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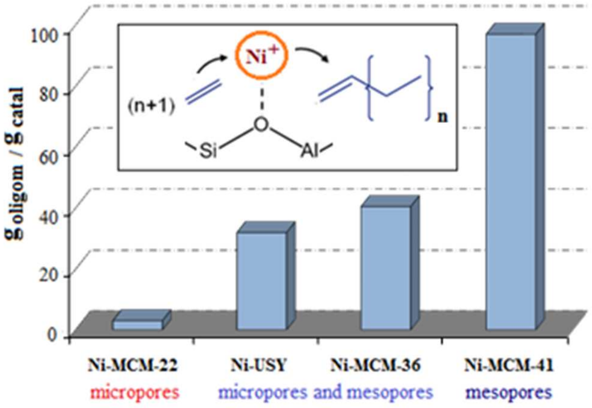

Nickel-based solid catalysts for ethylene oligomerization – a review

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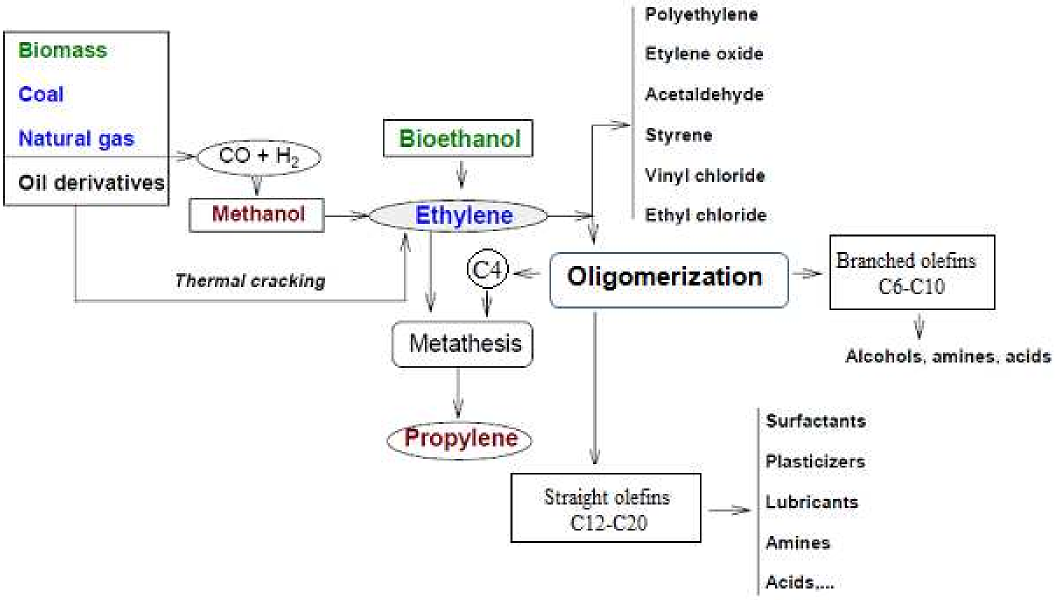
Abstract

Ni-based inorganic porous materials are the most important heterogeneous catalysts for the ethylene oligomerization. In spite of extensive research carried out in previous decades on these catalysts, only few aspects were reviewed in the literature. We illustrate here the main properties of these materials and their catalytic performances in oligomerization reactions performed under mild conditions.

The major groups of oligomerization catalysts, including NiO on various carriers and Ni-exchanged zeolites, sulfated-alumina or silica-alumina are described in the first part of this review. The nature of the active sites and their role in the ethylene oligomerization process are pointed out. In a second part, the literature dealing with the catalyst performances under various reaction parameters is reviewed. The influence of catalyst properties (in particular the catalyst pore size) and reaction conditions (i.e. temperature and pressure) on the productivity and the product distribution in oligomerization is methodically discussed. The excellent performances of Ni-exchanged ordered mesoporous silica-alumina, which are the best oligomerization catalysts known today, are carefully emphasized.

1. Introduction

With annual worldwide capacity running over 140 million tons, ethylene is among the most important basic organic chemicals. Currently, ethylene is produced in the petrochemical industry by steam thermal cracking of gaseous or liquid saturated hydrocarbons. However, emerging methods involving alternative sources such as natural gas, coal and biomass are envisaged. For example, the methanol (which is easily produced from all these sources *via* syngas) can be efficiently converted into ethylene by a zeolite-catalyzed process.[1-3] The bio-ethanol conversion into ethylene is also a very promising application (Scheme 1).[4,5]



Scheme 1. Ethylene: feedstocks and major derivatives

Ethylene is the raw material for a wide range of chemical products and intermediates. Industrial reactions of ethylene include in order of scale polymerization, oxidation, halogenation/hydrohalogenation, alkylation, hydration, oligomerization, and hydroformylation. Ethylene oligomerization is of considerable academic and industrial interest because it is one of the major processes for production of linear and branched higher olefins, which are components of plastics (C4-C6 in copolymerization), plasticizers (C6-C10 through hydroformylation), lubricants (C10-C12 through oligomerization) and surfactants (C12-C16 through arylation/sulphonation). The ethylene oligomers are also starting materials for other important chemicals, such as propylene, alcohols, amines and acids.

Ethylene oligomerization can be carried out in the presence of homogeneous and heterogeneous catalysts. The product selectivity strongly depends on the type of catalyst and operating conditions. The commercial processes for making long chain-olefins from ethylene oligomerization use organic solvents and homogeneous catalysts, such as trialkylaluminium (Chevron and Ethyl) and nickel complexes (Shell).[6-11] During the past decades new efficient homogeneous catalysts including complexes of nickel, titanium, zirconium, chromium, cobalt and iron have been developed.[12-23]

With respect to the green chemistry principles (solvent-free process, catalyst recycling, easy separation of reaction products and catalyst, etc.), heterogeneous catalysis is an environmentally friendly alternative to the traditional methods. Consequently, significant research efforts have been directed to the development of heterogeneous processes for ethylene oligomerization. Three main classes of solid catalysts have been reported: (i) solid acids,[24-30] (ii) nickel complexes immobilized on polymers and oxides,[31-35] and (iii) nickel supported on inorganic porous materials.[36-43]

Acid catalysts, such as supported phosphoric acid, zeolites, silica-aluminas and macroporous sulfonic resins demonstrated high potential for the oligomerization of C3+ olefins. Unfortunately, with acid catalysts, particularly at mild temperatures, the oligomerization rate of ethylene is much lower compared with that of other olefins.[24] Generally the oligomerization of ethylene is carried out at higher temperatures and the best acid catalysts are zeolites.[25-30] Under these conditions, besides oligomerization, reactions such as isomerization, disproportionation, cracking, aromatization occur, and a broad spectrum of products and large amounts of coke are formed.

The solid catalysts obtained by anchoring organometallic nickel compounds on polymeric matrices (Polymer-supported nickel complexes) are generally less active and less stable with respect to the homogeneous ones. Moreover, the product consisted in complex mixtures oligomers-polymers.[44-49] Similarly, when nickel complexes have been heterogenized on inorganic supports (SiO_2, Al_2O_3, SiO_2/Al_2O_3) poor activity/selectivity and doubtful stability were obtained in the ethylene oligomerization.[50] More recently, Rossetto *et al.* reported that nickel-β-diimine/silica is an active catalyst in ethylene oligomerization, but it is less active than its homogeneous analog.[51] De Souza *et al.* showed that $Ni(MeCN)_6(BF_6)_2$ on MCM-41 mesoporous silica is highly active in ethylene dimerization and trimerization in the presence of $AlEt_3$.[52,53]

As regards Ni-based inorganic materials, they revealed very interesting properties in the ethylene oligomerization, especially under mild operating conditions. Despite the large number of publications devoted to these catalysts, only few aspects were reviewed in the literature. Sanati *et al*. have reviewed the heterogeneous catalysts used in the oligomerization of ethylene, propylene, butenes and higher molecular weight olefins, but their paper focused mainly on solid acid catalysts.[24] Review articles written in the early 1990s by O'Connor,[25] Skupinska[6] and Al-Jarallah *et al.*[7] described for the most part the homogeneous oligomerization catalysts and only a little bit the heterogeneous catalysts.

