolite. On the other hand, Cr–P-SE catalysts exhibit S_{BET} and porous volume values which exceed the zeolite support ones. Gervasini [14] reported a similar behavior with cobalt and nickel loaded ZSM-5 zeolite and considered that such solids exhibit some degree of mesoporosity. In our study, according to DTA/TGA/MS results, Cr ions were merely deposited on the external surface of the ZSM-5 zeolite as Cr_2O_3 oxide aggregates, and such metallic phase might contribute to the textural data calculus.

Table 2				
Textural	properties	of the	investigated	solids.

_					
	Sample	$S_{\rm BET}~(m^2/g)$	Microporous surface (m ² /g)	Microporous volume (cm³/g)	Porous volume (cm ³ /g)
	NH4 ⁺ –ZSM-5 Cr–A-SE Cr–N-SE Cr–A-AE Cr–N-AE	312 336 353 248 291	239 197 212 161 213	0.139 0.113 0.121 0.092 0.121	0.240 0.525 0.528 0.198 0.225

3.4. TEM study

TEM images of Cr-P-SE catalysts are presented in Fig. 3.

Randomly shaped oxide particles, which are heterogeneously dispersed, are observed in the TEM images of Cr–N-SE catalyst. Furthermore, there are some surface regions which contain oxide particles having a significant size (see image #FX2945).

On the other hand, TEM images of Cr–A-SE reveal some surface regions which are poor in chromium (see image #FX2931). At the opposite, in the TEM images #FX2932 and FX2933, some surface regions contain metallic species without any apparent phases.

It seems that the thermal treatment during solid-state reaction favored the formation of Cr_2O_3 oxide particles, and the dispersion of these metallic species is governed by the nature of chromium precursor.

3.5. Structural properties

X-ray diffraction patterns of the investigated materials are shown in Fig. 4. Most catalysts exhibit diffraction peaks which are typical of crystalline ZSM-5 [15] (Fig. 4a). This result indicates that Cr species, stabilized after thermal treatment, are dispersed over the zeolite in the form of small oxide clusters (less than 4 nm)



Fig. 4. XRD patterns of (a) NH₄⁺–ZSM-5, (b) Cr–A-SE, (c) Cr–N-SE, (d) Cr–A-AE and (e) Cr–N-AE, (*) Cr₂O₃.



Fig. 5. ²⁷Al MAS NMR spectra of both Cr–P-SE catalysts and support.



Fig. 6. DRS spectra of Cr-P-SE catalysts, Fig. in-set: Cr-P-AE catalysts spectra.

that do not show X-ray diffraction. Nevertheless, XRD pattern of Cr–N-SE catalyst (Fig. 4c) reveals clear additional peaks at 2θ = 34, 36, 42, 51 and 56°, attributable to α -Cr₂O₃ [13]. Based on thermal analysis results, the decomposition of Cr nitrate led to Cr₂O₃ oxide which exhibited an agglomeration because of the potential oxidizing power of nitrate ions.

²⁷Al MAS NMR spectra of both Cr–P-SE catalysts and zeolite support are shown in Fig. 5. NMR spectrum of NH₄⁺–ZSM-5 zeolite shows a strong signal at $\delta \sim 60$ ppm which corresponds to

tetrahedral coordinated framework aluminum [16]. The weak signal situated at \sim 0 ppm corresponds to octahedral aluminum atoms extracted from the framework [16].

According to NMR spectrum of the zeolite support, the intensity of tetrahedral aluminum peak decreases after metal loading. It has been reported that exchanging paramagnetic species (like Cr^{n+} , with n < 6) with aluminosilicates [17], and Na⁺, Ca²⁺ cations with zeolites [18] modify the tetrahedral aluminum environment and decreases the corresponding peak intensity. On the other hand, the octahedral aluminum peak intensity does not exhibit any significant change after chromium loading. As XRD patterns have clearly showed up, there is no significant damage of the zeolite structure.

