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Nickel and molybdenum containing mesoporous catalysts for ethylene oligomerization and metathesis

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An original Ni-AlSiO₂ mesoporous catalyst (Si/Al = 6.5, 2.0 wt% Ni) was prepared using a commercial mesoporous non-ordered silica as a support. It exhibited notable catalytic behaviour for the oligomerization of ethylene in both batch and flow mode. Thus, at 150 °C and 3.5 MPa, the catalyst was highly active (up to 130 g of oligomers per gram of the catalyst per hour), selective (C4, C6, C8, and C10 olefins, no cracking products) and stable (high conversion for 9 h on-stream). However, the catalytic performances were slightly lower compared to those obtained with the catalyst prepared using a mesostructured SBA-15 silica as a model support. When nickel-catalyzed oligomerization was coupled with a metathesis reaction catalyzed by $MoO_x/(Al)SiO_2$ or $MoO_x/(Al)SBA-15$, ethylene was efficiently converted into propylene. To determine the physico-chemical properties of catalysts, various techniques were used, such as powder X-ray diffraction, N₂ sorption, ²⁷Al MAS NMR, Raman spectroscopy and X-ray photoelectron spectroscopy.

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Introduction

Ethylene is one of the most important basic organic chemicals. It is involved in a large number of industrial applications and among them, the oligomerization reaction is of considerable interest. Indeed, ethylene oligomers (*i.e.* olefins C_{2n} , n = 2-10) are valuable starting materials for a variety of chemicals, including lubricants, surfactants, alcohols, amines, and acids. Ethylene oligomerization is typically catalyzed by transition metals contained in both homogeneous and heterogeneous catalysts. Of particular note are Ni-based complexes1 and Ni-exchanged porous materials,² which exhibited very high activity and selectivity in this reaction. Various heterogeneous catalysts, including Ni-amorphous silica-alumina,3 Ni-(Al)-mesostructured materials,⁴⁻⁸ and Ni-zeolites,⁹⁻¹¹ were capable of oligomerizing ethylene, even under mild conditions. For these catalysts it was shown that the pore size is a crucial variable affecting their activity and stability.² For example, the Ni-exchanged zeolites suffered severe deactivation (due to the blocking of their micropores with heavy products),⁹⁻¹¹ while the catalysts with larger pores, *i.e.* Ni-Al-mesoporous materials, exhibited very high productivity in the ethylene conversion to oligomers.⁴⁻⁶ Typically, with Ni-based

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^b Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 71 D. Mangeron Ave., 700050, Iasi, Romania solid catalysts ethylene oligomerization leads selectively to C4-C10 olefins with an even number of carbon atoms. In order to enlarge the product range, we developed some catalytic cascade processes, in which nickel-catalyzed ethylene oligomerization was assisted by a second catalyzed reaction. For example, we proposed an original procedure in which ethylene oligomerization (over Ni-AlMCM-41) was combined with the acid-catalyzed co-oligomerization of the resulting C4-C10 olefins (over protonated AlMCM-41) to obtain hydrocarbons in the distillate range.¹² On the other hand, we reported in a recent paper that ethylene can be directly converted into propylene by one-pot catalytic cascade reactions, using two heterogeneous catalysts.¹³ In a single flow reactor ethylene was first selectively dimerized/isomerized over the Ni-AlSBA-15 catalyst to form 2-butenes, which reacted then with the excess of ethylene in a metathesis reaction catalyzed by MoO₃-SiO₂-Al₂O₃, to produce propylene. It is worth noticing that a higher growth rate is in demand for propylene compared to ethylene during the last few decades and the need to develop sustainable sources of raw materials highly stimulated the interest for the conversion of ethylene to propylene through simpler procedures, without any addition of other hydrocarbons. The state of the art of these processes has been discussed in our previous contribution.13

In some earlier studies, we showed that Ni-exchanged mesoporous materials, such as Ni-AlMCM-41, Ni-AlMCM-48 and Ni-AlSBA-15, with a carefully controlled texture, are "ideal" solid catalysts for ethylene oligomerization.^{4–6} The aim of the present work was to develop new oligomerization catalysts based on a