The aim of the present paper is to provide an overview of the current knowledge on the Ni-based materials used as heterogeneous catalysts in the mild ethylene oligomerization. The behaviour in ethylene oligomerization exhibited by the microporous Ni-exchanged zeolites will be compared with that shown by the catalysts having larger pores, such as Ni-sulfated-alumina, Ni-amorphous silica-alumina and NiO on various oxide carriers. Oligomerization processes performed in various ways (static, flow, slurry) will be discussed taking into account the key variables that govern the catalyst behaviour, i.e. reaction parameters, catalyst pore size, number/type of active sites, etc.

2. Ni-supported materials as catalysts for ethylene oligomerization

As mentioned above, ethylene oligomerization can be efficiently catalyzed by homogeneous and heterogeneous catalysts containing transition metals, in particular nickel. Indeed, porous materials, such as NiO on various carriers or Ni-exchanged materials like zeolites, sulfated-alumina, amorphous silica-alumina and mesostructured silica-alumina have been widely investigated in the past decades.

2.1. NiO and $NiSO_4$ on supports

The original Ni-based heterogeneous catalysts for ethylene oligomerization consisted of nickel oxide supported on silica. Morikawa first reported that NiO supported on Kieselguhr is able to catalyze the dimerization of the ethylene even at room temperature.[54] Bailey and Reid from Phillips Petroleum Company revealed that NiO supported on silica gel exhibited catalytic activity at temperatures in the range of 0° to 150 °C.[36] They suggested that the presence of alumina in support appeared necessary to ensure the properties of the catalyst. Moreover, only the catalysts activated by heating in an oxidizing atmosphere at 400-500 °C were able to catalyze the ethylene oligomerization. The product mixture consisted of dimers, trimers and tetramers. Ozaki and Shiba,[55,56] and later Uchida and Amai[57-59] showed that NiO/SiO_2 is an effective catalyst for the dimerization of ethylene at room temperature. The mechanism of this reaction was investigated by Kimura *et al.* by means of the deuterium tracer.[60]

In a series of studies it has been shown that the support plays a major role in the ethylene oligomerization with NiO. Thus, Matsuda *et al.* reported that only NiO supported on acidic silica and/or alumina exhibited activity for ethylene dimerization.[61] Silica-alumina was found to be an excellent support for NiO.[62-71] Moreover, the alumina content in support seemed to influence the catalyst behavior.[69,70]

Other oxides were used as efficient supports for NiO: γ-Al_2O_3,[72] silica pillared vacancy titanate[73] and B_2O_3-Al_2O_3.[74] In a series of studies, Sohn *et al*. investigated the ethylene dimerization at room temperature in the presence of NiO supported on carriers including TiO_2 and Al_2O_3-TiO_2 modified with WO_3,[75,76] ZrO_2 and La_2O_3-ZrO_2 modified with WO_3,[77-79] ZrO_2 modified with MoO_3,[80] TiO_2 and ZrO_2 treated with H_2SO_4,[81,82] TiO_2 modified with H_2SO_4, H_3PO_4, H_3BO_3, and H_2SeO_4.[83] The catalytic activity of these materials was evaluated in relation with their acid site density and strength, or with their thermal stability.

$NiSO_4$/support is also an important Ni-based heterogeneous catalysts for ethylene oligomerization. Usually these catalysts were prepared by impregnation with nickel sulfate on different supports such as γ-Al_2O_3,[35,84-87] SiO_2-Al_2O_3,[88] ZrO_2,[89] Fe_2O_3,[90] Fe_2O_3-ZrO_2,[91] CeO_2-ZrO_2,[92] TiO_2-ZrO_2.[93] Their catalytic activity strongly depended on the acidity of the surface.

2.2. Ni-exchanged materials

In order to obtain catalysts with isolated Ni sites, different microporous and mesoporous supports were exchanged with Ni^{2+} ions. Ni-exchanged zeolites showed good qualities as heterogeneous catalysts in the ethylene oligomerization, but a major disadvantage is their significant deactivation. Indeed, the microporous character of these materials leads to intracrystalline diffusion limitations which results in a rapid enrichment of polymeric waxes in the micropores. One of the approaches to overcome this problem was the use of catalysts with larger pores, such as Ni-sulfated-alumina, Ni-amorphous silica-alumina and Ni-mesostructured materials. These materials will be briefly presented below.

2.2.1. Ni-zeolites

Nickel exchanged faujasite X and Y were the first zeolites used as catalysts for the ethylene dimerization and oligomerization. Russian researchers found that these materials, with well dispersed Ni sites, are more active than NiO/SiO_2 and suggested that the active sites were the Ni^{2+} ions bonded to the oxygen anions of the zeolite framework.[67,94,95] The selective conversion of ethylene into dimmers over Ni-containing zeolites with faujasite topology, at low temperature and pressure has been also studied by various research groups in order to examine either the nature of the active sites or the kinetics of the reaction.[37,38,96-99]

The oligomerization of ethylene over zeolites performed under more severe conditions led to hydrocarbons with higher molecular weight. For example, with Ni-Beta zeolite, at 120 °C and 35 bar, the main products were C6-C10 oligomers.[100] Heveling *et al.* reported that the oligomerization of ethylene over Ni-Y catalysts at temperature higher than 300 °C can be directed towards diesel-range products (C12-C18).[28]

More recently Lallemand *et al*. compared Ni-containing zeolites having various topologies and pore sizes.[101-103] They showed that materials having large cavities (i.e. Ni-dealuminated Y)[101,102] or mesopores (i.e. Ni-MCM-36)[103] are more active and stable catalysts than the purely microporous Ni-Y and Ni-MCM-22 zeolites.

2.2.2. Ni-silica-alumina

The oligomerization activity of catalysts prepared by the ion exchange of Ni^{2+} onto silica-alumina supports has been firstly reported by Lapidus *et al*. in 1970s.[69,70] The catalytic behavior has been related to the quantity of acid sites present (i.e. the alumina content) in the mixed oxide support. A series of studies focused on this catalytic system has been later accomplished by the Nicolaides' group. In order to optimize the catalyst formula and the oligomerization process, they studied the effect of the acid strength of the support,[104,105] the reaction parameters,[39,106] the composition and the texture of catalyst[107] and the nickel concentration[28,108] in laboratory tests carried out either in a fixed-bed flow reactor[106-108] or a slurry reactor.[109]

2.2.3. Ni-mesoporous materials

Hartmann *et al.* have shown that Ni-MCM-41 and Ni–AlMCM-41 revealed catalytic potential for ethylene dimerization.[110] After a 24-h reaction period, in a static gas-phase reactor the ethylene conversion was near 5%. More recently, in a series of detailed studies, our group showed that Ni-exchanged mesostructured materials with carefully controlled texture and concentrations of nickel and acidic sites exhibited very interesting properties as heterogeneous catalysts for ethylene oligomerization.[43,111-114] Thus, catalysts with different topologies, including Ni-AlMCM-41, Ni-AlMCM-48 and Ni-AlSBA-15, effectively activated the ethylene in oligomerization processes performed in slurry batch mode or in a CSTR, under mild conditions. The general method used for preparing these catalysts starts from Al-containing mesostructured silica, which is modified by ionic exchange and thermal treatment (Fig. 1). Lin *et al.* reported the synthesis of Ni-AlSBA-15 materials by impregnation of the parent AlSBA-15 with nickel nitrate, followed by calcination at 450 °C.[115] These materials were effective catalysts for the ethylene oligomerization performed in a fixed-bed reactor.