3.6. DRS and Raman studies

UV–vis DRS spectra of prepared catalysts are illustrated in Fig. 6. Besides the support band (<230 nm), Cr–A-SE catalyst spectrum exhibits DRS bands at 278, 324, 346, 404, 466 and 582 nm, while bands at 279, 307, 349, 465 and 603 nm were observed in the DRS spectrum of Cr–N-SE catalyst. In both spectra, the three first bands are typical for chromate $O^{2-} \rightarrow Cr^{6+}$ charge transfer, while bands situated at ~465 nm evidencing the presence of polychromate species [19,20]. Finally, DRS bands situated at 582 and 603 nm are assigned to the *d*–*d* transition of Cr³⁺ ions (probably situated in the exchange sites) or to Cr₂O₃ [19,21]. In the case of Cr–A-SE catalyst, we were unable to explain the presence of the DRS band situated at 404 nm.

DRS spectra of Cr–P-AE catalysts exhibit two bands at 271 and 378 nm, typical for chromate species, and a shoulder at 454 nm evidencing the presence of dichromate and/or polychromate species [19,21–23].

Raman spectra of Cr–N-PM catalysts are illustrated in Fig. 7. Zeolite support does not exhibit any Raman features in the region of $200-1100 \text{ cm}^{-1}$ and, therefore, all the observed bands are assigned to chromium species vibrations.

Cr–A-SE and Cr–A-AE catalysts do not exhibit any Raman features, because of fluorescence phenomenon.

In our previous study [6], we reported Raman spectra of mechanical mixtures of CrO_3 –ZSM-5 and Cr_2O_3 –ZSM-5 (5 wt.% of Cr). Raman spectrum of CrO_3 –ZSM-5 solid exhibited two bands at 374 and 1000 cm⁻¹, attributed to the symmetric vibrations of monochromate species and Cr—O vibrations of polychromates, respectively [21,24]. Nevertheless, Raman spectrum of Cr_2O_3 –ZSM-5 solid exhibited a band at 553 cm⁻¹, ascribed to Cr—O–Cr vibrations of Cr_2O_3 [21,24,25].

Raman spectrum of Cr–N-SE catalyst exhibits two bands at 372 and 555 cm^{-1} , attributable to Cr–O vibrations of monochromate and octahedral Cr(III) species, respectively [21,24,26].



Fig. 7. Raman spectra of Cr-N-PM catalysts.



Fig. 8. DRIFTS spectra of NH4⁺-ZSM-5 and chromium loaded catalysts.

Such results are in good agreement with DRS ones. Nevertheless, in the case of Cr–N-AE catalyst, two bands dominate the corresponding Raman spectrum at 377 and 811 cm⁻¹, evidencing the presence of monochromate species [22,24].

3.7. DRIFTS study

DRIFTS spectra of Cr–ZSM-5 catalysts and parent zeolite are reported in Fig. 8.

The spectrum of zeolite support exhibits two bands. The first one, situated at 3591 cm^{-1} , is assigned to the vibration of strong Brönsted acid sites [27,28], while the second band, situated at 3725 cm^{-1} , is attributed to terminal silanol groups Si–OH [29,30].

Exchanging chromium in aqueous phase (Cr-P-AE catalysts) involves a decrease of 3591 and 3725 cm⁻¹ band intensities,



Fig. 9. TPR profiles of reference oxides.

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Catalyst	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	H_2/Cr	H ₂ amount (mmol H ₂ /g)
Cr–A-SE	294	361	419	460	0.44	0.26
Cr-N-SE	281	350	-	460	0.29	0.12
Cr-A-AE	-	-	-	471	1.68	0.21
Cr-N-AE	-	-	-	436	1.73	0.03

evidencing that a part of Cr ions is exchanged with strong Brönsted acid sites, while the other part is grafted on silanol groups.

In the DRIFTS spectrum of Cr–A-SE catalyst, the band situated at 3725 cm⁻¹, attributable to terminal silanol groups, does not undergo any significant change, suggesting that Si–OH groups do not participate significantly in the solid-state reaction. Nevertheless, the 3591 cm⁻¹ band intensity decreases, evidencing that Cr ions are exchanged with Brönsted acid sites, in agreement with ²⁷Al MAS NMR results which indicate the modification of Al atoms environment.

