Ethylene selective dimerization on polymer complex catalyst of Ni(4,4′-bipyridine)Cl$_2$ coactivated with AlCl(C$_2$H$_5$)$_2$

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Abstract

The activity and selectivity of several catalysts based on Ni(4,4′-bipyridine)Cl$_2$ complex co-activated with AlCl(C$_2$H$_5$)$_2$ and supported on different molecular sieves such as Y, L, mordenite, mesoporous MCM-41 and on amorphous silica–alumina utilised in the dimerization of ethylene at 298 K and initial pressure of the monomer 12 atm is presented. Chemo- and stereo-selectivity effects expressed as selectivity for dimers and oligomers, and respectively, the concentration of 1-C$_4$H$_8$ in C$_4$H$_8$ fraction and the molar ratios 2-*trans*-C$_4$H$_8$/2-*cis*-C$_4$H$_8$ are discussed. The results are correlated with the steric and diffusion hindrances induced by the micro- and meso-porous structure respectively, of the porous solid matrix.
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1. Introduction

The heterogeneizing of homogeneous transition metal complexes by their synthesis inside the nanometer-size voids of porous hosts is currently under study as functional mimics of enzymes [1–7]. Heterogeneized complexes present high activity and selectivity when utilised as catalysts [8–16] or as electrocatalysts [17–19].

Metal chelate complexes, such as Fe, Cu, Co, Ni—phtalocyanines and metal-Salen encapsulated in the supercage structure of synthetic faujasite-type zeolites X or Y, have been extensively studied as "ship-in-a-bottle" zeolite-based catalysts and they were tested in hydrogenation, regio- and enantio-selective oxidation of olefins and as catalysts for fine chemical synthesis [1–3,6,7,10–12,18–21].

Heterogeneized complexes on zeolite supports were utilised relatively less for dimerization and oligomeriza-tion of light olefins. Nickel complexes with phosphine and acetylacetonate ligands co-activated with aluminium alkyls solved in hydrocarbons [15,22–31] or impregnated on oxide supports SiO$_2$, Al$_2$O$_3$, SiO$_2$–Al$_2$O$_3$ [11,21,32–34] were mainly utilised for such reactions involving chain growth. In homogeneous catalysis, the oligomerization of olefins has already been concretised in several processes with industrial application such as DIMERSOL (IFP) [35–38], ALPHAB-UTOL (IFP) [39,40], IDEMITSU [40], Gulf [41], ETHYL CO [41], SHOP (SHELL) [42]. The DIMERSOL process, which is performed in the presence of a Ziegler–Natta-type catalyst based on nickel co-activated with an alkyl aluminium compound, produces hexenes, heptenes and octenes and was developed in three variants: DIMERSOL E yielding high-octane number gasoline by oligomerization of C2–C3 fraction, DIMERSOL G specific for total oligomerization of propylene to reformulated high-octane number gasoline and DIMERSOL X for the oligomerization of C4 fraction [37,38]. The ALPHABUTOL process, also developed by IFP, allows reaching 80–85% conversions of ethylene to dimers, with high selectivity to 1-butene (93%) at 50–55 °C,

2.4–2.8 Mpa, 5–6 h reaction time, in the presence of titanium complex using tri-ethyl-aluminium as co-catalyst [39,40]. In both processes, the catalyst is continuously injected in the feed and it is removed from the reaction products by vaporising the liquid withdrawn from the reactor in two steps, first in a classical exchanger and then in a thin-film evaporator [37–40]. The recovery of the catalyst is not stated.

The construction of coordination polymers formed by open supramolecular coordination networks from molecular blocks of Me(4,4′-bipyridine)X_2 (Me=Fe, Co, Ni, Cu; X=Cl, NO_3, ClO_4, N_3, O_2CCF_3) were reported, recently being crystalline materials having pore size, shape and functions. They are stable up to $400\,^\circ C$ and their structure is a no-interpenetrating two-dimensional network containing transition metal centres octahedral coordinated by four bridging chlorine and two bipyridine ligands in *trans* positions [43–47].

