Alumno-mesostructured Ni catalysts for the direct conversion of ethene to propene

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Ni/MCM-41 and Ni/AlMCM-41 were synthesized at different Si/Al ratios and tested in the direct conversion of ethene to propene (ETP-reaction). It was intended to evaluate the effect of modifying the catalyst acidity on the ETP-reaction rather than optimizing its performance. All catalysts were characterized by powder XRD, N2-physisorption, 29Si and 27Al MAS NMR, TEM, NH3-TPD, pyridine-DRIFT, H2-TPR, and TPO. Ni/MCM-41 showed low catalytic activity due to its low acidity. Ni/AlMCM-41 catalyst with a Si/Al ratio of 60 had high catalytic activity. Characterization results revealed that the catalyst structure does not have effect on the catalytic activity. Al could be incorporated into the MCM-41 framework up to Si/Al ratio of 16. Two different Ni-composites on the surface of the MCM-41 and AlMCM-41 were observed. Deeper characterization is required to know the Ni state. Important deactivation was observed at 450 °C. The nature of the carbonaceous species and reaction mechanism require deeper characterization.

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1. Introduction

The chemical industry is based mainly on ethene and propene as block-building chemicals. Both compounds are produced as co-products in the steam cracking of different hydrocarbon steams and in the refinery-based catalytic cracking. The petrochemical industry is presently facing a major squeeze in propylene availability as a result of the growth in propene derivatives, especially polypropylene [1]. Owing to this strong global demand, there is concern that the supply of propene from its traditional sources will not be sufficient to keep pace with demand [1,2]. Consequently, to meet the increasing demand for the production of propene, the on-purpose technologies will be of great interest. Several strategies have been proposed for propene production, the dehydrogenation of propane [2], the catalytic cracking of C4 alkenes to propene [3,4], and the metathesis of ethene and 2-butene [3,5]. The dehydrogenation of propane requires relatively large capital investments as well as high operating costs. The catalytic cracking of C4 alkenes produces a broad spectrum of by-products and it is difficult to implement [6], and the metathesis process requires 2-butene and ethylene in equal quantities. Also, Sugiyama et al., and Iwamoto et al., have shown that it is possible to obtain propene directly from ethanol by using Ni-doped MCM-41 and FSM-16 catalysts [7,8] which open a new alternative to produce propene from renewable sources.

Recently, the direct conversion of ethene to propene without any addition of other hydrocarbons (ETP-reaction) was found to offer an attractive alternative. This reaction was observed, at first, in a few early papers on olefin metathesis catalysts, over supported molybdenum and tungsten catalysts [9,10]. Recently, Iwamoto et al. [11–13] found that Ni ions loaded on MCM-41 prepared by template ion exchange catalyze the direct conversion of ethene into propene in the presence of water vapor. Because MCM-41 is not stable in presence of water [14], the long-term stability of the catalyst is questionable. Taoufik et al., have reported the direct transformation of ethene into propene over a tungsten hydride supported on alumina [15], but the conversion was low after 10 h on stream, reaching around 10% of conversion. Oikawa et al. [16] and Lin et al., showed that silicoaluminophosphate microporous molecular sieve, SAPO-34, and H-ZSM-5 zeolite are highly active for the ETP-reaction, but they present a serious deactivation with time on stream [17,18]. More recently, intensive work has been done in order to understand the nature of the catalytic active sites and the reaction mechanism of the ETP-reaction on Ni/MCM-41 catalysts [19–21], and the nature and mechanism of formation of the active sites on Ni/MCM-41 are being subject of discussion [22,23].
Since its discovery in 1992 by Mobil researchers [24,25], MCM-41 has attracted the attention because of its regular pore size in the mesoporous region, high specific surface area, and the capacity to introduce other elements other than silica in its framework structure [14]. In this sense, Al can be incorporated in its structure and therefore develop acidity [26,27]. Hartmann et al., showed that nickel-containing MCM-41 and AIMCM-41 are active in the ethylene dimerization and in the 1-butene isomerization, which is possible, because of the acidity of the catalysts [28]. More recently, Frey and Hinrichsen [29] studied the ETP-reaction on Ni/AIMCM-48 and found that the ethene conversion reached over 40% with a propene selectivity up to 56%, but no acidity characterization was done.

In this research, the acidic properties of the AIMCM-41 and the Ni-active sites were used in the direct transformation of ethene to propene. All catalysts were prepared by the template ion exchange method [30]. The Si/Al ratio was modified in a wide interval in order to change effectively the acidity of the catalysts. The proposed reaction mechanism of the direct transformation of ethene to propene suggested by Iwamoto consists in the following individual stages: first, two ethene molecules dimerize to 1-butene on nickel sites, this 1-butene isomerizes to 2-butene on acid sites, and finally, a metathesis step between 2-butene and ethene produces two molecules of propene on nickel sites [12]. Therefore, a joint modification of the acidity and the catalytic properties of the nickel pursue the potential to enhance the direct conversion of ethene to propene. In this work, results of applying the nickel-based MCM-41 and AIMCM-41 catalysts in the ETP-reaction are discussed. A wide spectrum of characterization techniques was used in order to explain the observed results.

2. Experimental

In this section, the methodology for the synthesis, characterization, and catalytic testing of the Ni/MCM-41 and Ni/AIMCM-41 in the ETP-reaction is described.