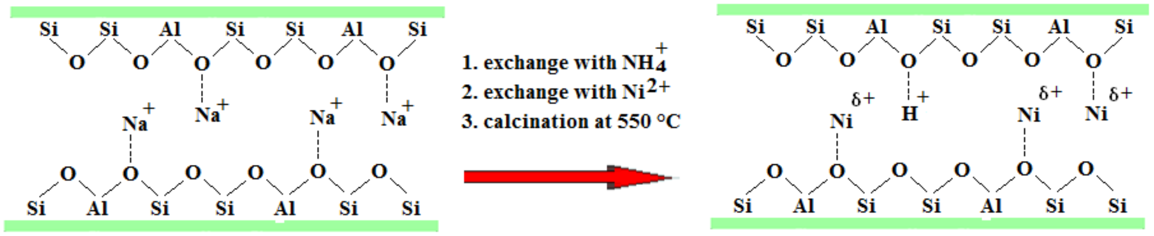


Fig. 1. General protocol for preparing Ni-mesoporous materials.[112]

2.2.4. Ni-sulfated alumina

Zhang *et al.* studied the ethylene oligomerization on a catalyst prepared by ion-exchanging Ni^{2+} onto a sulfated alumina support.[41,116] In a continous slurry reactor, at low temperature and pressure, a catalyst with 1.7 wt% Ni revealed high activity and stability against deactivation. The nature of the active sites in a such catalyst was investigated by Davydov *et al.* by means of FTIR spectroscopy of adsorbed CO.[87]

3. Nature of the active sites for ethylene oligomerization

It is well-known that the catalytic properties of nickel-modified materials strongly depend on the nature of the nickel species. For example, for the hydrogenation of unsaturated organic compounds zerovalent Ni^0 sites are needed.[117] On the other hand, there are catalytic reactions e.g. conversion of methanol to ethane,[118] selective NOx reduction[119-121] and lower olefins oligomerization[37,41,86,87,109,110,122-124] requiring nickel ions as active sites. Moreover, the oxidation state of the nickel ions appears to be crucial for the catalytic performance in these reactions.

In the case of the ethylene oligomerization catalyzed by Ni-based materials, extensive studies have been accomplished, and different opinions concerning the oxidation state of Ni have been expressed (Table 1). In erlier works on supported $NiO/Al_2O_3–SiO_2$ catalysts, isolated Ni^{2+} ions in a high coordinative unsaturation with Al^{3+} ions in the neighbourhood[71] or Ni^{2+} ions assisted by acid sites[69,70] were suggested to be the active sites. In a recent study, Martinez *et al.* proposed Ni^{2+} cations in exchange positions in Ni-Beta zeolite as active sites. The monovalent Ni^+ species were assigned the role of spectators.[100] Other authors considered that for Ni-Y highly dispersed Ni^0 is the catalytic site in the ethylene oligomerization.[96]

Table 1. Nature of the catalytic sites in Ni-based catalysts for ethylene oligomerization

Catalyst	**Catalyst treatment**	**Catalytic sites**	**Characterization method for Ni**	**Reference**
$NiO/Al_2O_3–SiO_2$	thermal	Ni^{2+} and Al^{3+}	ESCA, UV-Vis	71
Ni-Beta	thermal	Ni^{2+}	$FTIR/CO/C_2H_4$	100
Ni-Y	thermal	Ni^0	ESR	96
NiO/SiO_2	thermal; photochemical	low valent Ni and acid site	deuterium tracer	60
$NiO/\gamma\text{-}Al_2O_3$	thermal; photochemical	low valent Ni	EPR	72
Ni-X	thermal	Ni^+	ESR	37
Ni-clionoptilolite	thermal	Ni^+	ESR	134
Ni-SAPOs	H_2:thermal/photoreduction	Ni^+	EPR	135
Ni-CaY	thermal	Ni^+	ESR	38
$NiSO_4/Al_2O_3$	thermal	Ni^+	ESR	127
$NiSO_4/Al_2O_3$	thermal; CO reduction	Ni^+	FTIR/CO	86
$NiSO_4/Al_2O_3$	thermal	Ni^+ and acid site	FTIR/CO, XPS	87
$NiSO_4/Al_2O_3$	thermal	Ni^+ and acid site	FTIR/CO	84,85
$NiSO_4/SiO_2\text{-}Al_2O_3$	thermal	Ni^+ and acid site	FTIR/CO	88
Ni-MCM-41	thermal	Ni^+ and dehydrated Ni^{2+}	FTIR/CO	112

However, there are many more arguments supporting the view that low valent nickel ions, most likely Ni^+ species, are the sites responsible for the ethylene oligomerization. For example, a linear relationship between the rates of ethylene conversion and the Ni^+ concentrations in the catalyst has been reported in several studies.[37,38,125] In addition, it was observed that the reaction rate decreased when Ni^+ was further reduced to Ni^0.

Ni^+ is not a common oxidation state of nickel, but it can be produced by the reduction of Ni^{2+} ions present as extraframework sites in various microporous and mesoporous materials. According to literature data,[126,127] only isolated Ni^{2+} ions are able to be partially reduced to Ni^+. This behavior can be correlated with the oligomerization results. For example, using both exchanged and impregnated Ni-MCM-41, Lacarriere *et al.* showed that the catalytic sites for ethylene oligomerization are the nickel cations in exchange positions and that nickel oxide species are most probably inactive in this reaction.[114] A similar finding has been reported for NiO/B_2O_3-Al_2O_3,[74] Ni-Beta[100] and Ni-amorphous silica–alumina.[28]

Generally, the formation of Ni^+ ions is highly sensitive to the reduction methods and conditions, as well as to the support nature.[38,41,122,128] A number of methods have been used to transform Ni^{2+} into Ni^+: reduction with Na or Cs vapor, γ-irradiation at -196 °C, photo reduction by ultraviolet light at -196 °C under hydrogen, reduction with molecular hydrogen, CO and hydrocarbons. Dehydration under dry conditions at elevated temperatures is a very simple procedure, and it has been usually used in the oligomerization studies. It was suggested that the formation of the Ni^+ cations during the thermal treatment takes place through a dehydration mechanism.[121,126,129] In Ni-exchanged microporous and mesoporous aluminosilicates, the nickel ions are present in the 2+ oxidation state, surrounded by n H_2O molecules as ligands ($n \leq 6$) [130,131]. When the temperature is increased, the ligands are released[5,32] (eq. 1) and the water removed reduces Ni^{2+} to Ni^+ (eq. 2) :[121,126,129]

$$Ni^{2+}(H_2O)_n \rightarrow Ni^{2+}(H_2O)_x + (n-x)H_2O \qquad (1)$$

$$2Ni^{2+} + H_2O \rightarrow 2Ni^+ + 2H^+ + ½O_2 \qquad (2)$$

In order to explore the Ni ions, appropriate techniques, including deuterium tracer electron analysis, electron paramagnetic/spin resonance (EPR/ESR), or IR spectroscopy of probe molecules were employed. For example, Kimura *et al.* investigated the mechanism of the ethylene dimerization in the presence of NiO/SiO_2 by means of the deuterium tracer.[60] They suggested that the active sites consist of a low valent nickel and an acid. Elev *et al.* worked with NiO/γ-Al_2O_3 activated by thermal- and photoreduction with hydrogen.[72] EPR measurements on the reduced samples indicated the presence of low valent nickel among the active centers. Bonneviot *et al.* studied the dimerization of ethylene over Ni-exchanged X zeolite.[37] By means of EPR spectroscopy, they showed that the Ni^{2+} ions can be reduced to

Ni^+ by either thermal or photochemical treatment. Ni^+ ions are able to form complexes with olefin molecules and thus the catalyst becomes very active even at room temperature.

Choo *et al.* investigated the formation of monovalent nickel in Ni-zeolites, such as ferrierite, mordenite and clinoptilolite, using ESR spectroscopy.[132,133] A high reducibility of Ni^{2+} in zeolites was observed upon both thermal and hydrogen reduction. The g values of Ni^+ ions in ESR spectra, at about 2.1 and 2.5, are similar for all zeolite topologies. For Ni-clinoptilolite, Ni^+ sites can be also obtained via direct reduction of Ni^{2+} by ethylene at temperatures higher than 100 °C.[134] Over this catalyst, the conversion of ethylene to *n*-butenes reached a maximum at a reaction temperature of 350 °C. This temperature corresponds to the highest ESR intensity of Ni^+ species.