To our knowledge, until now there is no information concerning the catalytic activity of the above-mentioned complexes. Therefore, based on the fact that Ni complexes are already known as active catalysts in olefin oligomerization, we considered interesting to use Ni(4,4′-bipyridine)X_2 polymer complex as catalyst for ethylene oligomerization. We assumed that such complex co-activated with $AlCl(C_2H_5)_2$ could present specific catalytic activity due to the accessibility of nearly all transitional metal atoms. Special effects of selectivity might be obtained if such coordinative complex would be embedded in a porous matrix-like molecular sieves. The interaction of the active complex species with the crystalline field of the molecular sieve lattice induces a steric hindrance, which may affect both the symmetry of the complex and its interaction with the substrate and could be responsible for its selectivity properties. We report herein the activity and selectivity in ethylene dimerization for some complex catalysts Ni(4,4′-bipyridine)Cl_2 co-activated with $AlCl(C_2H_5)_2$ synthesised in the presence of zeolite L, mordenite (M), zeolite Y, MCM-41 molecular sieve and amorphous silica–alumina (SiAl).

2. Experimental

2.1. Catalyst preparation

All chemicals utilised for catalyst preparation are as purchased without purification: $NiCl_2\cdot6H_2O$ pa (Merck), 4,4′-bipyridine pa (LOBA FEINCHEMIE), $AlCl(C_2H_5)_2$ 98% (Merck–Suchardt). The supports zeolite L (Si/Al = 3.25), mordenite (M) (Si/Al = 5), zeolite Y (Si/Al = 2.31) and silica–alumina (SiAl) (Si/Al = 3.2) were synthesised by the Institute of Research for Petroleum Refining and Petrochemistry (INCERP)–Ploieşti–Romania and MCM-41 (initial ratio Si/Al = 30) was synthesised by S.C. Zecasin, SA, Bucharest, Romania. Before the preparation of supported complex catalysts, the supports were calcined at $460\,^\circ C$ during 4 h.

Ni(4,4′-bipyridine)Cl_2 was prepared according to the method described by Zhang et. al. [46]. Thus, a methanol solution of 4,4′-bipyridine (31.2 mg; 0.2 mmol; 12 ml methanol) was slowly added dropwise to a stirred aqueous solution of $NiCl_2\cdot6H_2O$ (47.5 mg; 0.2 mmol; 15 ml distilled water). A light single-phase pale green–yellowish polycrystalline sample was obtained. The insoluble product was filtered, washed with distilled water, methanol and acetone and further dried under vacuum. This method yielded 65–68% Ni(4,4′-bipyridine)Cl_2.

The supported complex catalysts were prepared according to the method described above by adding the support powder (0.32–0.35 g) in the $NiCl_2$ solution at the beginning of the preparation, thus allowing to obtain a content of 3.5–3.8 wt.% Ni in the final solid. The obtained solid was washed with distilled water, methanol and acetone to remove the weakly hold amounts of un-reacted $NiCl_2$ and 4,4′-bipyridine from the surface of the support. In this paper, the supported complex catalysts are referred to as K/S, where S is the abbreviation of the name of the support, e.g. L, M, Y, SiAl, and MCM-41, respectively.

2.2. Catalysts characterization

Ni(4,4′-bipyridine)Cl_2 was characterized by elemental analysis, XRD, diffuse reflectance UV–vis, and FTIR spectroscopy.

Elemental analysis was performed on a Carlo Erba equipment. The XRD analysis was performed with a Philips equipment using Cu Kα radiation. All measurements were made in a 2θ range of 5–80° at the operating power of 40 kV/40mA. The refinement of the diffraction patterns was performed using JADE (Windows) software.

The diffuse reflectance UV–vis spectra were recorded at room temperature with a JASCO V570 spectrometer in the range 250–850 nm. The spectrometer is equipped for reflectance studies with an integration sphere coated with MgO taken as a reference. Infrared spectra in the region 400–4000 cm^{-1} were recorded on a Bio–Rad FTS 135 spectrometer. Samples were prepared using the KBr disc technique. Resolutions of 8 cm^{-1} and 16 scans were used.

2.3. Catalytic activity tests

The catalytic activity tests were performed in static regime at 298 K, under pressure in a 100 ml stainless steel autoclave provided with a magnetic stirrer, using an amount of 0.2 g of catalyst. The initial pressure of ethylene was 12 atm. Coactivation was realised in situ using the appropriate amounts of $AlCl(C_2H_5)_2$ in order to yield a molar ratio Al/Ni = 5/1 in the catalyst. The experiments were stopped after different reaction times, and the gaseous phase from the autoclave was analysed by gas chromatography. The remaining solid catalyst was washed with *n*-heptane and the extract containing *n*-heptane, oligomers and traces of ethylene and butylenes

Table 1
Results of elemental analysis for Ni(4,4′-bipyridine complex)Cl_2

Composition (wt. %)	C	H	N	Ni
Calculated	42.00	2.80	9.80	20.55
Experimental	41.30	3.15	8.96	20.42

solved in the liquid phase was also analysed. Ethylene (99% purity) produced at PETROBRAZI, Ploieşti, Romania, was used as reactant. The analysis of the reaction products was performed on a thermoquest chromatograph equipped with FID detector, using a capillary column Al_2O_3-Plot (30 m length).