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non-ordered inexpensive commercial silica. Note that this is the first time that this support is used for preparing Ni-based oligomerization catalysts. The results were compared with our earlier investigation using the Ni-AlSBA-15 catalyst.⁶ Additionally, $MoO_x/(Al)SiO_2$ and $MoO_x/(Al)SBA-15$ materials were prepared and characterized. The Ni-based catalysts were coupled with MoO_x -containing metathesis catalysts in one-pot catalytic cascade reactions in order to convert ethylene into propylene.

Experimental

Materials and catalysts

The commercial silica gel (Davicat (R) SI 1454; Lot # SP550-10019ID35; a particulate size of 200 μ m) was used as received from Grace-Davidson. It is denoted in this study as SiO₂. SBA-15 silica was synthesized according to the conventional method, using the (EO)₂₀(PO)₇₀(EO)₂₀ triblock copolymer (Pluronic P123, Aldrich), tetraethyl orthosilicate (TEOS, Aldrich) and HCl 2 M (Aldrich), at a molar ratio of 1TEOS:0.016P123:4.9HCl:40.5 H₂O.^{14,15} The mixture was stirred for 24 h at 40 °C, and then it was maintained for 48 h at 100 °C in a Teflon-lined autoclave under static conditions. The solid product was filtered, washed with water, dried in an oven at 80 °C overnight and calcined in air flow at 550 °C for 8 h.

AlSiO₂ and AlSBA-15 samples were obtained by grafting SiO₂ and SBA-15 with sodium aluminate (54 \pm 1% Al₂O₃, Carlo Erba), according to the procedure described by Andrei et al.⁶ In a typical experiment, silica (4.0 g) was suspended at 25 °C for 15 h, under stirring in 400 mL of aqueous solution containing 1.1 g sodium aluminate, corresponding to a Si/Al ratio of 5. The samples which resulted in sodium form (Na-AlSiO₂ and Na-AlSBA-15) were subjected to successive ion exchange with NH₄NO₃ (99+%, Acros Organics) and Ni(NO₃)₂·6H₂O (98%, Alfa Aesar). Typically, 2 g of Na-AlSiO₂ were contacted three times, for 2 h at 25 °C, under constant agitation, with 100 cm³ of the 0.5 M aqueous solution of NH₄NO₃ to obtain the ammonium form, NH₄-AlSiO₂. The sample in ammonium form was subjected to successive nickel-ion exchanges with a 0.5 M aqueous solution of nickel nitrate, following the same procedure as above. The exchanged samples were calcined under air for 5 h at 550 $^\circ\mathrm{C}$ to achieve the oligomerization catalysts denoted in this study Ni-AlSiO₂ and Ni-AlSBA-15.

Supported MoO_x catalysts, denoted the MoO_x/support (support = SiO₂, AlSiO₂, SBA-15 and AlSBA-15), were prepared using the wet impregnation method, with an ammonium molybdate aqueous solution ((NH₄)₆Mo₇O₂₄·4H₂O, Aldrich-Sigma). Prior to impregnation the supports were dried under vacuum. After impregnation, the slurry was stirred at room temperature for 1 h and then the solvent was removed at 80 °C. The catalysts thus obtained, having a Mo loading of 10%, were calcined in air at 550 °C for 8 h.

Material characterization

The composition of materials (dissolved in solution) was determined by elemental analysis using the inductively coupled