ESR-Ni^+ sites were also detected by other research groups in active oligomerization catalysts such as dehydrated Ni-SAPOs,[135] prereduced Ni-CaY zeolites[38] and $NiSO_4/Al_2O_3$.[86] For the last catalyst, Cai *et al.* showed that Ni^+ is formed by partial reduction of Ni^{2+} with ethylene. The reduction of Ni^{2+} to Ni^+ in $NiSO_4/\gamma\text{-}Al_2O_3$ was also performed by evacuation at 600 °C.[127]

IR spectroscopy of adsorbed CO is considered to be one of the most suitable techniques to explore the nature of nickel species because it permits simultaneous detection of Ni^{2+}, Ni^+ and Ni^0.[122,126,136] According to literature data, the C-O-stretching modes of nickel carbonyls appear in distinct spectral regions: 2220-2180 cm^{-1} for Ni^{2+}-CO, between 2160 and 2110 cm^{-1} for Ni^+-CO and below 2100 cm^{-1} for Ni^0-CO. This technique was used to examine the nature of the active sites in Ni-sulphated alumina,[84,87] Ni-Y,[112] Ni-MCM-41[112] and Ni-Beta zeolite.[100] According to Davydov *et al.* isolated Ni^+ species are the active sites in the oligomerization process.[87] These sites are formed in a reduction process (heating in vacuum or with CO at temperature not higher than 400 °C), in which Brönsted acid sites are involved.

Sohn *et al.* suggested that the active sites responsible for ethylene dimerization can be generated by thermal treatment at high temperature and they consist of Ni^+ and an acid site.[84] In a detailed study, Lallemand *et al.* used the IR spectroscopy to evaluate the effect of the thermal treatment on the oxidation state of nickel in Ni-Y and Ni-MCM-41.[112] It has been established that during the thermal activation under dry atmosphere, the Ni^{2+} ions were dehydrated or/and reduced to Ni^+ ions. The thermal reduction of Ni^{2+} to Ni^+ was effective in Ni-Y (Fig. 2), but it was only partial in Ni-MCM-41. It was also found that the catalytic activity in the ethylene oligomerization performed in batch mode, at 150 °C strongly increased when the catalyst activation temperature increased from 200 °C to 550 °C. Based on spectral and catalytic measurements the authors suggested that both Ni^+ and dehydrated Ni^{2+} species in Ni-MCM-41 catalyst are catalytic sites in ethylene oligomerization.

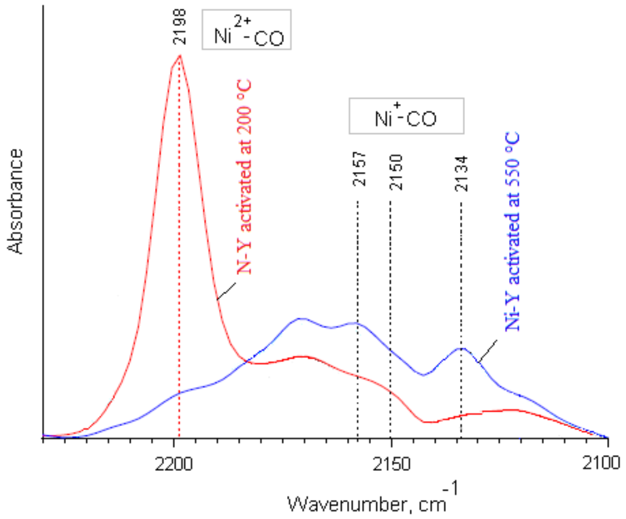


Fig. 2. DRIFT spectra (carbonyl region corresponding to the adsorbed CO at 30 °C on Ni-Y activated at 200 °C and 550 °C. Reproduced with permission from ACS

Note that, in most of published studies, to obtain effective catalysts for oligomerization, the Ni-based materials were thermoactivated before reaction at temperatures higher than 500 °C.

4. Catalysis and processes in ethylene oligomerization

The ethylene oligomerization over Ni-based catalysts has been carried out in wide ranges of temperatures (from 20 °C to 360 °C) and pressures (from 0.4 to 40 bar), in static, slurry or dynamic reactors. The reaction conditions, as well as the catalyst properties have a strong effect on the activity/productivity and the oligomer distribution (Table 2). NiO on supports are rather poor catalysts for ethylene oligomerization: the productivity was less than 3.5 g_{oligom} g_{catal}^{-1} h^{-1} and TOF values varried between 5 and 33 h^{-1}. Better results were obtained with Ni-exchanged alumina: productivity up to 11.5 g g^{-1} h^{-1} and TOF up to 1500 h^{-1}. Purely Ni-zeolites (Ni-Y, Ni-Beta, Ni-MCM-22) exhibited moderate activity, but the solids with microporous and mesoporous, i.e. Ni-Y (Si/Al = 30) and Ni-MCM-36 showed excellent behaviour with TOF of 10 500 h^{-1} and 16 000 h^{-1}, respectivelly. The best catalysts were the Ni-exchanged mesoporous materials with MCM-41 and MCM-48 topology. In batch mode, at 150 °C and 35 bar of ethylene, productivities between 110 and 158 g g^{-1} h^{-1} and TOF between 15 700 and 47 380 h^{-1} were reported.[111,114]

The nature of the oligomers depended on the catalyst, but also on the reaction mode and parameters. Depending on these factors, the ethylene oligomerization can be selectively directed to dimers (C4),[41,71,77-86,88,91,92] intermediate olefins (C6-C10)[43,102-104,109,111] or even to diesel-range products (C12-C18).[28,74,100] The effect of various elements on the oligomerization process will be discussed more in detail here below.

4.1. Role of the pore size of the catalyst

Among the properties of catalysts having a crucial effect on the activity and the stability, the porosity seemed to be the most important. We compared the catalytic behaviour of Ni-based catalysts with diverse topologies and porosities and the experimental data obtained under similar conditions are ploted in Fig. 3.[101-103,112,114]

Table 2. Comparison of catalytic performances in the oligomerization of ethylene of Ni-based catalysts with different compositions

Catalyst	Ni (wt%)	Reaction mode	T (°C)	P (bar)	Activity (g g^{-1} h^{-1})^a	TOF (h^{-1})^b	Oligomers (wt.%)				Reference
							C4	C6	C8	C10+	
NiO/SiO_2- Al_2O_3	3.9	flow	275	1.0	x^c	n.i.^{d}	81.8	16	1.7	0.5	69
	7.8	flow	275	1.0	x^e	n.i.	83.9	12.5	1.8	1.8	69
$NiO-ZrO_2/WO_3$	18	static	20	0.4^f	2.8	32.6	100	-	-	-	77,78
$NiO-ZrO_2/MoO_3$	3.9	static	20	0.4^f	0.4	21.5	100	-	-	-	80
$NiO/Al_2O_2-TiO_2/WO_3$	15.6	static	20	0.4^f	0.9	12.1	100	-	-	-	76
$NiO-ZrO_2/ SO_4^{2-}$	18	static	20	0.4^f	0.7	8.1	100	-	-	-	82
$NiO-TiO_2/SO_4^{2-}$	36.5	static	20	0.4^f	0.9	5.2	100	-	-	-	81
$NiO/Al_2O_3-SiO_2$	4	flow	40	20.7	0.325^g		50	16	13	21	62
$NiO/Al_2O_3-SiO_2$	3.6	batch	150	28	3.2	187	85.4	9.6	2.3	2.7	63
NiO/silica-titanate	n.i.	batch	150	11-28	3.2		13.2	20.7	16.7	49.4	73
$NiO/B_2O_3-Al_2O_3$	3.0	flow	200	10	0.33	23.1	73.8	20.2	5.1	0.9	74
	3.0	flow	200	40	n.i.		10	10	25	55	74
Ni-NaY	5.6	flow	70	41	0.4	15.0	67.3	32.7	-	-	97
Ni-Y	5.6	flow	60	28	0.3	11.2	67	13	5.5	14.5	98
Ni-NaY(Si/Al=2.8)	3.7	flow	115	35	25.1	1422	37	20	17	26	28
Ni-Y (Si/Al=31.5)	0.6	static	20	0.4^f	0.75	262	100	-	-	-	99
Ni-Y (Si/Al=30)	0.6	batch	50	40	30	10482	67	10	14	9	102
Ni-Beta(Si/Al=12)	1.7	flow	120	26	0.57	70	72.3	13.4	7.2	3.1^h	100
	2.5	flow	120	26	1.6	132	38.1	8.4	13.8	36.3^h	100
Ni-silica-alumina	0.27	flow	300	11.5	3.7	2873	72.2	14.1	6.2	3.4^i	104
Ni-silica-alumina	1.56	flow	110	35	1.9	266	27	17.6	25	30.4	105,106
Ni-silica-alumina	1.6	CSTR	160	35	11.5	1507	31	17	19	33	109
Ni-MCM-22	0.55	batch	150	40	2.2	876	81	5	13	1	103
Ni-MCM-36	0.5	batch	70	40	10	4193	81	8	6	5	103
	0.6	batch	150	40	46	16072	45	25	15	15	103
Ni-SBA-15	5	flow	120	30	1.0	42	n.i.	n.i.	n.i.	35.1	115
Ni-MCM-48	0.5	batch	150	35	113	47379	42	37	14	7	111
Ni-MCM-41 (3.5A)^j	2	batch	150	35	150	15723	45	33	15	7	114
Ni-MCM-41 (10A)^j	2	batch	150	35	158	16561	40	33	16	11	114
Ni-MCM-41	0.5	CSTR	30	20	3	1257	56	24	10	10	113
Ni/sulphated alumina	1.7	CSTR^b	50	0.7	6.1	752	88.8	11.2	-	-	41
$NiSO_4/Al_2O_3$	6.4	static	20	0.4^f	1.4	46	100	-	-	-	84
$NiSO_4/Al_2O_3-ZrO_2$	3.1	static	20	0.4^f	3.3	223	100	-	-	-	137