Starting from different Cr precursors and H^+ –ZSM-5 zeolite (Si/Al = 15), similar results have also been reported [6].

3.8. H₂-TPR study

TPR profiles of reference oxides (CrO_3 and Cr_2O_3) and Cr-P-PM catalysts are shown in Figs. 9 and 10, respectively. TPR results are compiled in Table 3.

TPR profile of Cr_2O_3 oxide exhibits two reduction peaks at 288 and 348 °C. The first one is attributed to the reduction of Cr(VI) present in the surface of chromia [6,31], while the second one corresponds to the reduction of Cr(III) to Cr(II) [6,31]. TPR profile of



Fig. 10. TPR profiles of chromium loaded catalysts.



Fig. 11. Ethylene conversion (\blacksquare) and CH₃CN selectivity (\Box) as a function of reaction temperature. Conditions: 0.1 g catalyst, 10% NH₃, 10% C₂H₄, 10% O₂, total flow rate: 100 cm³/min.

 CrO_3 oxide exhibits three reduction peaks at 289, 474 and 587 °C, which corresponds to the reduction of Cr(VI) to Cr(III) [32–34].

TPR profile of Cr–A-SE catalyst exhibits reduction peaks at 294, 361, 419 and 460 °C. According to Ilieva et al., the peak situated at 294 °C corresponds to the reduction of Cr(VI) species anchored to the surface of chromia [6,31]. The reduction peak situated at 361 °C corresponds to the reduction of Cr(III) to Cr(II) [31], in agreement with the TPR study performed with Cr_2O_3 reference oxide (Fig. 9). TPR peak at 419 °C could be attributed to the reduction of Cr oxo-cations [6]. At relatively high temperature (460 °C), the reduction of chromate species strongly bounded to the support occurs [19,32–34].

TPR profile of Cr–N-SE catalyst exhibited three reduction peaks at 281, 350 and 460 $^{\circ}$ C, attributable to the reduction of Cr(VI) species anchored to the chromia surface [6,31], Cr(III) ions [31] and chromate species strongly bounded to the zeolite [19,32–34], respectively.

TPR quantitative study performed with Cr–P-SE catalysts (Table 3) indicates that H_2/Cr molar ratio values are lower than theoretical value required for a total reduction of Cr(VI) to Cr(III) according to: $2CrO_3 + 3H_2 \rightarrow Cr_2O_3 + 3H_2O$. Probably, a part of Cr species seems to be in exchange sites and reduced with H_2 according to:

$$[HO-Cr-O-Cr-OH]^{2+} + H_2 \rightarrow 2[Cr(OH)]^+ + H_2O$$

In this context, Weckhuysen et al. reported [19] that Cr species were hardly reduced because of the residual acidity of Cr–MOR and Cr–Y catalysts. According to DRIFTS study, the amount of bridging hydroxyls might be higher on Cr–A-SE catalyst since a small amount of OH groups have been replaced by Cr ions. Consequently, the difficult reduction of Cr(VI) species is indicated by the presence of residual hydroxyls.

TPR profiles of Cr–P-AE catalysts exhibit unique zone of H₂ consumption between 250 and 600 °C, with a maximum at 471 and 436 °C, respectively for Cr–A-AE and Cr–N-AE catalyst. In addition, H₂/Cr molar ratio values are close to the theoretical value required for a total reduction of Cr(VI) to Cr(III). According to DRIFTS spectra of Cr–P-AE catalysts, bridging hydroxyls groups have been replaced by Cr ions after aqueous exchange. Such catalysts, which are less acidic, contain only one type of cationic Cr(VI) species located at the exchange sites of the zeolite. Weckhuysen et al. [19] reported that dichromates or larger Cr(VI) clusters are more easily reduced if they are located at the external surface of the zeolite.

3.9. Catalytic activity

Catalytic performances of prepared catalysts, in ethylene ammoxidation ($C_2H_4 + O_2 + NH_3 \rightarrow CH_3CN + 2H_2O$), as a function of reaction temperature, are compiled in Table 4 and Figs. 11 and 12. Data were collected under stationary conditions after a stabilization period of 1 h.