2.1. Synthesis of MCM-41 and AIMCM-41

MCM-41 and AIMCM-41 were prepared by a modification of the method used by Noreña-Franco et al. [31]. Tetrabutylammonium silicate was prepared with a mixture of 5.4 g of a solution of tetrabutylammonium hydroxide 40 wt.% (Sigma–Aldrich, TBAOH) and 0.6 g of silica fumed (Sigma–Aldrich). The latter component was mixed with another solution formed by 3.42 g of cetyltrimethylammonium bromide (Merck, CTABr ≥97%) and 9.1 g of deionized water. The resultant mixture was stirred by hand during 15 min and had a molar composition of 1 SiO2:0.035 TBAOH:0.000–0.063 NaAlO2:25 H2O. Sodium aluminate (NaAlO2:Al2O3 50–56% and Na2O 40–45%) was used as aluminum source, and its amount was adjusted for having different Si/Al ratios (150, 60, 16 and 5). After that, the mixture was transferred into a Teflon bottle and aged 48 h at 100 °C. The white solid was recovered by vacuum filtration and washed with deionized water. The final powder was dried at 80 °C for 6 h (as-synthesized AIMCM-41). A sample was calcinated in air at 225 °C for 3 h and at 540 °C for 6 h at a heating rate of 1 °C min⁻¹ in order to carry out the corresponding characterization. Siliceous MCM-41 was synthesized in the same manner but without any use of NaAlO2.

2.2. Synthesis of the Ni/MCM-41 and Ni/AIMCM-41

Ni/MCM-41 and Ni/AIMCM-41 were prepared by template ion exchange method [30]. In a typical procedure, 3.0 g of as-synthesized MCM-41 or AIMCM-41 was mixed with 30 ml of deionized water. The latter mixture was put in contact with 30 ml of a 0.03 M nickel solution under dropwise conditions and vigorous stirring. Nickel nitrate (Merck, Ni(NO3)2·6H2O ≥ 99.0%) was used as Ni precursor. The resulting mixture was transferred into a Teflon bottle and treated at 80 °C for 20 h without stirring. The light-green solid was recovered by vacuum filtration, washed with 300 ml of deionized water, and dried at 80 °C for 24 h. The final product was calcinated at 600 °C for 6 h in air. The rate of heating was 5 °C min⁻¹.

2.3. Catalytic activity testing

Catalytic experiments were carried out in a fixed-bed reactor consisting of a quartz tube with an inner diameter of 0.6 cm at atmospheric pressure. Each experiment was carried out with 0.5 g of catalyst and at a constant GHSV of 1.41 h⁻¹ gcat⁻¹. The feed was a mixture of 10% ethene (99.95%) in nitrogen (99.999%). The length of the catalytic bed was around 12 cm. The temperature was modified in the interval from 50 to 475 °C by increments of 25 °C. The analysis of the reaction products was carried out by an online gas chromatograph (Agilent 6890 GC/TCD with a 5973 MSD) equipped with a 30 m length HP-Plot Q column (Agilent Technologies). Experiments with different GHSV were carried out at 350 °C with constant mass of catalyst and by varying the volumetric flow rate. Deactivation experiments were performed for equivalent reaction conditions but at three different constant temperatures (250, 350 and 450 °C) for 60 h on stream.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were collected on an X’Pert PRO diffractometer by PANalytik using Ni-filtered CuKα radiation. The generator was operated with a voltage of 40 kV and a current of 40 mA. All samples were scanned in the region of [1–10°] 2θ with a step size of 0.016° using a scanning time of 10 s per step. Nitrogen physisorption isotherms were measured at −196 °C using a Quantachrome Nova2200e analyzer. Prior to adsorption, the samples were degassed for 24 h at 110 °C in vacuum. Between 10 and 20 mg of sample was used for the measurements. Specific surface areas were calculated from the linear parts of BET plots while the total pore volume was evaluated using the isotherm at a relative pressure of 0.995. Elemental analysis based on Atomic Absorption Spectroscopy (AAS) was carried out using a Varian SpectrAA 800 system. The template-free samples were dissolved in nitric acid. The NMR spectra were recorded applying a Bruker Avance 300 NMR spectrometer at room temperature. The spectrometer was equipped with a 4 mm CP/MAS probehead BL4. The samples were introduced in 4 mm ZrO2 rotors. The 29Si CP-MAS spectra were recorded at 59.62 MHz. The proton 90° pulse was set to 2.7 μs, and the decoupling strength during acquisition was 69 kHz. The following conditions were applied: 15 kHz spinning rate, recycle delay of 8 s, and contact time 5 ms. The 29Si shifts were externally referenced to Q6B. The 27Al MAS NMR spectra were recorded at 78.21 MHz at spinning rate of 8 kHz. The 90° pulse width 0.58 μs and 36,000 scans were collected with a relaxation delay of 2 s. The 27Al shifts scale was externally referenced to [Al(H2O)6]³⁺. Spectra were acquired with a time domain of 8 k data points and Fourier transformed using 16 k data points. TEM analyses were performed by using a Philips/FEI CM200 microscope. A sample of powdered catalyst was suspended in ethanol followed by ultrasonic dispersion. A drop of this suspension was placed on a carbon-coated copper grid and it was allowed to dry. The apparatus was operated at an acceleration voltage of 200 kV and equipped with a CCD camera for the imaging acquisition and analysis by SIS Olympus processing system. An EDAX DX-4 system was used for
Energy Dispersive X-ray analysis (EDX). Pyridine diffuse-reflection FTIR spectra were collected using a Smart collector and a high temperature Environmental Chamber equipped with ZnSe windows (Thermo Electron GmbH, Germany). The FTIR analyzer used in the experiments was a Nicolet 6700 equipped with a Ge/KBr beamsplitter and a DLaTGS detector (Thermo Electron GmbH, Germany). The stainless gas lines (He and He + pyridine) were connected to the cell. Initially, the powder catalyst was pre-treated at 400 °C for 60 min under a constant He flow, during the complete analysis, of 25 ml min⁻¹. The catalyst was cooled down at 50 °C, and then, the He was saturated with pyridine at room temperature and fed to the cell for 60 min. Finally, only He flow was passed through the cell during 30 min at 50 °C and the IR spectra were collected with a resolution of 4 cm⁻¹ and 100 scans. The last procedure was repeated at 100 and 150 °C for all catalysts. The presented IR spectra were recorded against the background collected by using KBr dehydrated in situ for 2 h at 400 °C under He flow. Surface acidity was investigated by Temperature Programmed Desorption of ammonia experiments (NH₃-TPD). The samples were pre-treated at 500 °C in helium for 2 h followed by cooling to 100 °C. Ammonia (1 vol.% NH₃ in He) was then adsorbed at the same temperature for 2 h. Physisorbed molecules were removed by switching back to a pure helium flow (also at 100 °C) for 1 h. Finally, the temperature was raised to 650 °C with a temperature ramp of 10 °C/min. Desorbed ammonia was detected with a TCD. Temperature Programmed Oxidation (TPO) was carried out in the same device with a 5 vol.% of O₂ in He. The samples were pre-treated for 1 h at 100 °C under He flow followed by cooling to 50 °C. Then, the mixture of O₂ and He was passed through the sample and the temperature was raised to 1000 °C with a temperature ramp of 5 °C/min. Change in O₂ composition was detected with a TCD. Catalyst reducibility was studied by Temperature Programmed Reduction (TPR) in a BEL-CAT Catalyst Analyzer (BEL Japan Inc.) using hydrogen. The samples were pre-treated for 1 h at