plasma optical emission spectroscopy (ICP-OES) method, on a Perkin Elmer Optima 7000 DV apparatus. The XRD measurements were performed on a Bruker AXS D8 diffractometer, using CuKa radiation and a Ni filter. The textural characterization was achieved by using a conventional nitrogen adsorption/ desorption method, at -196 °C, on a Micrometrics ASAP 2020 automatic analyzer. The structural and textural parameters were calculated from nitrogen isotherms and XRD data, as previously described.6 27Al MAS NMR spectra were recorded for the calcined samples at room temperature using a Varian 600 MHz WB Premium Shielded spectrometer, using 3.2 mm o.d. ZrO₂ rotors with a rotation speed of 20 kHz. A pulse width of 1 µs was used, with a recycle delay of 1 s. The number of scan was 2600 and the chemical shifts were referenced to an aqueous solution of Al(NO3)3. The Raman spectra were measured using a confocal microspectrometer (Labram HR, Jobin-Yvon) in air at 25 °C. The sample volume was illuminated using an argon-krypton-ion laser beam $(\lambda = 647.1 \text{ nm})$ focused by an objective (*50LF, N.A. = 0.5, Olympus). The scattered light was collected using the same objective and dispersed with a 1 cm⁻¹ spectral resolution using a grating of 1800 lines mm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 (Thermo Electron) spectrometer equipped with an Al Ka source (1486.6 eV).

Catalytic experiments

The catalytic oligomerization of ethylene was performed in both semicontinuous (slurry batch reactor) and continuous modes (fixed bed reactor). In the first case, the oligomerization reaction was conducted in a 0.3 L well-mixed gas-slurry autoclave. Prior to each experiment, the catalyst (powder) was pretreated successively in a tubular furnace (550 °C, 8 h) and in an oligomerization reactor (200 °C, 3 h) under nitrogen flow at atmospheric pressure. The reaction was performed at 150 °C and 3.5 MPa, using 0.5 g of the catalyst and 0.1 L of dry oxygenfree *n*-heptane as a solvent, under constant stirring (1000 rpm). During the experiment ethylene (quality N25 from Air Liquide) was continuously fed so that the total pressure was maintained constant in the reactor. After reaction, the autoclave was cooled to -20 °C and the products were collected, weighted and analyzed by GC on a Varian 3900 chromatograph (FID, DB-1, 60 m \times 0.32 mm, 3 µm film thickness).

In the flow mode, ethylene oligomerization was performed in a stainless steel fixed bed reactor (i.d. 5 mm) using 0.5 g of the Ni-based catalyst (0.15–0.25 mm sieve fraction). The pressure was regulated *via* a back-pressure regulator. Before each test, the catalyst was activated in the reactor at 550 °C under nitrogen flow for 8 h. The reaction was conducted at 150 °C and 3.0 MPa of ethylene, without inert carrier gas. Oligomerizationmetathesis reactions were performed at 80 °C and 3.0 MPa, in a similar mode, but using two consecutive catalyst beds consisting of the Ni-based catalyst and the Mo-based catalyst, respectively. The complete reactor effluent was analyzed online by gas chromatography (Varian CP-3800, FID), using a CP-PoraPLOT Q capillary column (25 m, 0.53 mm, 20 µm) and an auto-sampling valve. Deactivation rates (in h⁻¹) were estimated from the parameter $((a_0 - a_t)/(a_0 \times t))$ (where a_0 is the initial conversion and a_t the conversion after *t* h on stream). For the quantification of the products captured, the spent catalyst (20 mg) was analyzed by thermogravimetry (TGA) using a NETZSCH TG 209C apparatus. The temperature program started with an isothermal period of 5 min at 50 °C followed by a temperature ramp up to 900 °C at 10 °C min⁻¹ in synthetic air (20 mL min⁻¹).