[a] $g_{oligomers}\ g_{catalyst}^{-1}\ h^{-1}$; [b] $mol_{C2H4}\ molNi^{-1}\ h^{-1}$; [c] ethylene conversion = 15%; [d] n.i. - not indicated
[e] ethylene conversion = 23.8%; [f] initial pressure; [g] $g_{oligomers}\ mL_{catalyst}^{-1}\ h^{-1}$ [h] 3.4-4% cracking products; [i] 4.1% cracking products, [j] pore diameter

As shown in this figure, the average activity, expressed in terms of oligomers quantity per unit mass of catalyst and time, strongly increased when the pore size of catalyst increased.

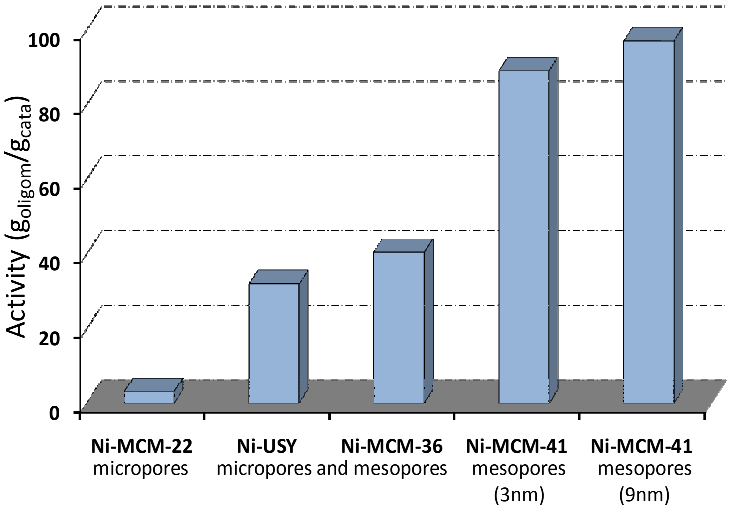


Fig. 3. Activities of Ni-exchanged materials with different topologies and pore sizes (1.5-2 wt% Ni; reaction conditions: 150 °C, 35 bar, 1 h of reaction, batch mode)

With Ni-MCM-22 (a zeolite having only micropores) a very small amount of oligomers was obtained.[103] The activity significantly increased in the presence of zeolites having both micropores and mesopores, such as Ni-dealuminated Y (Ni-USY) and Ni-MCM-36,[102,103] and it was much higher for the mesoporous Ni-MCM-41 materials.[112,114] Measurements done on the spent catalyst showed that the microporous catalysts have been very fast deactivated by pore blocking with heavy reaction products.[103] Note that similar rapid deactivation suffered the Ni-Y catalyst in the oligomerization reaction perfomed in dynamic mode.[97,98] In contrast, the large pores in nickel-mesoporous catalysts facilitate the diffusion of larger oligomers, which results in a low deactivation rate and higher activity of these catalysts. Similar high stability against deactivation has been exhibited by others catalysts with mesopores, like nickel/sulphated alumina[116] and Ni-silica-alumina.[106]

4.2. Role of the Ni concentration

The effect of the nickel concentration on the catalyst performances has examined in many studies.[69,74,88,100,106-108,114] Lapidus *et al.* compared catalysts with 5% and 10%NiO/SiO_2-Al_2O_3 in oligomerization reactions performed at 275 °C.[69] The ehylene conversion was 30.4 % and 23.8%, respectively. When they used Ni-Y zeolithe, the conversion was 39.2% and 29.4% for 4.7 wt% and 8.1 wt% Ni, respectively.[95]

Nicolaides *et al.* showed that the addition of nickel ions in excess of those introduced by ion-exchange in silica-alumina lead to major changes in the activity and selectivity of catalysts.[107] The ethylene conversion increased with increasing nickel content up to a maximum at a Ni content of 1.5 wt%. Above this nickel content the conversion fell fairly sharply. The 1-hexene selectivity mirrored the ethylene conversion level in that the higher the conversion, the lower was the selectivity. The same research group reported that at the lower nickel concentration the activity per nickel site is higher than at the higher nickel concentration.[108] In addition, increasing the Ni concentration resulted in a marked shift to a lighter product.

According to Heveling *et al.*, over Ni-Y, at 150 °C, the oligomerization proceeded by a selective growth reaction following Schulz-Flory statistics and the growth factor α increased with the nickel loading.[28] High nickel loadings favour the formation of diesel-range olefins in the product spectrum.

We studied the role of nickel loading on the activity in ethylene oligomerization using MCM-41 catalysts (Si/Al = 9, pore size of 3.5 nm) with different Ni concentrations, prepared by both ion exchange and wet impregnation.[114] The catalyst activity *vs.* Ni loading is plotted in Fig. 4. The activity increases when the nickel content increases up to 2 wt%. Then, the activity reaches a plateau and beyond 5.5 wt% nickel, the activity decreases. The decreasing activity observed for highly loaded Ni-catalysts was caused by partial blocking of pores by bulk NiO particles. The TPR measurements indicated that up to 2 wt% nickel in the material, nickel is present only as charge-compensating cation, and beyond, NiO appears. Similar remarks can be made for the TOFs obtained with different catalysts. It is about 15 000 h^{-1} for nickel loadings lower than 2% and it falls drastically to 5 600 h^{-1} for catalysts with 5.6 wt% of nickel. These results suggest that the active Ni species for oligomerization are the nickel cations in exchange positions and that nickel oxide species formed by impregnation are most probably inactive in this reaction.

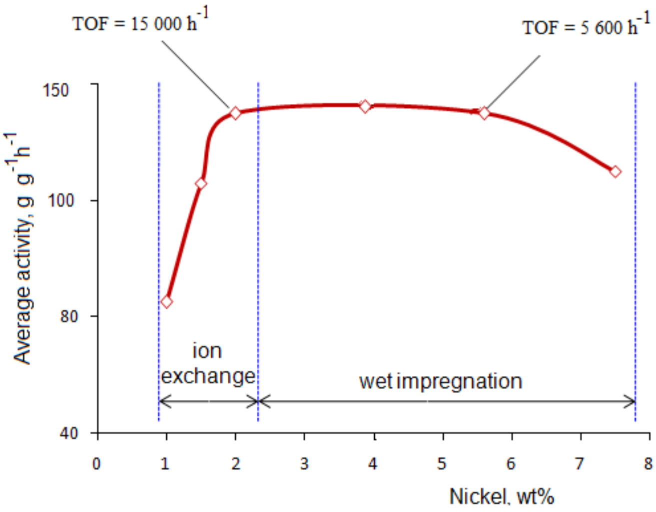


Fig. 4. Activity of Ni-MCM-41 catalysts in ethylene oligomerization as a function of nickel loading (reaction conditions: 150 °C, 35 bar, reaction time 1 h, batch mode). Adapted from ref. 114

Note that similar findings have been reported by Sohn *et al.* for $NiSO_4$-based catalysts,[88,91] Lavrenov *et al*. for NiO/B_2O_3-Al_2O_3[74] and Martinez *et al.* for Ni-Beta catalyst.[100] Thus, the activity of Ni-Beta (Si/Al = 12, at T = 120 °C, P = 26 bar, WHSV = 2.1 h^{-1}) increased linearly with increasing the Ni loading up to 2.7 wt% and then leveled off until a constant conversion of 85% was reached at loading above 5 wt%. Heveling *et al.* found that Ni-exchanged silica-alumina (0.73 wt% Ni) was superior in terms of conversion and TOF compared with Ni-impregnated silica-alumina (3.84 wt% Ni).[106] Based on these results, but without specifying the nature of the active species, they considered that the metal was more efficiently used in the ion-exchanged catalyst than in the impregnated one.