The zeolite support does not exhibit any activity in ethylene ammoxidation. Furthermore, Cr–P-PM catalysts are relatively



Fig. 12. CH₃CN yields as a function of reaction temperature. Conditions: 0.1 g catalyst, 10% NH₃, 10% C₂H₄, 10% O₂, total flow rate: 100 cm³/min.

Catalyst	TatalystEthylene conversion (X) (%)			CH_3CN selectivity (S) (%)			CH ₃ CN Yield (%)					
Temp. (°C)	425	450	475	500	425	450	475	500	425	450	475	500
Cr–A-SE	7	10	13.7	16.1	77	84	90	92.5	5.4	8.4	12.3	14.8
Cr-N-SE	5.5	9.7	16.7	19.5	22	45.5	83	92.5	1.2	4.4	13.8	18
Cr–A-AE	4.2	10.2	18	25.7	27	66	86	92	1.1	6.7	15.5	23.6
Cr–N-AE	0.1	5	11.2	23.7	5	35	74	95	0	1.7	8.3	22.5

Table 4Ethylene ammoxidation results.

Conditions: 0.1 g catalyst, 10% NH₃, 10% C₂H₄, 10% O₂, total flow rate: 100 cm³/min.

active and selective toward acetonitrile and do not exhibit any significant change in catalytic properties even at 500 °C, after 10 h on stream.

At 425 °C, Cr–A-AE is a poor active catalyst in ammoxidation, with both low C₂H₄ conversion (4.2%) and acetonitrile selectivity (27%), whereas Cr–A-SE catalyst exhibited, at the same temperature, slightly higher C₂H₄ conversion (7%) and acetonitrile as main reaction product (acetonitrile selectivity of 77%). On the other hand, catalysts issued from Cr nitrate exhibited, at 425 °C, very low catalytic activity. In fact, at 5.5% of ethylene conversion, Cr–N-SE catalyst yielded only 1.2% of acetonitrile, while Cr–N-AE catalyst is inactive.

At 450 °C, Cr–A-AE catalyst exhibited 66% of selectivity toward acetonitrile at 10.2% of ethylene conversion. Such catalytic properties are similar to those obtained in the presence of Cr–A-SE catalyst, but they slightly exceed those of Cr–N-PM ones.

At 500 °C, it is clear that Cr–P-AE catalysts yielded higher C_2H_4 conversion and acetonitrile yields when compared to Cr–P-SE solids.

4. Discussion

Solid-state exchange of Cr(III) ions into ZSM-5 has been studied by the mean of thermal analysis coupled to MS. The mechanism of such exchange depended on the nature of chromium precursor. For example, because of the low thermal stability of Cr nitrate salt, solid-state exchange with NH₄⁺–ZSM-5 zeolite occurs at relatively low temperatures. After decomposition of Cr nitrate, Cr ions (present mostly in the form of Cr^{3+}) balancing the negatively charged ZSM-5 framework and occupy the exchange sites. The production of the strong oxidizing agent NO₂ caused these Cr^{3+} ions to be either oxidized to Cr(VI) species, or aggregated into (nano)crystals of Cr₂O₃ (detectable by XRD).

When a mixture of Cr acetate and zeolite is heated, Cr³⁺ ions might have migrated either to the external surface of the zeolite or continued to reside at the internal surface. During solid-state reaction herein, volatile compounds such as acetic acid and water were produced. The hydrate water of the mixture provides surface hydroxyl groups that act as binder making Cr(III) crystals aggregates. We believe that the external surface of the zeolite might contain Cr(III) oxide as characterization techniques revealed. Raising of the temperature and the prolongation of solid-state reaction time caused that a part of Cr(III) ions migrates inside the zeolite channels to be exchanged with Brönsted acid sites and stabilized in the form of (hydro)oxo-cations such as [HO–Cr–O–Cr–OH]²⁺, mono and polychromate species.