Results and discussion

Material characteristics

Ni-exchanged oligomerization catalysts. The chemical, structural and textural characteristics of SBA-15, AlSBA-15 and Ni-AlSBA-15 materials were widely examined in our previous study.⁶ They are typical of the SBA-15 topology, with very well-ordered arrays of mesoporous channels. The main properties of these materials are summarized in Table 1. Fig. 1 shows the nitrogen sorption isotherms of SiO₂, AlSiO₂ and Ni-AlSiO₂ materials. All samples show a type IV isotherm with a H1 type hysteresis loop, typical for the mesoporous, but non-ordered materials. The isotherms point out a significant change of the textural features of AlSiO₂ and Ni-AlSiO₂ materials compared to the parent silica. These changes are quantified in Table 1 and reveal a decrease of the total pore volume and of the BET surface area. The modifications, similar to those observed in the case of the SBA-15 type materials, can be attributed to a loss of (ultra)microporosity and a decrease of the surface roughness by a dissolution-redeposition of silica upon treatment in sodium aluminate solution.^{6,16} Using the ionic exchange procedure described in the experimental section, the amount of nickel incorporated in Ni-AlSiO₂ and Ni-AlSBA-15 samples was 2.0 and 2.5 wt%, respectively. Insertion of aluminium atoms into the silica network was confirmed by ²⁷Al MAS NMR. The NMR spectrum of AlSiO₂ and Ni-AlSiO₂ exhibited an intense signal centred at 55 ppm, which is characteristic of tetrahedrally coordinated aluminium species and only a small signal at about 0 ppm (which is associated with octahedrally coordinated aluminium species) (Fig. 1). As previously reported for SBA-15 materials,⁶ this result proves that the treatment with sodium aluminate is a very efficient method for the postsynthesis alumination of the silica.

 MoO_x supported metathesis catalysts. The properties of metathesis catalysts (samples with a loading of 10 wt% Mo) are summarized in Table 2. As expected, compared to the unmodified supports (see Table 1), the catalysts containing MoO_x species showed a decrease of the pore volume and surface area.



Fig. 1 Nitrogen physisorption of (a) SiO_2 , (b) $AlSiO_2$ and (c) $Ni-AlSiO_2$ (left). ²⁷Al MAS NMR of (a) $AlSiO_2$ and (b) $Ni-AlSiO_2$ (right).

However, no significant changes in the isotherm shape (results not shown) were observed for both SiO₂ and SBA-15 types of materials.

DRUV-Vis and Raman spectroscopy were used as methods for identifying the MoO_x species presents in catalysts. The UV-Vis spectra of both $MoO_x/SBA-15$ and $MoO_x/AlSBA-15$ (Fig. 2) feature a strong absorption band at about 250 nm, which is assigned to the highly dispersed tetrahedral MoO_x species.^{17,18} $MoO_x/SBA-15$ features an additional band at approximately 330 nm, which can be ascribed to the polymerized octahedral MoO_3 species.^{17,18}

Fig. 2 shows also the UV-Vis spectra recorded for MoO_x/SiO_2 and $MoO_x/AlSiO_2$ catalysts. Both samples display large bands in the range of 200 and 400 nm. The intense band at wavelength higher than 300 nm indicates that the Mo species are mainly octahedral MoO_x and even bulk α -MoO₃ in both MoO_x/SiO_2 and $MoO_x/AlSiO_2$ samples.

The Raman spectra recorded for $MoO_x/SBA-15$ and $MoO_x/$ AlSBA-15 are reported in Fig. 3. Both samples display a band at 960 cm⁻¹, which is assigned to the highly dispersed MoO₃ monomers.^{19–21} The Raman spectrum of the MoO_x/SBA-15 sample displays three additional bands at 995, 819 and 367 cm⁻¹, which proves that this catalyst also contains polymerized octahedral MoO_x and small crystallites of bulk α -MoO₃,^{19,22,23} which is in agreement with the UV-Vis results.

The Raman spectra of MoO_x/SiO_2 and $MoO_x/AlSiO_2$ (not shown) exhibited a band at 960 cm⁻¹ together with intense bands at 995, 819 and 367 cm⁻¹. The nature of the MoO_x species in these catalysts was also checked by X-ray diffraction at diffraction angles from 5 to 70° (Fig. 3). For both catalysts, the diffraction lines of the crystalline phase of MoO_3 (*e.g.* at 23.3, 25.7, 27.3 and 33.78°) are visible,^{19,24} confirming the UV results. However, the low intensity of these signals suggests that only a small part of Mo is present as the crystalline phase.