### Table 1: N₂-adsorption data and Ni composition of the Ni/MCM-41 and Ni/AlMCM-41.

<table>
<thead>
<tr>
<th>Catalyst Si/Al ratio</th>
<th>BET specific surface, m² g⁻¹</th>
<th>PV⁻¹ cm³ g⁻¹</th>
<th>BJH-PD, nm</th>
<th>NLDFT-PD, nm</th>
<th>Ni content, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>∞</td>
<td>1087.1</td>
<td>1.2</td>
<td>3.0</td>
<td>4.1</td>
<td>4.0</td>
</tr>
<tr>
<td>150</td>
<td>1385.2</td>
<td>2.0</td>
<td>3.0</td>
<td>3.9</td>
<td>4.4</td>
</tr>
<tr>
<td>60</td>
<td>918.8</td>
<td>1.4</td>
<td>3.0</td>
<td>4.1</td>
<td>4.6</td>
</tr>
<tr>
<td>16</td>
<td>928.4</td>
<td>1.3</td>
<td>3.0</td>
<td>4.1</td>
<td>3.7</td>
</tr>
<tr>
<td>5</td>
<td>533.3</td>
<td>0.6</td>
<td>3.0</td>
<td>3.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

⁻¹ Pore volume.
⁻² Pore diameter determined by Barrett–Joyner–Halenda method (BJH) from the desorption branch.
⁻³ Nonlocal density functional theory (NLDFT) from the desorption branch.
⁻⁴ Determined by Atomic Absorption Spectroscopy (AAS).

![Fig. 1. XRD patterns (a) and N₂-physisorption isotherms (b) of Ni/MCM-41 and Ni/AlMCM-41 at different Si/Al ratios.](image)

![Fig. 2. Conversion of ethene on Ni/MCM-41 and Ni/AlMCM-41 at different Si/Al ratios as a function of temperature. Ethene conversion = (ethene consumed/ethene fed) × 100.](image)
600 °C in synthetic air (25 ml/min) followed by cooling to 100 °C in a pure argon stream (25 ml/min). After switching to 10 vol.% of H₂ in Ar (total flow rate: 25 ml/min), temperature was increased linearly with 10 °C/min from 100 to 1100 °C. All TPO and H₂-TPR data were normalized to the respective sample weight and expressed in arbitrary units.

3. Results and discussion

Fig. 1 reveals the structural characterization of the Ni/MCM-41 and Ni/AlMCM-41 catalysts. The crystalline Ni/MCM-41 and Ni/AlMCM-41 are characterized by a broad band at low angles in the XRD spectrum and by a Type IV N₂-adsorption isotherm [24,25]. In Fig. 1a, the XRD spectra and in Fig. 1b the N₂-adsorption isotherms of the synthesized catalysts are given. From the spectra 1a, it is possible to observe that the catalyst without Al has a highly hexagonal ordered structure with the classic diffractions (100), (110), (200) and (210) [25]. For the catalysts Ni/AlMCM-41, the intensity of all diffractions is diminished, which means that the hexagonal phase in these catalysts is less ordered compared to the catalyst without Al. Therefore, it is concluded that the hexagonal ordering degree of the MCM-41 is very sensitive to the presence of Al during the synthesis, even at high Si/Al ratios.

The N₂-adsorption measurements for these catalysts are characterized by a type-IV isotherm according to IUPAC classification [32]. Such behavior corresponds to the MCM-41 materials and they present capillary condensation at relative pressure between 0.30 and 0.35 [25]. The N₂-adsorption data and Ni content of the Ni/MCM-41 and Ni/AlMCM-41 are summarized in Table 1. Two different methods were used to determine the pore size distribution, Barret–Joyner–Halenda method (BJH-method), and the nonlocal density functional theory (NLDFT) from the desorption branch. From these results, it is observed that BJH-pore diameter is the same for all catalysts, which is an indication that this method underestimate the pore diameter size and the NLDFT is more accurate to determine the pore diameter of the MCM-41 materials [33].