3. Results and discussion

The elemental analysis of the synthesized complex Ni(4,4′-bipyridine)Cl_2 gives the results presented in Table 1 comparatively to the calculated values. The slight discrepancy between the observed and calculated C, H, and N values is likely caused by the presence of water molecules in the crystal lattice.

The powder XRD analysis of the neat complex gives the values $a = 11.974$; $b = 11.335$; $c = 3.584$ in agreement with the data published [47]. The complex has an orthorhombic symmetry, belonging to space group C_{mmm} (N° 65).

The electronic spectrum of the complex (Fig. 1) presents the characteristic bands for two d–d spin, allowed transitions: υ_1 ($^3A_{2g} \rightarrow {}^3T_{1g}$ (P)) at 409 nm and υ_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$) at 713 nm. The band at 298 nm is due to the charge transfer from ligand to metal. The other bands noticed correspond to π–π* transitions characteristic to the ligand [48]. This bands are also noticed in the spectra of the supported complex catalysts, e.g. K/Y, and respectively K/MCM-41. Their intensity is lower due to the low concentration of complex in the
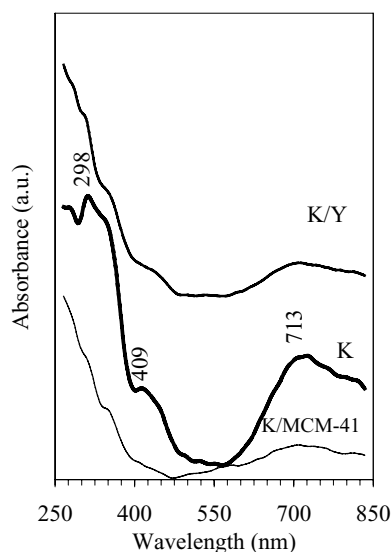
catalyst. The bands characteristic for Ni^{2+} in octahedral coordination appear at wavelengths higher than 1000 nm [49] and are not shown in Fig. 1.

The FTIR spectrum of the complex (K) presents the main bands characteristic to 4,4′-bipyridine ligand [50], which are a little bit shifted and split due to the coordination of the ligand to the metallic ion (Fig. 2). In the spectra of the supported complex catalysts the bands corresponding to the complex are overlapped by the strong bands of the carrier. As an example, in Fig. 2, the spectrum of K/Y is presented and compared to the spectra of the neat complex and of the parent zeolite. Several new bands appear in the regions where the neat complex presents its highest intensity bands, e.g. 637, 809, 1420, 1609 and 2366 cm^{-1}. Their intensity is not too pronounced, since the amount of the complex on the support is rather small (19.2 wt.%). The bands of the complex at 494 cm^{-1} and those in the region 1000–1223 cm^{-1} are overlapped by the bands corresponding to the support at 484 and 1006–1110 cm^{-1}, respectively. Due to this overlapping, in the spectrum of the supported complex only broader and higher intensity bands compared to those of the parent zeolite are noticed at 484 and 1028 cm^{-1}. In the spectrum of the supported complex, the vibrations corresponding to the hydroxyl groups have a low intensity and the bands appear to be shifted to higher wavenumbers, e.g. 3555 and 3627 cm^{-1} compared to 3140 cm^{-1} and 3446 cm^{-1} in the spectrum of the parent zeolite, respectively. The bands corresponding to Ni–O vibrations appear in the near infrared region of the spectrum, which was not investigated.