Table 1	Properties of parent and modified SiO_2 and SBA-15 samples^a
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Sample	D, nm	$S_{\rm BET}$, m ² g ⁻¹	V, mL g ⁻¹	$V_{\rm mes}$, mL g ⁻¹
SiO ₂	6.0^{b}	400	0.81	0.69
$AlSiO_2^c$	6.0^{b}	330	0.65	0.55
$Ni-AlSiO_2^d$	6.0^{b}	320	0.67	0.57
SBA-15 ^e	8.4	740	1.05	0.81
AlSBA-15 ^e	7.9	440	0.73	0.59
Ni-AlSBA-15 ^f	7.9	460	0.78	0.63

Table 2Main properties of Mo-based metathesis catalysts^aD, $S_{BET,}$ V, $V_{mes},$ Mo,Samplenm $m^2 g^{-1}$ mL g^{-1} mL g^{-1} atoms nm

Sample	D, nm	$s_{\text{BET}},$ m ² g ⁻¹	v, mL g ⁻¹	$v_{\rm mes},$ mL g ⁻¹	atoms nm ⁻²
MoO _x /SiO ₂	5.9^{b}	180	0.62	0.56	3.5
MoO _x /AlSiO ₂	5.9^{b}	200	0.49	0.43	3.1
MoO _x /SBA-15	7.9	540	0.90	0.74	1.2
MoO _x /AlSBA-15	7.7	300	0.55	0.45	2.1

^{*a*} Pore diameter (*D*), specific surface area (S_{BET}), total pore volume (*V*), mesoporous volume (V_{mes}). ^{*b*} Average pore diameter. ^{*c*} Si/Al = 6.5 (mol/mol). ^{*d*} 2.0 wt% Ni. ^{*e*} Si/Al = 7.0 (mol/mol). ^{*f*} 2.6 wt% Ni.

^{*a*} Pore diameter (*D*), specific surface area (S_{BET}), total pore volume (*V*), mesoporous volume (V_{mes}). ^{*b*} Average pore diameter.



Fig. 2 DRUV-vis spectra of $MoO_x/SBA-15$ and $MoO_x/AISBA-15$ (left). DRUV-vis spectra of MoO_x/SIO_2 and $MoO_x/AISIO_2$ (right).



Fig. 3 Raman spectra of $MoO_x/SBA-15$ and $MoO_x/AlSBA-15$ (left). X-ray patterns of MoO_x/SiO_2 and $MoO_x/AlSiO_2$ (right).

Summarizing, various MoO_x species coexist in all samples: monomeric, polymeric, and crystalline Mo oxide. Highly dispersed (monomeric) species are preferentially produced on the AlSBA-15 type support. This behavior can be related to the surface density of the MoO_x species on supports: 2 Mo nm⁻² for AlSBA-15 and 3–3.5 Mo nm⁻² for SiO₂/AlSiO₂ (Table 2). On the other hand, for each class of materials, the aluminated supports (material exhibiting acidic properties) allowed us to prepare catalysts with MoO_x species better dispersed than the purely silica supports. This is in good agreement with previous studies,^{18,22} which claimed that highly dispersed MoO_x species are preferentially formed on acidic supports.

The oxidation state of molybdenum in the MoO_x species was investigated by XPS. The spectrum of the $MoO_x/SBA-15$ catalyst (considered as example for this study) in the Mo 3d region is shown in Fig. 4. Similar spectra, consisting of a single couple of two well-resolved bands $(3d_{3/2} \text{ and } 3d_{5/2})$, were obtained for all metathesis catalysts. The values of the binding energies (BE) of catalysts are slightly higher than those of the bulk α -MoO₃ (Table 3). These results suggest that in all samples the Mo atoms are essentially in a single oxidation state, most probably $Mo^{6^+, 2^5}$ It is important to note that the species Mo^{6^+} are considered as precursors for generating the active site in metathesis reactions.²⁶ On the other hand, according to Thielmann *et al.*,²³ the BE shifted to higher values compared to bulk α -MoO₃ indicating the presence of isolated and only small (not bulk) clusters of dispersed molybdenum oxide species.