The N₂-adsorption data depend on the Si/Al ratio. The BET specific surface was around 1000 m² g⁻¹ for almost all catalysts, which is typical for MCM-41 materials [25]. More detailed data are given in Table 1. The catalyst with a Si/Al ratio of 5 showed the lowest value of BET specific surface, pore volume, and pore size. Therefore,
from the XRD and N$_2$-physisorption results, it is concluded that the Ni/MCM-41 and Ni/AlMCM-41 with a Si/Al ratio of 150, 60, and 16 presented the classic structure of the MCM-41 materials.

The Ni content depends also on the Si/Al ratio and the catalyst with a Si/Al ratio of 60 revealed the highest Ni content, 4.6 wt.%. For lower Si/Al ratios than 60, the Ni content decreased reaching 2.8 wt.% for the catalyst with a Si/Al ratio of 5. This fact must have an impact in the catalytic behavior and might be also responsible of the differences in catalytic activity.

In the next section, catalytic activity experiments in the ETP-reaction for all catalysts will be presented. Deeper characterization has been carried out in order to understand the obtained results.

3.1. Catalytic activity

Figs. 2 and 3 illustrate the conversion of ethene and the selectivity of the major reaction products (propene and butenes) in the ETP-reaction as a function of temperature for the catalysts with different Si/Al ratio. The Ni/MCM-41 catalyst revealed a low conversion of ethene and low propene selectivity. Thus, the results are not comparable to the observations of Iwamoto et al., and Lehmann et al., but they used a different synthesis procedure and different conditions during the synthesis, as well as different source of silica [11,12,19]. The addition of small amounts of Al during the synthesis of the support has a strong impact on the catalytic behavior of the Ni/MCM-41 catalysts.

It can be seen in Fig. 2 that the conversion of ethene increased with an increasing amount of Al (lower Si/Al ratios). The same behavior is observed for the selectivity of propene, depicted in Fig. 3a, which reached a maximum at a Si/Al ratio of 16. This fact may also explain the differences between the results obtained in this work and the results obtained by Iwamoto et al., and Lehmann et al., for Ni/MCM-41. For Si/Al ratios lower than 16 both, the conversion and selectivity of propene diminished. This reduction in the catalytic activity might be influenced by the reduction of the specific surface and the reduction of the Ni content. The

![Graphs showing catalytic activity](image-url)
selectivity of butenes is also given in Fig. 3. From this figure, it is possible to observe that the selectivity of the two different butenes isomers is also directly influenced by the Si/Al ratio. The selectivity of 2-butene is the sum of the selectivities of cis-butene and trans-butene. These selectivities can be grouped in three different intervals, low temperatures (50–150 °C), intermediate temperatures (150–300 °C), and high temperatures (300–475 °C).

The Ni/MCM-41 catalyst showed a high selectivity of 1-butene in the low temperature region, indicating a dimerization reaction of ethene. With increasing temperature, the selectivity of 1-butene decreases (Fig. 3b) and the selectivity of 2-butene increases (Fig. 3c), reaching a maximum in the interval of intermediate temperatures. This is an indication that the 1-butene is being isomerized to 2-butene. No formation of iso-butene was observed indicating a low acidity of the catalysts. According to Hulea and Fajula [34], Ni-exchanged AlMCM-41 is an efficient bifunctional catalyst for the ethylene oligomerization. Therefore, this type of reactions may also take place for the reaction conditions investigated in this work. In the interval of high temperature, it is observed that the selectivity of 2-butene is diminishing and the selectivity of propene is increased, reaching a maximum at around 375 °C (Fig. 3a). This result suggests that on Ni/MCM-41, a metathesis reaction between 2-butene and another molecule of ethene is taking place, as it has been reported by Iwamoto [12]. The maximum in Fig. 3a indicates that propene is consumed at higher temperatures to form probably long-chain hydrocarbons according to Hulea and Fajula [34].

The selectivity of 1-butene was lower than 20% for all Ni/AlMCM-41 catalysts at all temperatures investigated. This behavior indicates that the isomerization step is fast in comparison with the dimerization and metathesis steps, which is in concordance with the results reported in the literature regarding the isomerization of 1-butene [28,35]. The selectivity of 2-butene strongly depends on the Si/Al ratio. A higher selectivity is obtained for lower Si/Al ratios reaching a maximum at Si/Al = 60. In the region of low temperatures, the selectivity of 2-butene is high and showed a light decrement in the interval of intermediate temperatures. This behavior was observed for all Ni/AlMCM-41 catalysts. For the
region of high temperatures, this decrement is more pronounced, indicating probably that 2-butene is consumed for the production of propene through a metathesis step.

Fig. 4 shows the yield of propene, 1-butene, and 2-butene as a function of temperature at different Si/Al ratios. From this figure, it is possible to observe that the Ni/AlMCM-41 catalyst with a Si/Al ratio of 60 provides the highest yield of propene in the region of high temperatures, Fig. 4a. These results show that the Si/Al ratio, i.e., the number of active sites of the catalysts and their relative acidity, has a strong influence on the product distribution in the ETP-reaction.