The catalysts prepared in aqueous phase, using zeolite support and 0.01 M solutions of Cr precursors exhibited low metal retention because of diffusional restrictions. After ion exchange, hydrated Cr cation, such as $Cr(H_2O)_6^{3+}$ [19], could be present in the cavities and/or channels of the zeolite. The following way can be proposed [19]:

$$Cr(H_2O)_6^{3+} + n^-O-Zeo \rightarrow Cr^{3+} + (O-Zeo)_n(H_2O)_m + (6-m)H_2O$$

During this process, besides Brönsted acid sites, Cr ions were anchored with silanols groups according to DRIFTS results. Drying procedure results in a decrease of the ligand field strength of $Cr(H_2O)_6^{3+}$ complex which migrates to cationic sites on the surface of the zeolite after a thermal treatment at 500 °C. DRS and Raman studies indicate that monochromates, dichromate and/or polychromate species were founded at the zeolite surface.

The difference between catalytic properties of low and overexchanged catalysts is obvious. At relatively low temperature (425 °C), catalysts prepared in aqueous medium exhibited substantially low activity. Since Cr(III) species were not detected in the case of Cr–P-AE catalysts, it is more likely that these species are actives at low temperatures. This idea confirms the agreement that the improved catalytic properties of Cr–A-SE catalyst are mainly related to the dispersed Cr(III) species. Characterization by DRS and H₂-TPR is clearly in favor of the formation of such species. However, Cr–N-SE catalyst, having a higher concentration of Cr(III) sites, consequently yielded CO₂ as main product at low temperatures. Probably, residual nitrate ions poisoned these sites for further CO₂ formation. Similar results have been reported in our previous study [6].

At 450 °C, the catalysts issued from Cr nitrate exhibited low catalytic activity since the negative effect of nitrate ions was not entirely prevented.

As the reaction temperature increases, the prepared solids improve their catalytic properties. Among them, catalysts issued from aqueous exchange, which are very poor on chromium, exhibited substantially higher ethylene conversions, nitrile yields and selectivities. This behavior can be correlated with the nature of Cr species which are, essentially, mono/di and polychromate species.

In the case of Cr–P-SE catalysts, besides Cr^{3+} ions and mono/poly-chromates, Cr oxo-cations could be considered as active sites. In fact, the catalyst we reported earlier [6], e.g. issued from H⁺–ZSM-5 (Si/Al = 15) and CrCl₃, was very active in ethylene ammoxidation. We have attributed the improved catalytic properties of this catalyst, which is also poor on chromium, to the presence of Cr oxo-cations at the exchange sites.

Nevertheless, higher concentration of Cr(III) oxide species around the active sites thereby creating a diffusion block for ethylene molecules, and inhibits the catalytic activity of Cr–P-SE catalysts.

5. Conclusion

The exchanged chromium content and the nature of metallic species introduced in the ZSM-5 zeolite depended on the catalysts preparation method. In fact, upon aqueous exchange, low exchange levels were reached. Sitting of chromium ions in exchange sites led to the consumption of both Brönsted acid sites and silanol groups as DRIFTS spectra have showed up, and the thermal treatment led essentially to the formation of chromate species with different degrees of polymerization as DRS and Raman results revealed. Indeed, the reduction of different Cr ions with H₂ was demonstrated by H₂-TPR analysis.

After solid-state reaction, higher exchange levels were reached. DRS, Raman, TPR and DRIFTS results showed that Cr species are essentially oxo-cations, mono and/or polychromates, and Cr(III) ions either in the zeolite exchange sites or located on the outer surface as Cr₂O₃ oxide (XRD and TEM results).

The prepared materials exhibited generally good catalytic properties in the studied reaction. Among them, those prepared from aqueous exchange exhibited the highest activity. Improved catalytic properties were not related to the level of metal exchanged, as expected, but depended on chromium speciation. It seems that Cr(VI) species play a key role in the ammoxidation of ethylene, whereas, in the case of Cr–P-SE catalysts, higher concentration of Cr(III) oxide species, around the active sites, inhibits the catalytic activity.

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