Catalytic results

Ethylene oligomerization in the batch mode. Ni-AlSiO₂ was used as a catalyst in ethylene oligomerization tests performed at 150 °C, under 3.5 MPa of ethylene, using *n*-heptane as a solvent. The reaction was run for 60 min. Table 4 compares the



Fig. 4 Mo 3d XP spectrum (normalized with respect to the Si 2p emission) of a $MoO_x/SBA-15$ sample.

Table 3	XPS binding	energy for	metathesis	catalysts
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	Binding energy	
Sample	Mo 3d _{5/2}	Mo 3d _{3/2}
α-MoO ₃	232.80	235.90
MoO_x/SiO_2	233.02	236.06
$MoO_x/AlSiO_2$	233.31	236.31
MoO _x /SBA-15	233.13	236.28
MoO _x /AlSBA-15	233.12	236.17

average catalytic activity and the oligomer distribution with those previously obtained with Ni-AlSBA-15.6 It is important to note that the results obtained with Ni-AlSBA-15 were the highest ever reported in the literature with Ni-based microporous and mesoporous catalysts. The result obtained with the Ni-AlSiO₂ catalyst is inferior in terms of average productivity (per weight of the catalyst) compared to the Ni-AlSBA-15 catalyst. Also the turnover frequency (TOF, expressed as the number of molecules of ethylene transformed by the nickel site per hour) was slightly lower with Ni-AlSiO₂ compared to Ni-AlSBA-15, though still remarkably high. To estimate the TOF values, each Ni ion introduced to the silica-alumina support was considered as a single active site. Note that the high TOF values exhibited by the Ni-exchanged mesoporous materials were often comparable to those obtained in ethylene oligomerization using Ni²⁺-based complexes as homogeneous catalysts.27-29

For both Ni-AlSiO₂ and Ni-AlSBA-15 catalysts, the oligomers consisted of C4, C6, C8 and C10 olefins, with small amounts of C12 olefins. Only traces of alkanes and odd carbon number alkenes were identified, indicating that the hydrogen transfer or the acid catalyzed cracking reactions are not occurring to a significant level. C4 and C6 olefins were the main products:

 Table 4
 Representative catalytic behaviour of Ni-based catalysts for ethylene oligomerization

	Si/Al, mol mol ⁻¹	Ni, wt%	$ \begin{array}{c} \text{A1,}^{a} \\ \text{g g}^{-1} \text{ h}^{-1} \end{array} $	$\operatorname{TOF}_{s^{-1}}$,	Selectivity to, wt%			
Catalyst					C4	C6	C8	C10+
Ni-AlSiO ₂	6.5	2.0	130	3.7	56	31	10	3
Ni-AlSBA-15	7.0	2.6	175	3.9	41	37	15	7

^{*a*} Average productivity $g_{\text{oligomers}} g_{\text{catalyst}}^{-1} h^{-1}$. Conditions: 150 °C, 3.5 MPa, reaction time 60 min, batch mode.

87% with Ni-AlSiO₂ and 78% with Ni-AlSBA-15. C4 fraction was exclusively linear (no isobutene detected) and 2-butene predominated as compared with 1-butene among C4 isomers. The linear hexenes (75%) also predominated as compared with other ethylene trimers.

Ethylene oligomerization in the flow mode. The catalytic behavior of the Ni-AlSiO₂ catalyst was also evaluated for ethylene oligomerization carried out in the flow mode, using a fixed-bed dynamic reactor. The reaction was conducted over 9 h on stream, at 150 °C, 3.0 MPa of ethylene, and a weight hourly space velocity (WHSV) of 10 h⁻¹. The initial conversion of ethylene was about 90% and it declined smoothly, with a deactivation rate of 19.3 × 10⁻³ h⁻¹ (Fig. 5). The product distribution (47% C4, 34% C6, 16% C8 and 3% C10+) did not change during the catalytic test. The average composition of butenes consisted of 18% 1-C4, 38% *trans*-2-C4 and 44% *cis*-2-C4.