Fig. 5 shows the change in product distribution as a function of the GHSV, i.e., the contact time dependence on the ETP-reaction. Clearly, high GHSV (shorter contact time) corresponds to a lower conversion of ethene and a lower selectivity of propene. The selectivity of butenes increases at higher GHSV. The catalyst with a Si/Al ratio of 60 and without Al revealed the highest and the lowest conversion of ethene, respectively. The highest selectivity of propene was observed with the rich Al catalyst (Si/Al ratios of 16 and 5), but there is no significant difference. At a constant ethene conversion of around 48%, it is possible to observe the effect of the Si/Al ratio on the selectivity of the major reaction products for the catalysts with Si/Al ratios of 150, 16, and 5. From this comparison, it is possible to observe that the selectivity of 1-butene increases with the Al content, indicating that the dimerization step is being favored with the Al content. The selectivity of propene increases also but at less extent. On the contrary, the selectivity of 2-butene diminished slightly. This result indicates that the Si/Al ratio modifies mainly the dimerization step and other types of reaction are taking place to produce propene.

At the reaction conditions used in this work, the major reaction products were 1-butene, 2-butene, and propene and their behavior during the ETP-experiment supports the reaction mechanism for the propene production suggested by Iwamoto [12]. In the next section, the catalyst characterization results will be used in order to understand the observed catalytic activity results.

Powder XRD and N2-physisorption results showed that the ordering degree of the hexagonal structure does not have a significant influence on the catalytic behavior of the Ni/MCM-41 and Ni/AlMCM-41 on the ETP-reaction. The Al-containing catalysts have the highest activity in the ETP-reaction even when their hexagonal ordering is low. Low Si/Al ratios have a negative influence on the ETP-reaction due to the reduction of the BET specific area and the difficulty to incorporate high amounts of Ni and Al into the MCM-41 framework [27].

3.2. Deeper characterization

Fig. 6 illustrates the $^{29}$Si CP-MAS NMR spectra (a) and $^{27}$Al MAS NMR spectra in direct detection (b) of Ni/MCM-41 and Ni/AlMCM-41 at different Si/Al ratios.
A shoulder of lower intensity with a chemical shift of around −91 ppm has been observed. This shoulder is assigned to Si(OSi)₃ OH units [37], and a very small contribution on this peak at around −87 ppm attributed to Si(OSi)₂(OAl)OH units could be observed [37]. The intensity of these peaks is diminishing for lower Si/Al ratios, which is an indication that the difficulty to incorporate Al into the MCM-41 framework was increased. Therefore, from these results, it is concluded that the Al incorporation is quite successful and the acidity of the Al-containing catalysts has to be increased.

The results presented above clearly show that the Al is being incorporated into the MCM-41 framework up to a Si/Al ratio of 16. This fact is probed with the ²⁷Al MAS NMR results, which are presented in Fig. 6b. The Al framework (tetrahedral coordinated) gives a peak at a chemical shift between 47 and 52 ppm and extra-framework Al (octahedral coordinated) at a chemical shift of 3 ppm [26,38]. From this figure, it can be clearly observed that there is no peak at 3 ppm for the catalysts with a Si/Al ratio of 150, 60 and 16, which means that all Al is being incorporated into the MCM-41 framework. For all last samples, the peaks are centered at around 50 ppm and they are width peaks; therefore, this result is associated with Al tetrahedral coordinated (framework Al) in a highly distorted environment [37]. For the catalyst with a Si/Al ratio of 5, a very broad peak of high intensity centered at 48.8 ppm is observed. This peak contains an important contribution of octahedral Al and pentahedral Al species (ca. 33 ppm) according to the results of Kosslick et al. [39,40]. The high-intensity peak centered at 50 ppm might be due to tetrahedral Al coordinated as extra-framework and forming a condensate phase that has been observed by Kloetstra et al., for AlMCM-41 with low Si/Al ratios [27]. This condensate phase causes an important reduction of the BET specific surface because it is blocking the pores of the MCM-41 as extra-framework Al tetrahedrally coordinated.
On Fig. 7 TEM micrographs of Ni/MCM-41 (7a) and Ni/AlMCM-41 with Si/Al ratio of 16 (7b) are depicted. This figure reveals the hexagonal structure of the Ni/MCM-41 and the low hexagonal ordering degree of the catalyst with a Si/Al ratio of 16. Ni-particles could not be observed. The condense phase observed by Kloetstra and coworkers [27] could not be recognized for the catalyst with a Si/Al ratio of 16. Thus, it is concluded that at this Si/Al ratio, only tetra-coordinated Al belonging to the MCM-41 framework could be observed. EDX analysis revealed a local Si/Ni composition of 2/1 for Ni/MCM-41 catalyst and a local Al/Si/Ni composition of 4.2/28.8/2.3 for the Ni/AlMCM-41 catalyst with a Si/Al ratio of 16. These values are close to the experimental values determined by Atomic Absorption Spectroscopy (AAS) Table 1.

As it has been widely stated in the literature that MCM-41 is slightly acidic and the Al incorporation can modify its acidity [26,28,39,40], NH$_3$-TPD of Ni/MCM-41 and Ni/AlMCM-41 was carried out and the results are depicted in Fig. 8. These results show the total acidity of the catalysts (Brønsted and Lewis acid sites) and it is observed that their surface density and strength depend on the Si/Al ratio, which simultaneously have a strong influence on the ETP-reaction (Figs. 2–5).

In the NH$_3$-TPD spectra, two peaks, viz. at ca. 150–250 °C and at 270–370 °C are recognized. In the interval of low temperature, the amount of desorbed NH$_3$ increased with the Al content. This NH$_3$ desorption is associated with weak Brønsted and Lewis acid sites. The high-temperature interval corresponds to Brønsted and Lewis acid sites.
This type of acidity seems to have a strong effect in the ETP-reaction. The catalyst with a Si/Al ratio of 60 showed the highest acidity in the interval of high temperature and revealed the highest catalytic activity in the ETP-reaction. For the catalyst Ni/MCM-41, the surface density of the acid sites is low; therefore, the catalytic activity should be also low.