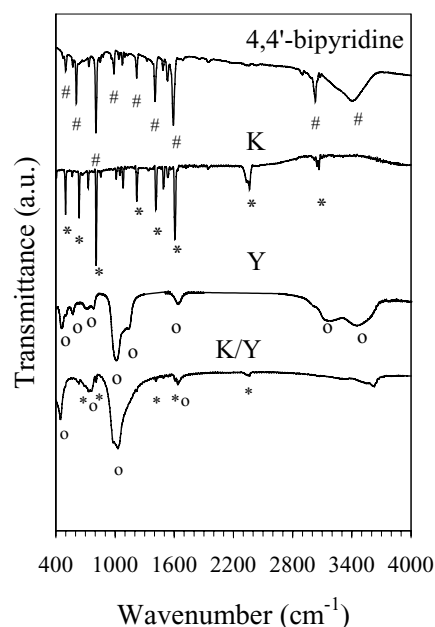The determinations of the activity and selectivity for ethylene dimerization under static regime in the presence

Fig. 1. DR-UV–vis spectra of K, K/Y and K/MCM-41.

Fig. 2. FTIR spectra of 4,4′-bipyridine, K, Y, and K/Y (most intense bands: ligand—(#); complex—(*); Y zeolite—(○).

Table 2
Results of the activity tests for ethylene dimerization. Complex catalyst Ni(4,4′-bipyridine)Cl$_2$ co-activated with AlCl(C$_2$H$_5$)$_2$; molar ratio Al/Ni = 5/1, T = 298 K, initial pressure of C$_2$H$_4$ = 12 atm, reaction time = 30 min

Catalyst	K	K/L	K/M	K/Y	K/MCM-41	K/SiAl
C$_2$H$_4$ conversion (%)	7.5	4	9	13.4	37	3.2
Intrinsic activity[a] $\left[\dfrac{\text{moles of C}_2\text{H}_4 \text{ transformed}}{\text{moles of Ni} \cdot \text{h}}\right]$	10.8	31.7	72.5	110.1	305.3	26.4
Selectivity to C$_4$H$_8$ (%)[b]	89	91	93	86	84	74
% 1-C$_4$H$_8$ in n-C$_4$H$_8$ fraction	88.8	65.5	64.3	50	16.7	37.5
$\left[\dfrac{trans\text{-}2-\text{C}_4\text{H}_8}{cis\text{-}2-\text{C}_4\text{H}_8}\right]$	1.4	2.5	1.9	1.7	2.0	2.2
Selectivity to oligomers C$_{5+}$ (%)[b]	0.8	0.3	0.6	1.9	5.8	12.8

Equilibrium composition at 298 K: %1-C$_4$H$_8$ in n-C$_4$H$_8$ fraction = 2.5%; $trans$-2-C$_4$H$_8$/cis-2-C$_4$H$_8$ = 3.22.

[a] The intrinsic activity was calculated taking into account the bulk Ni amount in the catalyst sample. The concentration of complex in supported catalysts was 19.2 wt.%. For all the tests 0.2 g catalyst were used.

[b] The carbon unbalance is due to the formation of by-products through side reactions such as disproportionation.

of Ni(4,4′-bipyridine)Cl$_2$ complex co-activated with AlCl(C$_2$H$_5$)$_2$, both unsupported and dispersed on different carriers are presented in Table 2.

Under identical reaction conditions the supported complex catalysts are more active than the unsupported complex, the catalytic activity is decreasing in the following order:

K/MCM − 41 > K/Y > K/M > K/L > K/SiAl > K.

The lower activity of K/SiAl may be a consequence of the fact that on the amorphous support the dispersion of Ni active sites is not distributed systematically as it is on the crystalline supports. Besides that, the highest selectivity of this catalyst for oligomer formation as well as its lower selectivity for 1-C$_4$H$_8$ and cis-2-C$_4$H$_8$ could be related to a cooperative effect between Ni and protonic sites of silica–alumina support.

In the reactions performed during 2 h under constant pressure of ethylene, e.g. 12 atm, by adding successive amounts of reactant, the catalytic activity varied insignificantly and the conversion values were almost identical to those determined after the first 30 min. In these experiments, the selectivity to n-C$_4$H$_8$ decreased slightly (Fig. 3a) while the selectivity for oligomers increased to 2.8% on the unsupported complex catalyst, being 2.6–5.2% for the complex catalyst supported on microporous zeolites, 12.4% for the complex supported on MCM-41, and respectively 15% for the complex supported on amorphous carriers (silica–alumina) (Fig. 3b).