The Ni loading in catalyst also affected the product distribution. Thus, when the Ni concentration increased from 1.0 wt% to 2.5 wt% in Ni-Beta, the amount of butenes in products decreased from 69.9% to 38.1%, whereas the yield of C10+ oligomers increased from 2.1% to 37.2%.[100] With a Ni-silica-alumina catalyst, the dimers/trimers ratio varied linearly with the nickel content.[108]

4.3. Role of the acid sites

Generally, Ni-supported materials contain both Ni and acid catalytic sites. There is agreement that the Ni sites are indispensable for ethylene oligomerization. But, what is the role of the acid sites? A large number of studies showed that the acidity of catalyst is also crucial for this reaction. Thus, it was reported that the ethylene oligomerization activity of the nickel-exchanged silica–alumina is proportional to the acid strength of the surface.[97,104]

For catalysts prepared by the ion exchange of Ni^{2+} onto silica-alumina supports Lapidus *et al.* suggested that the catalytic behavior can be related to the quantity of acid sites present (i.e. the alumina content) in the mixed oxide support.[69,70] They suggested that the active sites in ethylene oligomerization include both Ni^{2+} ions and acid centers. Sohn *et al.* showed that the activity of NiO and $NiSO_4$ supported on different carriers can be closely correlated with their acid site density and strength.[75,85,88-93] As previously reported by Kimura *et al.*, they suggested that the active sites in ethylene dimerization consist of low valent Ni ion and acid sites.[60]

Davydov *et al.* showed the essential role played by the acid sites, which are required to promote the Ni^{2+}/Ni^{+} redox cycle and to stabilize the Ni^{+} ions involved in the ethylene oligomerization.[87] Ng et al. suggested that a Ni^+–H^+ couple is involved in the oligomerization mechanism of ethylene.[97]

In oligomerization studies performed under mild reaction conditions, in a slurry batch reactor, in the presence of Ni-AlMCM-41,[43] Ni-Y[102] and Ni-MWW[103] we found that both nickel and acid sites are required for the activation of this reaction. Moreover, the balance between the acid and nickel site densities is a key factor that influences the activity, selectivity, and stability of the catalyst (Table 3).

Table 3. Effect of the acidic properties of catalyst on the average activity

Catalyst	**Si/Al (mol mol^{-1})**	**Acidity[c] (mmol g^{-1})**	**Ni/acid site (mol mol^{-1})**	**Average activity (g g^{-1} h^{-1})[d]**
Ni-Y[a]	6	1.02	0.25	15
	15	0.58	0.29	20
	30	0.35	0.29	30
Ni-MCM-41[b]	10	0.72	0.14	21
	18	0.59	0.14	25
	26	0.45	0.19	41
	49	0.34	0.21	64

Oligomerization conditions: [a] 50 °C, 40 bar; [b] 150 °C, 35 bar; [c] from ammonia TPD; [d] $g_{oligom}\ g_{catal}^{-1}\ h^{-1}$

For Ni-based zeolites, a too high density of acid sites may be detrimental to activity by promoting the formation of long chain oligomers, responsible for pore blocking and catalyst deactivation.[102,103] In the case of Ni-containing mesoporous materials, we found that the amount of oligomers strongly increased when the acidic site concentration decreased from 0.72 to 0.3 mmol g^{-1}.[43] In addition, a too low acidity was detrimental for the catalytic activity. Indeed, a high acid/nickel ion sites ratio results in rapid surface deactivation of Ni-containing materials due to acid-catalyzed reactions, which are responsible for the formation of strong adsorbed long-chain oligomers.[43,103] Consequently, only a carefully selected acid sites density has a beneficial influence on the stability of Ni-based catalyst and implicitly on the oligomerization activity.

4.4. Effect of the temperature

The reaction temperature plays a decisive role in determining activity, stability and selectivity of catalysts. According to literature data, the catalyst performances changed with the temperature in different ways. Over narrow ranges of temperature, a single mode of variation was observed. Thus, Zhang and Dalla Lana reported that on nickel/sulphated alumina in a slurry reactor, the ethylene conversion decreased with the increase in reaction temperature for the range of 5-50 °C.[116] This decrease has been attributed to the lower ethylene solubility in solvent (n-heptane) and to catalyst deactivation at higher temperature. At low temperature high selectivity to 1-butene was attained, while the selectivity to C6 increased with temperature. Ng and Creaser found that on Ni-Y, at 40 bar, in a fixed-bed reactor, the reaction rate increased from 6.04 (at 50 °C) to 13.19 mmol g^{-1} h^{-1} (at 70 °C).[97,98] In CSTR mode, with Ni-SiO_2-Al_2O_3, at 35 bar, Heydenrych *et al.*, reported that the ethylene conversion slightly decreased between 120 and 160 °C.[109]

For broader ranges of temperature, polymodal dependences between the activity and the reaction temperature were observed. For example, working in a fixed-bed reactor, in the temperature range 40-360 °C, over both Ni-Y[100] and Ni-SiO_2-Al_2O_3,[106] Heveling *et al.* identified two distinct temperature regions of high catalytic activity. One was at a low temperature, a volcano-type curve with a conversion maximum at about 120 °C, and the other at a higher temperature (> 300 °C). For reactions performed in batch mode we found that the ethylene conversion followed volcano-type curves, with maxima at about 50 °C and 150 °C, for Ni-Y and Ni-MCM-41, respectively (Fig. 5).[43,102]

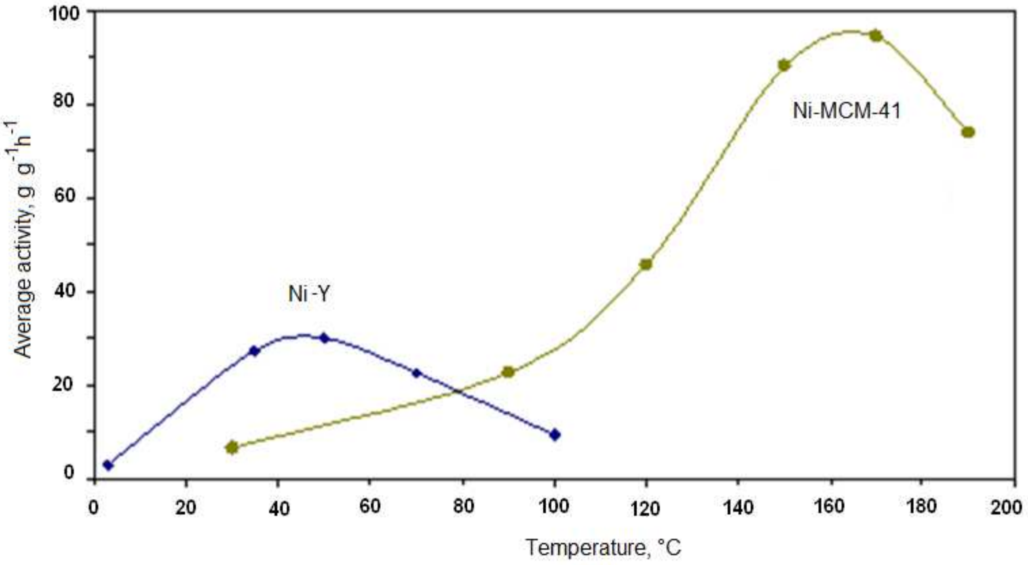


Fig. 5. Effect of the reaction temperature on the amount of oligomers (batch mode, reaction time 60 min, pressure 40 bar).