From these results, it can be concluded that the ETP-reaction requires a catalyst providing an intermediate acidity.

It is well known that the Al incorporation into the MCM-41 framework produces Brønsted acid sites [39,40] and they can catalyze the ethene dimerization and oligomerization reactions in zeolite materials [41–43]. Therefore, it is important to distinguish between Brønsted and Lewis acid sites on the surface of the catalysts. Pyridine diffuse-reflectance FTIR of Ni/MCM-41 and Ni/AlMCM-41 was carried out and the results are depicted in Fig. 9. The figure illustrates the spectra of the catalyst powder before and after saturation with pyridine at 50, 100, and 150 °C as a function of the Si/Al ratio. All catalysts exhibit two characteristic bands at 3745 cm\(^{-1}\) corresponding to Si–OH groups and at 3550–3700 cm\(^{-1}\) corresponding to Al–OH and Si–OH–Al groups [44]. Before the pyridine adsorption, the intensity of these bands increases for lower Si/Al ratio but for the catalyst with a Si/Al ratio of 5 their intensity was found to be the lowest. The catalyst with a Si/Al ratio of 60 offered the highest intensity of both bands.

New bands in the interval of 1400 and 1650 cm\(^{-1}\) were observed after the pyridine treatment while the bands in the interval 3800 and 3550 cm\(^{-1}\) almost disappeared. All catalysts presented absorption bands at 1580 cm\(^{-1}\), 1489 cm\(^{-1}\), 1460 cm\(^{-1}\), and 1448 cm\(^{-1}\) of different intensity. The peak at 1448 cm\(^{-1}\) is related to binding to Lewis acid sites, and the peak at 1596 cm\(^{-1}\) is significant due to the adsorption to hydroxyl groups with a weak acidic character [25,45]. The band at 1460 cm\(^{-1}\) may be indicative of pyridine chemisorption at Lewis sites of higher acid strength [39,40]. Finally, the band at 1580 cm\(^{-1}\) is consistent with the presence of a liquid layer of pyridine, which also contributes to the band around 1448 cm\(^{-1}\) [47]. At 50 °C, all the bands associated with Lewis acid sites showed high intensity because the sample was saturated with pyridine at this temperature. The band associated with the Brønsted acid sites, 1489 cm\(^{-1}\), increased for lower Si/Al ratio because of the Al incorporation into the MCM-41 framework which is in agreement with the \(^{27}\)Al NMR results. At 100 °C, the intensity of the band at 1596 cm\(^{-1}\) diminished for lower Si/Al ratio indicating that the acidity of the catalyst was weak for the catalysts with high Al content. At 150 °C, almost all bands disappeared, indicating the weak acidity of all catalysts. At this temperature, the band at 1489 cm\(^{-1}\) (associated with the Brønsted acid sites) became more intense. According to the catalytic activity results, this type of acidity has the most important effect on the ETP-reaction.

To study the reducibility of Ni on Ni/MCM-41 and Ni/AlMCM-41, H\(_2\)-TPR was carried out. On the basis of manifold H\(_2\)-TPR results made for Ni on MCM-41, AlMCM-41 and silica [48–51], the TPR
peak regions of nickel on silica can be summarized as follows: Ni-
oxide could be reduced between 327 and 527 °C, the cationic form
of Ni on the silica surface could be reduced between 527 and
627 °C, and the Ni ion forming some composite compounds might
be reduced between 627 and 727 °C. Fig. 10 illustrates the H2-TPR
results of Ni/MCM-41 and Ni/AlMCM-41 as a function of the Si/Al
ratio. A small peak in the temperature interval between 300 and
500 °C has been observed for all the catalyst. This peak is assigned
to Ni-oxide which is more pronounced to the catalyst with a Si/Al
ratio of 5. For all catalyst, a broad peak of high intensity is observed
in the interval of 500 and 750 °C, which might be due to the forma-
tion of bulk mixed nickel-silicates and nickel-aluminosilicate. This
affirmation is in concordance with the 29Si CP-MAS NMR. For the
siliceous catalyst (Si/Al = 1), the peak presented a maximum
reduction temperature of 625 °C with a shoulder at higher temper-
ature (700 °C). These results can be interpreted in a manner that Ni
is present as a mixture of its cationic form and it is forming Ni com-
posite compounds. For the catalyst with a Si/Al ratio of 16 and 5, this
shoulder has disappeared which is an indication that Ni is
present mostly in its cationic form and it is more homogeneously
distributed in the AlMCM-41. For the catalysts with a lower Si/Al
ratio (16 and 5), the maximum is shifted to higher temperature,
650 and 675 °C. Thus, Ni is forming composite compounds in the
AlMCM-41. From these results, it is concluded that Al plays an
important role in the Ni state in the MCM-41, and at Si/Al ratio
of 60, the Ni state that is more active in the ETP-reaction is formed.

Fig. 12. TPO of the Ni/MCM-41 and Ni/AlMCM-41 after the ETP-experiment (a) and after the deactivation experiments at 250, 350, and 450 °C.

### Table 3
N2-adsorption data of the Ni/AlMCM-41 catalyst with a Si/Al ratio of 60 after 60 h on stream.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>BET specific surface, m² g⁻¹</th>
<th>PVᵃ, cm³ g⁻¹</th>
<th>BJH-PDᵇ, nm</th>
<th>NLDFT-PDᶜ, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>848.8</td>
<td>1.2</td>
<td>3.0</td>
<td>4.0</td>
</tr>
<tr>
<td>350</td>
<td>777.1</td>
<td>2.3</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>450</td>
<td>769.4</td>
<td>2.6</td>
<td>3.0</td>
<td>3.8</td>
</tr>
</tbody>
</table>

ᵃ Pore volume.
ᵇ Pore diameter determined by Barret–Joyner–Halenda method (BJH) from the desorption branch.
ᶜ Nonlocal density functional theory (NLDFT) from the desorption branch.