Fig. 4 shows the results of the activity tests as a function of the reaction time. The complex supported on mesoporous solid MCM-41 presents an outstanding catalytic activity; ethylene conversion reaches 73.4% after a reaction time of 2 h. For all the other catalysts, ethylene conversion increases linearly in time up to 40–50% after 5 h for K, K/L, K/M, K/Y and respectively to 20% for K/SiAl (Fig. 4a). The relatively low conversions in the range 4–13.4% after 30 min reaction time and respectively 40–50% after 5 h reaction time for the complex catalysts supported on microporous zeolite
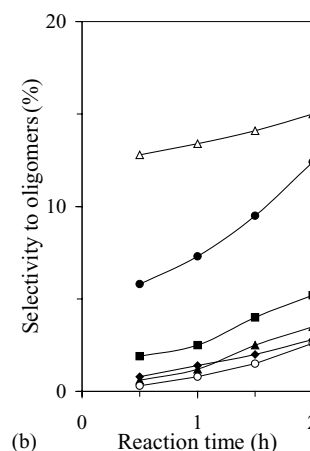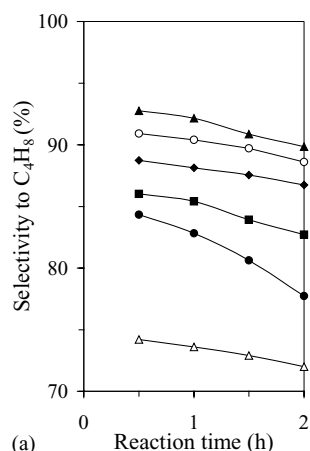

Fig. 3. Variation of the selectivities to n-C$_4$H$_8$ (a) and oligomers (b) as a function of the reaction time in catalytic tests performed under constant pressure of ethylene pC$_2$H$_4$ = 12 atm, T = 298 K, 0.2 g complex catalyst Ni(4,4′-bipyridine)Cl$_2$ coactivated with AlCl(C$_2$H$_5$)$_2$ ratio Al/Ni = 5/1 (◆) K; (■-) K/Y; (▲) K/M; (●) K/MCM-41; (○) K/L; (△) K/SiAl.

carriers as well as the limited conversion obtained for the complex supported on MCM-41, e.g. 37% after 30 min and respectively 73.5% after 5 h may be a consequence of the "secondary shape selectivity" effect. This effect is due to the strong adsorption of the oligomer by-products on the active sites, which leads to their partial blockage and restricts either the access of ethylene to the active zones or/and the internal back-diffusion of the butylenes from the pores to the gas phase [51].

As it is shown in Fig. 4b, all catalysts supported on microporous zeolites presented remarkable selectivity towards *n*-butylene formation. The low variations of this selectivity follow the reverse order of the increase of the catalytic activity. The catalysts that showed the lowest selectivity for *n*-butylene formation accompagnied by an enhancement of the selectivity for oligomers (see data in Table 2) are K/MCM-41, and respectively K/SiAl. In the case of K/MCM-41 this fact could be expected due to the mesoporous structure of the support, while in the case of K/SiAl the higher acidity of the support could be held responsible for this behaviour.

Fig. 4c shows that the unsupported complex presents a peculiar selectivity towards 1-butylene formation (e.g. the

concentration of $1-C_4H_8$ in C_4H_8 fraction is varying from 89.6% after 5 min reaction time, to 71.4% after 5 h value not presented in the figure). The catalytic systems supported on microporous zeolites and respectively amorphous silica–alumina, whatever is the carrier, present a moderate selectivity towards 1-butylene formation, the highest amount of 1-butylene in C_4H_8 fraction being in the range 40–65% depending on the catalyst. The lower values of the concentration of $1-C_4H_8$ in C_4H_8 fraction found for supported complex catalysts comparatively to the one obtained for the unsupported complex might be due to the specific adsorptive properties of the supports, which favour the adsorption of $1-C_4H_8$ on the catalytic mass and thus the isomerization of the double bond. The different initial concentrations of $1-C_4H_8$ in C_4H_8 fraction for supported complex catalysts are probably influenced by the spatial hindrances for the formation of the intermediates and the reaction products, and the internal molecular traffic for butylenes isomers, restrictions imposed by the characteristic porous structure of the supports. The concentration of $1-C_4H_8$ decreases linearly in time, this decrease being around 10% after 3 h reaction time, however, these values are at least 10 times higher than 2.5%, value specific for thermodynamic equilibrium at 298 K. From these data, it may be seen that for all catalysts, except K/MCM-41, 1-butylene is the product preferentially formed in the initial stage of the process and it is subsequently transformed into 2-butylene through a secondary reaction of isomerization. These results suggest that the reaction involving the migration of the double bond, which is slower than the increase of the carbon chain, is produced due to the adsorption of the alkyl-dimer intermediate on the catalytic active site, probably as a π-methyl–allyl complex having "sin" or "anti" conformation that may be stabilised by generating $1-C_4H_8$ or $2-C_4H_8$ *cis-* and *trans-*, respectively, as indicated in Scheme 1.