On the Ni-AlSBA-15 catalyst, the initial conversion of ethylene was about 93% and the deactivation rate was $1.6\times10^{-3}~h^{-1}$ (12 times lower than that of the Ni-AlSiO_2 catalyst). 6 The product distribution was similar for Ni-AlSiO_2 and Ni-AlSBA-15 catalysts.

The efficiency of the regeneration process was evaluated on the spent Ni-AlSiO_2 catalyst. It consisted of calcination at 550 $^\circ\mathrm{C}$ for 8 h with a mixture air-nitrogen (25/75, v/v) in the reactor. The regenerated catalyst exhibited initial catalytic properties similar to those of the original catalyst, but the deactivation rate slightly increased ($23 \times 10^{-3} h^{-1}$). Additional TG measurements under oxidizing conditions were carried out on the spent catalysts in order to evaluate the amount of products confined into the pores. As can be seen in Fig. 6, the total weight loss was about 30%, consisting of two fractions: 22% in the range of 50-300 °C (light and middle oligomers) and 8% in the range of 300-750 °C (heavy products). The TGA weight loss for the spent Ni-AlSBA-15 catalyst was only 10%. This major difference in the weight loss exhibited by these two catalysts may explain why Ni-AlSiO₂ (having narrower and non-ordered pores) showed a higher deactivation rate. On the other hand, the high stability of the Ni-AlSBA-15 catalyst can be related to the SBA-15 topology where the large interconnected mesopores facilitate the diffusion



Fig. 5Ethylene conversion and product spectrum vs. time on stream onNi-AlSiO2. $\langle \diamond \rangle$ % ethylene conversion, (\Box) % C4, (Δ) % C6, (X) % C8 (X)C10+; conditions: 150 °C, 3.0 MPa of ethylene, WHSV = 10 h⁻¹.



Fig. 6 TG and DTG curves of the spent Ni-AlSiO₂ catalyst.

of the products, particularly the bulkier ones, and results in a lower deactivation rate of these catalysts.

Ethylene oligomerization and metathesis. Another objective of this study was to investigate the direct conversion of ethylene to propylene in a single flow reactor, using two heterogeneous catalysts, through cascade dimerization, isomerization, and metathesis reactions (Scheme 1).

Two consecutive catalyst beds consisting of the Ni-based catalyst and the Mo/support catalyst, respectively, were placed in the reactor. Based on previous results obtained in oligomerization and metathesis reactions¹³ and preliminary experiments, the following parameters were chosen for conducting the oligomerization-metathesis reactions: T = 80 °C, p = 3.0 MPa and the flow rate = 33 mL min⁻¹ of pure ethylene. WHSV was 16.5 h^{-1} for the oligomerization catalyst (0.15 g) and 5 h^{-1} for the metathesis catalyst (0.50 g). A moderate conversion of ethylene is favorable, because it limits the formation of higher oligomers in the oligomerization step, and increases the conversion in the metathesis step. Different catalytic systems were tested and the results are summarized in Table 5. Under the present reaction conditions the major olefins were propylene and butenes (>80%). Small amounts of C5 and C6+ olefins were also formed. The presence of C5 and C7 olefins indicates that the Mo-based catalysts were also able to catalyze metathesis reactions involving olefins higher than C4. The best catalytic system in terms of selectivity to propylene was the couple Ni-AlSBA-15 and MoO_x/AlSBA-15. Moreover, the metathesis catalysts based on SBA-15 type supports are better than those prepared on commercial silica supports. MoO_x/AlSiO₂ and MoO_x/SiO₂ show low selectivity to C3, suggesting that they are less active metathesis catalysts. These results can be related to the properties of the metathesis catalysts discussed above. Indeed, MoOx/AlSBA-15 contains highly dispersed MoO_x (which are very active metathesis species),^{19,24}



Scheme 1 Reaction sequence: ethylene dimerization, butene isomerization and cross-metathesis.