Fig. 13. Conversion of ethene on Ni/AlMCM-41(Si/Al = 60) as a function of time on stream at different temperatures. GHSV; 1.41 h⁻¹ g⁻¹ cat, 10% ethene in nitrogen.
Characterization of the catalysts after the ETP-experiment was carried out. Table 2 summarizes the physical features of all catalysts after the ETP-experiment. An important reduction of the BET specific surface area was observed for the catalysts with a Si/Al ratio of 1 and 150. This change was less pronounced for the other catalysts. The pore volume increased and the pore diameter did not suffer important modifications. Modification of the N2-physisorption data might be mainly due to the blocking of the pores with long-chain hydrocarbons [34].

XRD results showed that the structure and ordering degree of the catalysts was retained after each experiment (spectra not depicted). The same conclusion follows for the deactivation experiments (results shown below). Ni or carbonaceous particles were not detected by conventional XRD because of the small content of Ni and carbon in the catalysts. Considering that Ni-oxide was observed by H2-TPR and its reduction starts at temperatures higher than 175 °C [52–54], after the ETP-experiments, Ni0 particles might be observed on MCM-41 and AlMCM-41. This fact is illustrated in Fig. 11 where Ni-particles could be observed for the catalyst with a Si/Al ratio of 60. Carbonaceous species could be also observed and Buchireddy et al. [55] suggested that these species result from growth of Ni particles during tar reduction. Therefore, Ni particles might promote the carbonaceous species formation on Ni/AlMCM-41 catalysts.

Fig. 12a illustrates the TPO results after the ETP-experiment for the catalysts with different Si/Al ratio. Two very broad peaks with a maximum centered in the interval of 400–500 °C and 600–700 °C were observed. The contribution at temperatures lower than 300 °C can be associated with the oxidation of Ni0 [56]. The interval of 300–500 °C might correspond to the oxidation of monoatomic carbon with a low rate of oxidation [57]. The oxidation peak at higher temperature could be assigned to the oxidation of filamentous carbon [53]. The catalysts with a Si/Al ratio of 60 and 16 presented the highest formation of carbonaceous species. From these results, it is concluded that carbon formation reactions are taking place besides to the formation of propene and butenes and they might deactivate the catalysts. Therefore, deeper deactivation studies should be done in order to explain the nature of the carbonaceous species formation during the ETP-reaction.
The standard characterization techniques for alumino-meso-structured materials with low Si/Al ratios are XRD, N$_2$-Physisorption, $^{29}$Si CP-MAS NMR and $^{27}$Al MAS NMR, and TEM [27]. NH$_3$-TPD, pyridine diffuse-reflectance FTIR, and H$_2$-TPR analysis were done to study the surface composition of the catalysts. In Figs. 2–5 can be observed that the catalyst with a Si/Al ratio of 60 leads to the highest conversion of ethene and the highest yield of propene. Preliminarily, XRD and N$_2$-physisorption results revealed that this catalyst is characterized by low hexagonal ordering, but it has an N$_2$ isotherm type IV and high specific surface, which are characteristics of the MCM-41 materials [24,25]. Therefore, it is concluded that the hexagonal ordering of the MCM-41 has not an important effect on the catalytic behavior of the Ni/AlMCM-41. As it has been already observed in Fig. 7, Ni/MCM-41 revealed a highly ordered hexagonal structure but its behavior on the ETP-reaction is poor. This fact supports the previous explanation.

The presence of Al in the catalysts has a strong impact on the ETP-reaction when it belongs to the MCM-41 framework. This incorporation is modifying its surface acidity as it has been showed by NH$_3$-TPD and pyridine diffuse-reflectance FTIR. The results of $^{29}$Si CP-MAS NMR showed that the Q$^3$ is the main unit in the Ni/MCM-41 which corresponds to surface (SiO)$_3$Si–OH (phyllosilicate phase) [36] and it has a low density and weak surface acidity, as it is observed in Figs. 8 and 9. This phase also has been observed by Lehmann et al., and Tanaka et al., on Ni/MCM-41 [20,21]. Thus, the low acidity of this catalyst might be responsible for its low catalytic activity.

The results of $^{27}$Al MAS NMR analysis indicate that Al is incorporated to the MCM-41 framework. The presence of Al in the catalysts generates an important modification of the Ni state (according to the H$_2$-TPR results) and a modification of their acidity. Therefore, these differences might be responsible to explain the differences in catalytic activity between the Al-containing catalysts. The Ni-oxides reduce at temperatures lower than 400 °C to form Ni$^0$ particles that have been observed by TEM; therefore, the differences in catalytic activity might be also influenced by the formation of Ni$^0$, which is not active in the ETP-reaction. Hartmann et al., reported that Ni$^{+1}$ is the active state of the nickel for the dimerization of ethene on Ni/AlMCM-41 and the Al tetrahedral coordinated in the MCM-41 framework improves its stability [28]. Thus, Ni$^{+1}$ could be the active state of nickel in the ETP-reaction for the catalyst with a Si/Al ratio of 60. For Ni/AlMCM-41 catalysts, it is
concluded that the isomerization of 1-butene is fast for all Si/Al ratios and for all temperatures investigated. At these reaction conditions, the 1-butene isomerization is in equilibrium [35].