As shown in Table 2, the oligomers distribution depends on the reaction temperature. Thus, at near-room temperature ethylene was selectively dimerized to butene.[38,77-86,102,113] More generally, under mild conditions, on weakly acidic catalysts, the ethylene oligomerization was highly selective, resulting almost exclusively in olefins with an even number of carbon atoms.[43,100,105,109,111,114] In addition, a Schulz-Flory-type distribution (C4 > C6 > C8 > C10...) was typically obtained. Only traces of alkanes, aromatics, and odd number alkenes were present in the oligomeric products. At higher temperature, and especially in the presence of strongly acidic catalysts, a broad range of saturated and unsaturated hydrocarbons are formed, including both even- and odd-carbon products.[28,39,40] That is suggestive of the occurence of secondary cracking reactions which are catalysed by the acid sites. The acid sites are also considered to be responsible for two other main secondary reactions: the isomerization and co-oligomerization of primary products.[43,99,102,103,106] Consequently, the high values of temperature resulted in increased catalyst deactivation.[39]

In order to highlight the effect of the temperature on the product distribution, we summarized in Table 4 the results obtained in our laboratory with different catalysts. The contribution of the temperature is evident from the changes in the distribution of oligomers and the isomers inside each Cn olefin group of products. At low temperatures, a near Schulz–Flory-type product distribution was obtained over all catalysts. At higher temperatures, the oligomerization was mainly directed towards the formation of C6 and C8 or C10+ olefins. Among the butenes, the proportion of 1-C4 decreases rapidly with increasing reaction temperature. These results indicate that 1-butene is the initial product of ethylene oligomerization and that its acid-catalyzed isomerization to *cis/trans* 2-butene becomes prominent when the reaction temperature increases.

Table 4. Oligomer distribution vs. reaction temperature

Catalyst	**Temperature, °C**	**Selectivity, %**					**Reference**
		1-C4	**2-C4**	**C6**	**C8**	**C10+**	
Ni-MCM-41[a]	50	31	26	32	9	2	43
	100	16	40	31	11	3	
	150	10	42	27	15	6	
	200	3	26	15	36	20	
Ni-USY[b]	35	82	10	5	2	1	102
	50	21	47	10	14	8	
	70	10	44	9	22	15	
Ni-MCM-36[c]	70	38	43	8	6	5	103
	150	12	42	15	15	17	

[a] batch mode, 35 bar, n-heptane solvent; [b,c] batch mode, 40 bar, n-heptane solvent

As shown in Table 4, small amounts of olefins having more than 10 carbon atoms are formed. In order to further increase the chain length of the produced olefins, we combined the effect of the Ni-MCM-41catalyst with that of an acid catalyst (H-MCM-41).[114] In the presence of two catalysts, the distribution of oligomers was directed towards longer-chain olefins with the formation of heavier olefins up to C18, with a Poisson type distribution centered on C12 (Fig.

6). In addition, the productivity increased from 113 $g_{oligom}\ g_{catal}^{-1}\ h^{-1}$ for the oligomerization of ethylene over Ni-MCM-41 to 180 $g_{oligom}\ g_{catal}^{-1}\ h^{-1}$ for the co-oligomerization with Ni-MCM-41 and H-MCM-41.

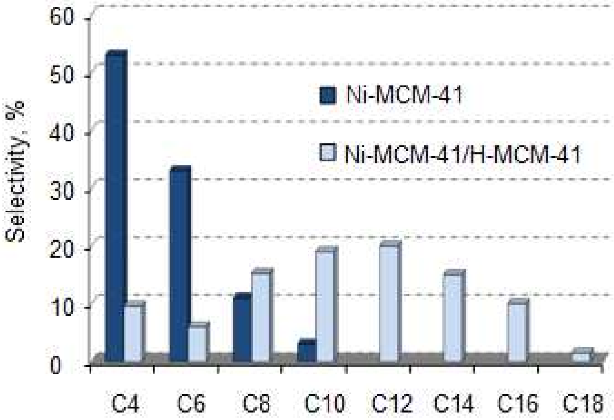


Fig. 6. Product selectivity in olefins oligomerization and co-oligomerization (150 °C, 34 bar of ethylene, *n*-heptane solvent)

4.5. Effect of the pressure

For reactions performed in the liquid phase, due to ethylene solubility dependence on pressure, the catalytic activity increased by increasing the olefin pressure. Thus, in slurry mode, with Ni-MCM-41, at 150 °C, using *n*-heptane as solvent, Hulea and Fajula found that the catalytic activity increased linearly when the ethylene pressure increased from 20 to 50 bar.[43] The favorable effect of the ethylene pressure was also emphasized when the oligomerization was performed in dynamic mode, in a fixed-bed reactor. For example, with reaction pressures in the range 10-35 bar, over Ni/silica-alumina, at 100 °C, the ethylene conversion increased from 5.4% to 41.9%.[107] In addition, the 1-hexene selectivity was the highest at the intermediate pressure of 15 bar. With the same catalyst, Espinoza *et al.* reported that the ethylene conversion slightly increased when the pressure increased from 11.5 to 26 bar.[39] Ng and Creaser evaluated the properties of Ni-Y zeolite at 70 °C in the pressure range of 7-40 bar.[97,98] The reaction rate (mmol g^{-1} h^{-1}) was 1.69 at 7 bar, 5.53 at 14 bar, 7.73 at 27.5 bar and 13.19 at 40 bar.

4.6. Kinetics

It is important to note that only few detailed reports on the kinetics of oligomerization reaction have been reported. The earlier researches on the reaction kinetics of ethylene were performed in the presence of Ni-Y zeolite and Ni-silica alumina, in fixed-bed type reactors.[39,98,124,139] Using IR techniques, Riekert found that the reaction over Ni-Y was of second order with respect to ethylene concentration and the activation energy was 88 kJ mol^{-1}.[138] Heveling *et al*. evaluated the activity of Ni-Y by analysis of product samples taken from reactor after 45 minutes of stream.[124] For an isothermal flow reactor model, at 150 °C, first order kinetics were found to be followed. First-order kinetic with respect to ethylene has also reported by Ng and Creaser on Ni-Y at temperatures ranging from 50 to 70 °C.[98] The apparent activation energy was observed to decrease from 58.6 to 42.1 kJ mol^{-1} with increase in time on stream. Espinoza *et al.* studied the oligomerization of ethylene over Ni-exchanged silica-alumina, in a fixe-bed type reactor over the temperature range 120-380 °C.[39] The reaction was found to be first order based on an isothermal integral flow reactor model.

Due to the high exotermicity of the oligomerization process, a stirred slurry reactor is more adapted than the fixed-bed reactor for establishing accurate kinetic data. Zhang and Dalla Lana investigated the reaction kinetics of ethylene oligomerization over nickel/sulphated alumina, in n-heptane solvent, at low temperature (5-50 °C) and atmospheric pressure in a laboratory slurry reactor.[116] A first-order dependence of ethylene consumption rate was determined, with an apparent activation energy of 16.3 kJ mol^{-1}. Heydenrych *et al.* measured the ethylene oligomerization kinetics on a Ni-exchanged silica-alumina catalyst, using a continous stirred tank reactor, under 35 bar and temperature varying from 120 to 180 °C.[109]

Three second-order reactions were used to correlate the observed rate of ethylene conversion and the Schulz-Flory-type product distribution: ethylene-ethylene dimerization, ethylene-oligomer reaction, and butene-butene dimerization. The activation energies for these reactions were 15.51, 11.71 and 66.6 kJ mol^{-1}, respectively. The maximum absolute rate of oligomerization of ethylene was 11.5 g_{oligom} g_{catal}^{-1} h^{-1}.