 Table 5
 Catalytic behaviour in the ethylene oligomerization-metathesis reaction

	After 1 h c	on str	After 3 h on stream				
Catalyst couple	C2 conv., ^{<i>a</i>} %	C3, ^b %	C4, ^c %	C2 conv., %	C3, %	C4, %	
Ni-AlSBA-15 + $MoO_x/SBA-15$ Ni-AlSBA-15 + $MoO_x/AlSBA-15$	41 43	54 71	35 23	39 40	29 35	55 63	
$\begin{array}{l} \text{Ni-AlSiO}_2 + \text{MoO}_x/\text{SiO}_2 \\ \text{Ni-AlSiO}_2 + \text{MoO}_x/\text{AlSiO}_2 \end{array}$	40 41	18 38	63 46	38 39	9 27	79 53	
^{<i>a</i>} Ethylene conversion. ^{<i>b</i>} Concentration of propylene in products. ^{<i>c</i>} Concentration of butenes in products. Conditions: 80 °C. 3.0 MPa.							

while the other catalysts contain mainly polymerized octahedral MoO_x and even a small amount of bulk α -MoO₃, which are known to be less active species in metathesis.

On the other hand, previous studies have reported on the relationship between catalytic activity and acidity of the catalytic materials.^{18,30–33} These results suggested that similarly structured MoO_x species exhibited higher activity when they were supported on stronger acidic supports.

The effects of the time on stream on the C3 and C4 selectivity profiles are given in Fig. 7 for the best catalytic couple. The initial selectivity to propylene was 71%, which is very close to that obtained with the catalytic system Ni-AlSBA-15 + MoO_3 -SiO₂-Al₂O₃ in a previous study.¹³ In that case, the selectivity to propylene decreased progressively from 70% to 46% at 5 h on stream. In the present study, with Ni-AlSBA-15 + MoO_3 /AlSBA-15 the selectivity to C3 decreased rapidly from 71% to 35% at 3 h on stream, and 24% at 6 h on stream (Fig. 7). The selectivity to butenes increased from 23% to 72%. These results indicate that the activity of the metathesis catalyst diminished with time on stream, while the oligomerization catalyst maintained its activity during the catalytic test. The low reaction temperature may contribute to the deactivation process by preventing fast product desorption from the metathesis active sites.

In summary, the results reported here are promising in terms of catalyst productivity and selectivity to C3–C4 olefins, but additional work is needed to optimize the metathesis catalyst and the reaction conditions in order to improve the catalyst lifetime and selectivity to propylene.



Fig. 7 Selectivity to C3 (\Box), C4 (\triangle), and conversion (\diamond) of C2 vs. time on stream. Catalysts: Ni-AlSBA-15 + MoO_x/AlSBA-15; conditions: 80 °C, 3.0 MPa of ethylene.

Conclusion

We showed that a mesoporous non-ordered inexpensive Ni-AlSiO₂ catalyst can be successfully prepared by post-synthesis alumination of commercial silica, followed by ion exchange with nickel. This solid proved to be a versatile, robust and efficient catalyst for the selective oligomerization of ethylene under mild conditions. Thus, productivity up to 130 g of olefins (C4-C10) per g of the catalyst per hour was obtained in the batch mode, at 150 °C. Using a fixed-bed flow reactor, the catalyst also showed good activity and stability. However, these catalytic behaviours are to some extent inferior to those exhibited by the expensive mesoporous Ni-AlSBA-15 catalyst. This difference is due to the narrow pore size of the silica-based catalyst, which suffered a more rapid deactivation with respect to the mesoporous model material. These results clearly illustrate that the structural features of Ni catalysts strongly affect the catalytic activity/stability in C2 conversion. By combining the oligomerization catalysts with the MoO_r/(Al)SiO₂ or the MoOx/(Al)SBA-15 metathesis catalyst, in an one-pot cascade process, at 80 °C, ethylene was converted into propylene.

The metathesis behaviour was governed by the texture and the acidity of the supports, as well as the nature of the MoO_x species. Thus, the catalysts based on SBA-15 type supports were again better than those prepared on commercial silica supports. The best catalyst was MoO_x /AlSBA-15, with highly dispersed MoO_x species and surface acidity.

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