Similar observations may be made concerning the molar ratio $2-trans-C_4H_8/2-cis-C_4H_8$, whose variation in time for all catalyst is presented in Fig. 4d. For all catalysts this ratio has values lower than the one corresponding to thermodynamic equilibrium, expressing the catalysts tendency towards the production of higher amounts of $cis-2-C_4H_8$ isomer than at equilibrium. The formation of $cis-2-C_4H_8$ is most favoured by the unsupported complex and less favoured by K/SiAl. In these two cases, the ratio between *trans-* and *cis-*isomers is constant in time. After one-hour reaction time, K/MCM-41 leads to ratios similar to those obtained with the unsupported complex. For catalysts supported on microporous supports, the selectivity for $cis-2-C_4H_8$ decreases with the reaction time, proving that the rate for *cis-*isomer formation is higher due to steric hindrances [52]. It is noteworthy that excepting K/SiAl, after 5 h reaction time there are no differences between the behaviour of the unsupported complex and the catalysts supported on crystalline carriers.

The reaction products obtained on complex catalysts supported on Y, MCM-41, and silica–alumina, respectively, which lead to the highest amounts of oligomers, were
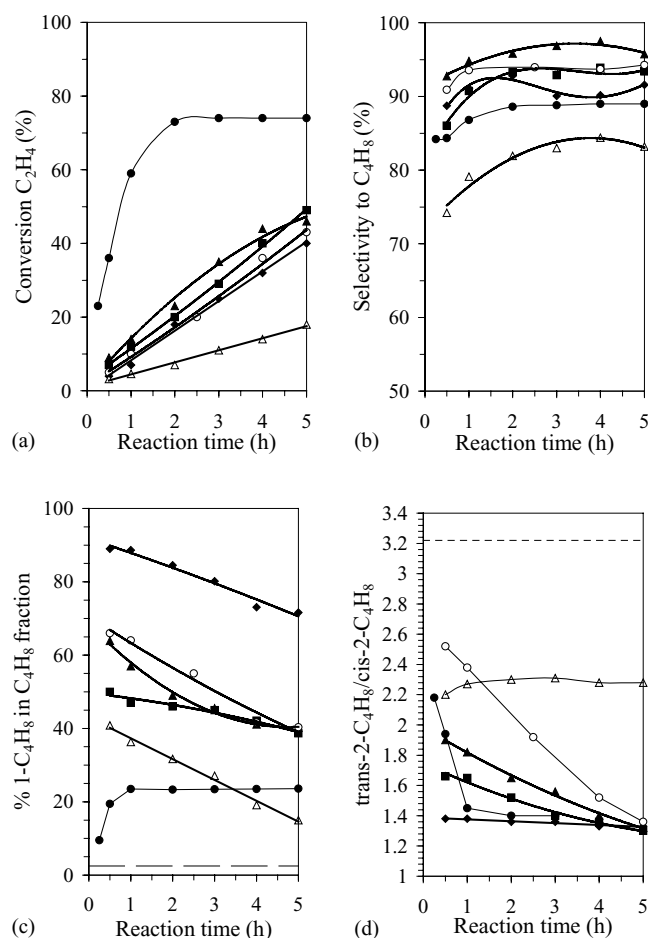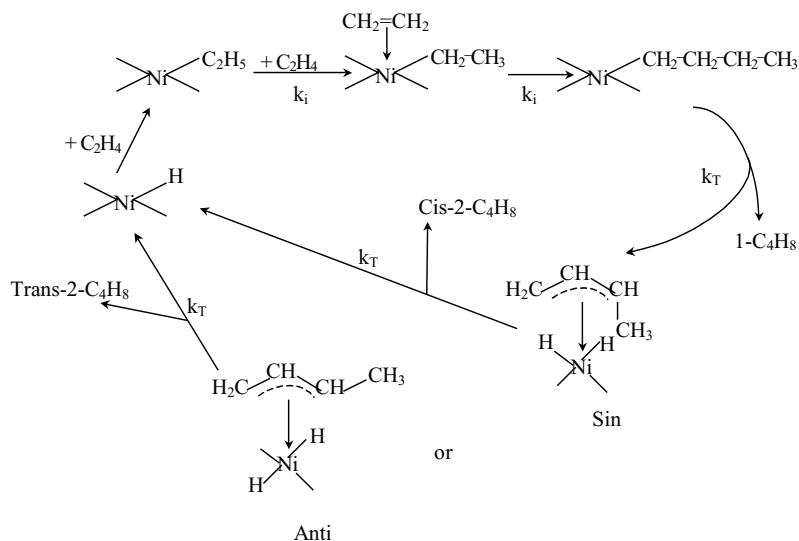