Currently, there is no report about Ni as active site for the metathesis of ethene and 2-butene. The results in this investigation showed that Ni could have indeed activity on this reaction stage of the ETP-reaction. These results are in accordance with the results obtained in [12,19]. Deeper characterization has to be done in order to investigate the Ni state of the Ni/AlMCM-41 catalysts, e.g., in situ EPR, diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO, and its role in the metathesis step during the ETP-reaction. The maximum in the selectivity and yield of propene, 38% and 25% respectively, on Ni/AlMCM-41 is a clear indication that propene is reacting to form other products, probably larger-chain hydrocarbons (oligomers). Therefore, not only the reactions involved in the reaction mechanism proposed by Iwamoto are taking place [12]. A deeper study of the reaction mechanism is required in order to understand and to optimize the behavior of the Ni/AlMCM-41 catalyst in the ETP-reaction.

The catalytic study was concluded by an investigation of the catalyst stability. The Ni/AlMCM-41 with a Si/Al ratio of 60 was selected because it presented the highest yield of propene. Table 3 summarizes the N\textsubscript{2} physisorption data after the deactivation experiments performed at three different temperatures. An important BET specific surface reduction was observed for all temperatures but in higher extent at 450 °C. An important reduction of pore diameter was observed that could be provoked by the deposition of carbonaceous species inside the pores [34]. Figs. 13–15 illustrate the conversion of ethene, the selectivity, and yield of the major reaction products, respectively. In these figures one can see that at 250 °C, there was a gradual deactivation. The main reaction products were 1-butene and 2-butene. The selectivity and yield of propene were less than 5%. At 350 °C, the conversion of ethene decreased from 78% to 62% after 60 h on stream. The major reaction products were propene, 1-butene, and 2-butene and their selectivity slightly changed with time. The selectivity of propene was almost constant during the 60 h on stream (around 18%).

At 450 °C, serious deactivation was observed and the conversion of ethene decreased from 87% to 35% after 60 h on stream. Important changes in selectivity were observed in the first 10 h on stream. The propene selectivity increased from 27% to 43%, which did not change after this time. In this period of time, the selectivity of butenes was low (less than 20%), which is an indication that other reactions took place. After 10 h on stream, the selectivity of propene remained constant and was higher than at lower temperatures. At 450 °C, the selectivities of 1-butene and 2-butene were lower than at 250 and 350 °C. This behavior suggests that 1-butene was isomerized to 2-butene and propene was probably formed through a metathesis step between 2-butene and ethene. This last step was favored at high temperature. 450–475 °C (see Figs. 3 and 4).

The reason for the deactivation of the catalysts at high temperature might be the occurrence of other types of reactions, e.g., oligomerization and coke formation. Hulea and Fajula [34] have shown that the Ni/AlMCM-41 with different Si/Al ratios are active for the ethene oligomerization and the presence of a uniform pore size distribution in the ordered mesoporous materials is very favorable for the oligomerization process [34]. For high temperature, these reactions might be highly favored to produce longer-chain hydrocarbons in the first 10 h on stream. These oligomers do not leave the pore and the conversion of ethene diminished.

Fig. 12b gives the TPO results for the catalyst with a Si/Al ratio of 60 at 250 °C, 350 °C, and 450 °C. At high temperature, the formation of carbonaceous species is much higher. These species clearly caused a serious deactivation of the catalyst under the reaction conditions investigated in this work. The colors of the catalysts changed after the deactivation experiments from very light gray to black depending on the temperature and time on stream. Therefore, the main reaction was definitely accompanied by coking processes. The results of these deactivation experiments support the reaction mechanism suggested by Iwamoto [12], but the strong deactivation of the catalysts at 450 °C revealed that other types of reactions are also taking place. Finally, it should be mentioned that experiments with respect to catalyst regeneration were performed successfully. The initial catalytic activity could be totally reestablished after 1 h of treatment with a mixture of 5% of oxygen in nitrogen at high temperature.

4. Conclusions

In this work, Ni/MCM-41 and Ni/AlMCM-41 were synthesized and tested in the direct conversion of ethene to propene. The acidity of the catalysts was efficiently manipulated by adjusting the Al content into the MCM-41 framework. Ni/MCM-41 revealed a low conversion of ethene and a low selectivity (or yield) of propene. This result showed that on this type of catalyst, the reaction mechanism is in accordance with the mechanism suggested by Iwamoto. The Ni/AlMCM-41 catalysts offered a high catalytic activity reaching a maximum at a Si/Al ratio of 60. This behavior is due to the acidity of the catalyst and to the stabilization of the Ni\textsuperscript{II} on the AlMCM-41 support. Lower Si/Al ratios have a detrimental effect on the course of the ETP-reaction because of the weaker acidity of the catalyst and because of the possibly different state of Ni in comparison with the catalyst with a Si/Al ratio of 60. Deeper characterization should be done in order to clarify the Ni state in the Ni/MCM-41 and Ni/AlMCM-41 catalysts. Hexagonal ordering of the final catalyst has no effect on the ETP-reaction. The maximum in the selectivity and yield of propene indicates that propene is involved in other reactions and not only dimerization, isomerization, and metathesis reactions are taking place. Therefore, further mechanistic investigations are required in order to understand the reaction mechanism on Ni/AlMCM-41 catalysts better. Ni/AlMCM-41 with a Si/Al of 60 showed very good stability at reaction temperatures lower than 350 °C. Serious deactivation of the catalyst was observed at 450 °C although the selectivity of propene stayed high. Different carbon species were observed, and they provoke a serious deactivation of the catalyst at high temperature. Regeneration of the Ni/AlMCM-41 catalyst could be carried out successfully.

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References