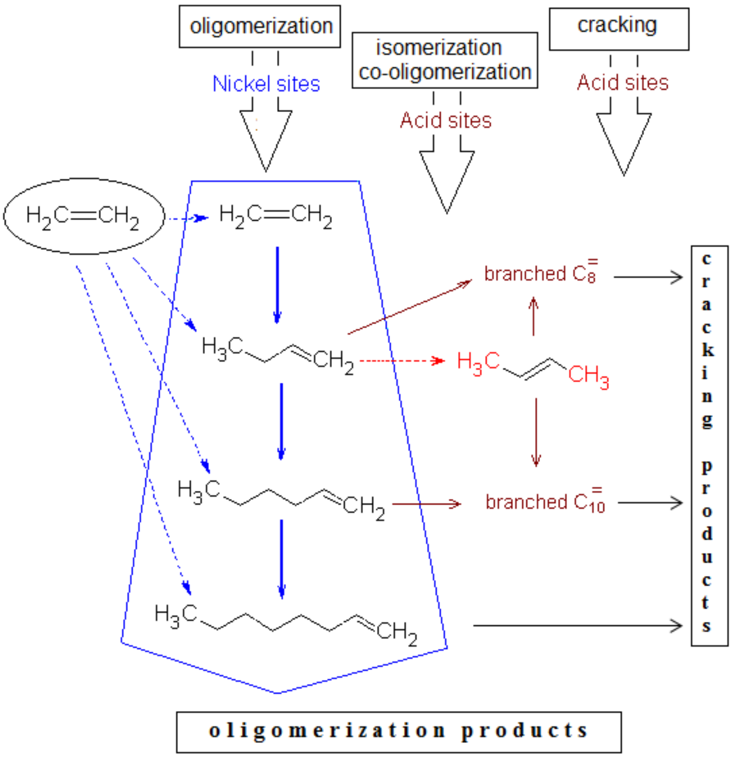
4.7. Catalyst deactivation in oligomerization processes

The catalyst deactivation (which is a major drawback in heterogeneous processes) has been evaluated in a number of studies on ethylene oligomerization. The deactivation resulted generally from strong adsorption of products on active sites and pore blocking with heavy molecules. Consequently, the catalyst lifetime is mainly governed by the pore size and reaction conditions. The microporous Ni-exchanged zeolites (Ni-Y, Ni-MCM-22) suffered very fast deactivation.[28,97,98,102,103] For example, NiY has lost about 50% of the initial activity after 2-3 h time-on-stream (tos), at reaction temperatures between 50 and 70 °C.[98] An exception was the Ni-Beta nanocrystalline zeolite, with high external surface.[100] This catalyst exhibited no signs of deactivation under reaction conditions (120 °C and 35 bar). In contrast, catalysts with mesopores, such as Ni-amorphous silica-alumina, Ni-mesostructured silica-alumina, Ni/sulphated alumina, showed very high stability against deactivation. Thus, using a Ni-exchanged silica-alumina catalyst, in a fixed-bed microreactor, at relatively low temperature (100-120 °C), high pressure (35 bar) and MHSV = 2, Heveling *et al.* reported excellent catalyst stability over 144 days of tos.[106] In order to compare the deactivation rates of a Ni-exchanged silica-alumina catalyst at different reaction conditions, Espinoza *et al*. monitored the ethylene oligomerization in a fixed-bed microreactor, at temperatures ranging from 240 and 380 °C and pressure from 1.7 to 26 bar.[39] The deactivation of the catalyst (between 50 and 70% over 100 h time on stream) was independent of the space velocity, but its rate increased with pressure and with temperature.

The performances of Ni-mesoporous materials have been also evaluated in pilot plants equipped with continous stirred tank reactors. Zhang *et al.* found that Ni/sulphated alumina exhibited very good oligomerization activity with no apparent deactivation at low temperatures (5-25 °C) during 34 h tos.[41] According to Heydenrych *et al.*, under more severe conditions (35 bar, 120-180 °C) Ni-exhanged silica-alumina exhibited only very little deactivation during experimental runs of 900 h tos.[109] Lallemand *et al*. reported that during catalytic tests performed at 30 °C and 35 bar, over 170 h on stream, Ni-MCM-41catalyst was highly active (ethylene conversion > 95%) and very stable to deactivation.[113]

4.8. Reaction pathways

As discussed above, the various product distributions obtained in the ethylene oligomerization on Ni-containing catalysts were mostly related to the reaction temperature and the nature of the active sites in catalyst.[28,43,74,88,97,100,102,103,112] The literature data suggest that several distinct rections occur, as shown in Scheme 2. The first reaction is based on the coordination chemistry on nickel sites. They act as active sites for both the initial oligomerization of ethylene and further oligomerization reactions involving butene–ethylene coupling, leading to linear olefins of medium-chain length. The second one is based on the acid catalysis. Over acid sites, the C4 and C6 olefins can be consumed through co-oligomerization reactions (mechanism involving carbenium ions), leading to the formation of octenes or higher branched olefins, respectively. These reactions are essentially favored by a stronger acidity or/and a higher acid sites concentration and higher reaction temperatures. The same factors are responsible for the isomerization of the initial product (1- butene, 1-hexene, …). The C4–C10 oligomers can be involved in further acid catalyzed reactions, leading to the formation of heavy hydrocarbons which are responsible for pore blocking and catalyst deactivation. The third type of reactions, occuring under severe conditions and involving the acid sites, consists in the cracking of the primary and secondary oligomers and H transfer.[74,100,104]



Scheme 2. Reaction pathway in the ethylene oligomerization process

5. Conclusions and outlook

This review, focusing on the catalytic behavior of Ni-based inorganic porous catalysts, shows through a number of examples the high potential of these materials for the ethylene oligomerization under mild conditions. NiO and $NiSO_4$ supported on mineral oxides, Ni-exchanged zeolites and mesoporous silica-alumina are the catalysts discussed in this paper.

After this extensive discussion, some concluding remarks can be done:

(i) Generally, the NiO-based catalysts showed inferior catalytic behavior compared to that exhibited by the Ni-exchanged porous materials.

(ii) The active sites are most probably Ni^{+} and dehydrated Ni^{2+} isolated species. Both can be easily obtained by thermal treatment at high temperature.

(iii) The activity and the lifetime of catalysts mainly depend on their pore topology and pore size. Microporous materials deactivate faster by pore blocking with heavy products.

(iv) The catalysts with mesoporous structure showed the best behaviour: TOF up to 47 000 h^{-1} and productivity higher than 150 g_{oligom} g_{catal}^{-1} h^{-1}. The high activity and the deactivation stability were ascribed to their mesoporous texture and to their very high nickel site dispersion. It is important to note that in terms of TOF (see Table 2), these materials exhibited behavior comparable to that showed by the nickel complexis in homogeneous catalysis (Table 5).

(v) Oligomerization is a flexible process: dimers, medium olefins or long-chain hydrocarbons can be obtained by tuning the catalyst properties (i.e. nickel sites - acid sites balance) and reaction conditions. In order to shift the products to olefins C10+, the oligomerization on Ni-catalysts can be coupled with co-oligomerization reactions involving the primary olefins over an acid catalyst.

(vi) 100-150 °C and 30-40 bar seem to be the optimal ranges for the temperature and the pressure, respectively.

(vii) The stirred slurry L-S system is the most adequate mode for performing the oligomerization.

(viii) The main drawback of these catalysts consists in their sensibility to poisoning with molecules such as water, carbon monoxide, acetylene, butadiene, oxygen, sulfur compounds.[62,112]

Despite the large number of studies and the remarkable results in this field, no industrial oligomerization application based on these catalysts was developed until now. The main research challenge is to produce the knowledge necessary to design the “ideal” catalyst and large-scale oligomerization processes.

Table 5 . Catalytic performances in ethylene oligomerization of Ni^{II} complexes with different ligands

Ligand	Cocatalyst	TOF (h^{-1})	Ref.
o-(Diphenylphosphino)benzoic/acetic acid	-	6 500	139
Aryl-substituted α-diimines	Modified MAO[a]	53 000-110 000	140
2-Pyrazolyl substituted 1,10-phenanthroline derivatives	MAO	1 300-9 900	141
N-[(2-Chlorophenyl)methylene]-N-(1-pyridine-2ylethyl)-amine	MAO	9 500	142
2-[(Diisopropylphosphino)methyl]-pyridine	MAO	9 000	142
Modified α-nitroketonate	MAO	26 600-41 300	143
α-Diimines	MAO	17 400-69 100	144
Phosphinoimines	MAO or $AlEtCl_2$	7 000- 61 000	145

[a] MAO = methylaluminoxane

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