Fig. 4. Time dependency of the catalytic activity: (◆) K; (■-) K/Y; (▲) K/M; (●) K/MCM-41; (○) K/L; (△) K/SiAl thermodynamic equilibrium.

Scheme 1.

submitted to a more detailed analysis whose results are presented in Fig. 5. Based on the mechanism presented in Scheme 1, the selectivity to dimers is higher when $k_T > k_i$; the formation of oligomers is enhanced when $k_i \approx k_T$.

In the liquid fraction, the amount of oligomers with odd number of carbon atoms was less than 5%. The complex supported on Y zeolite presented an appreciable selectivity towards C_6 oligomers formation. The complex dispersed on mesoporous support MCM-41 leads non-selectively to almost equal amounts of C6, C8, and C10+ oligomers, while higher amounts of heavy oligomers (C8 and C10+) were obtained in the case of the complex supported on the amorphous silica–alumina.

In order to determine if leaching of the complex $Ni(4,4'-bipyridine)Cl_2 \cdot 5AlCl(C_2H_5)_2$ occurred, the liquid fraction obtained in the catalytic tests after 5 h was submitted to the appropriate chemical treatment followed by UV–vis spectroscopy analysis to investigate the presence of Ni and Al traces. For all catalysts the results confirmed the absence of leaching, since the concentration of Ni in liquid fractions is under the detection limit, and only traces of Al (e.g. 10–20 ppm) could be detected.
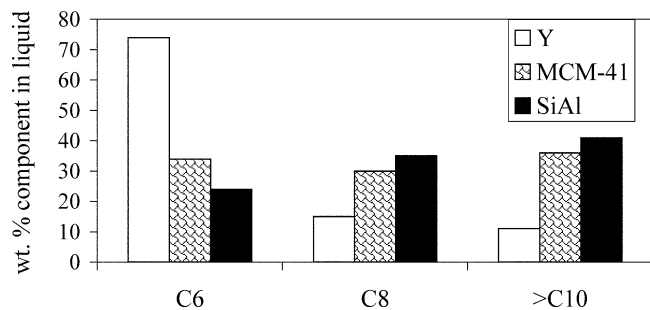
4. Conclusions

$Ni(4,4'-bipyridine)Cl_2$ polymer complex co-activated with $AlCl(C_2H_5)_2$ and dispersed on micro- or mesoporous supports is an active and selective catalyst for ethylene dimerization to n-butylenes under conditions of temperature and pressure milder than in the case of ALPHABUTOL process [39,40]. However, these Ni catalysts are less selective for 1-butylene compared to the Ti catalyst used by ALPHABUTOL.

The polymer complex structure, in which all the nickel atoms are potentially accessible to the monomer substrate, is responsible for the specific activity of these catalysts even at low concentrations of active complex phase.

There are significant differences between the behaviour of the complex species dispersed on crystalline supports such as microporous zeolites or mesoporous molecular sieve MCM-41 and respectively amorphous supports such as silica–alumina. Thus, the complex supported on crystalline carriers favours the formation of higher amounts of n-butylenes than the complex supported on amorphous silica–alumina, which is more favourable for the formation of oligomers. The n-butylene fraction obtained with the former catalysts is richer in $1-C_4H_8$ and cis-$2-C_4H_8$ compared to the corresponding values at thermodynamic equilibrium.

The effects of selectivity expressed as concentration of $1-C_4H_8$ in n-butylene fraction and $trans$-$2-C_4H_8/cis$-$2-C_4H_8$ respectively, may be tailored by supporting the complex on carriers with different structure and porosity.

The advantage of supporting the complex on carriers with regular structure of the pores consists in the easier separation of the catalyst from the reaction mixture.

Fig. 5. Comparison between the composition of the liquid oligomers obtained on K/Y, K/MCM-41 and K/SiAl.

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