

Ni(2,2'-bipyridine)₂Cl₂ encapsulated in Y zeolite new catalyst for ethylene dimerization

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Received 30 November 2004; accepted 24 March 2005

Available online 26 April 2005

Abstract

Catalysts containing Ni(2,2'-bipyridine)₂Cl₂ complex (K) encapsulated in Y zeolite cages (K_e/Y) or obtained by impregnation-complexation (K_i/Y), co-activated with AlCl(C₂H₅)₂ show good activity and selectivity for ethylene dimerization at 333 K and W/F = 37 g_{cat} h (moles C₂H₄)⁻¹ molar contact time. K_e/Y co-activated with AlCl(C₂H₅)₂ led to an ethylene conversion of 72.5% and 74.5% selectivity to C₄H₈, the prevailing isomer being 1-butylene.

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Keywords: Ethylene dimerization; Ni(2,2'-bipyridine)₂Cl₂; Y zeolite encapsulated complex catalysts; AlCl(C₂H₅)₂ activation

1. Introduction

In homogeneous catalysis, the dimerization and oligomerization of light olefins in the presence of nickel complexes with phosphorous- or nitrogen-containing ligands co-activated with alkylaluminium compounds has been already concretised in industrial processes such as DIMERSOL (IFP) [1–4] or SHOP (Shell) [5–8]. Nevertheless, all homogeneous processes present disadvantages related to the separation and the recovery of the catalyst. Therefore, the heterogeneization of homogeneous transition metal complexes by their synthesis inside the nanometer-size voids of porous solids becomes very attractive [9–12]. Recent papers showed that selective ethylene dimerization to *n*-butylenes can be performed in the presence of Y zeolite encapsulated complexes such as Pd(2,2'-bipyridine)Cl₂, Pt(2,2'-bipyridine)Cl₂ or Ni(4,4'-bipyridine)Cl₂ [13–15]. To our knowledge, the activity

of Y zeolite-encapsulated Ni complexes with 2,2'-bipyridine ligand for ethylene dimerization has not yet been reported. Nickel may form different complex combinations with 2,2'-bipyridine (2,2'-bpy), such as Ni(2,2'-bpy)Cl₂, Ni(2,2'-bpy)₂Cl₂ or Ni(2,2'-bpy)₃Cl₂ [16–19]. When encapsulated in Y zeolite, these complexes could present different activities depending on the coordination state of Ni in the structure and the steric hindrances induced. Therefore, this paper aims to investigate the activity of Ni(2,2'-bpy)₂Cl₂ (K) complex supported on Y zeolite for the selective dimerization of ethylene. The influence of the preparation method used for obtaining K/Y catalysts and the effects of the co-activation with diethyl aluminium chloride are also scrutinized.

2. Experimental

2.1. Catalyst preparation

Two samples of Ni(2,2'-bpy)₂Cl₂ supported on Y zeolite, e.g., K_e/Y and K_i/Y, were prepared using two

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methods: (i) the encapsulation through the “flexible ligand method” and (ii) the impregnation–complexation method [10,11]. The former consists in the reaction of the ligand with the transitional metal previously introduced inside the zeolitic cages by ionic exchange, while the latter is based on complexation of Ni species dispersed on the support by its impregnation with NiCl_2 aqueous solution.

The support was Y zeolite (Si/Al = 2.5, Na content 2.6×10^{-3} equiv $\cdot \text{g}^{-1}$, NH_4 content 2.6×10^{-3} equiv g^{-1}). The other reagents: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 2,2'-bpy, ethanol and acetone were p.a. grade from Merck.

For the preparation of K_eY , the zeolite was first submitted to three procedures of ionic exchange at 353 K for 2 h using fresh NiCl_2 aqueous solution (0.1 M). After the last procedure, the slurry mass was filtered, washed with demineralized water until no Cl^- ions were detected in the residual water and then dried at 423 K during 24 h. The content of Ni in the dried material designed as Ni–Y was 3.3%wt. The complexation of Ni^{2+} species was performed under inert atmosphere by mixing a portion of Ni–Y with an excess of 2,2'-bpy in a sealed glass tube while heating for 2 h at 363 K. During this period, a light blue colour was observed on the surface of the solid. The excess of uncomplexed ligand was removed by Soxhlet extraction (10 extractions, 2 h each) under nitrogen atmosphere with ethanol and then with acetone. After drying, the solid was submitted to ionic exchange with NaCl aqueous solution during 8 h aiming to re-exchange the uncomplexed Ni^{2+} and also to break the bonds to the zeolite lattice (Ni–O), consequently building up $\text{Ni}(\text{C}_2\text{H}_5)_2$ embedded in zeolite cages. The resulting solid was dried on P_2O_5 at room temperature. The final product, K_eY contains 2.2%wt. Ni determined by AAS. The results of the chemical and elemental analyses (%wt: N – 2.09, C – 8.95 and Cl – 2.65) corroborated with the analysis of the metal content showed that the ratio Ni:N:C:Cl is 1:4:20:2, therefore suggesting that the encapsulated Ni complex species is: $\text{Ni}(\text{C}_2\text{H}_5)_2\text{Cl}_2$.

For the preparation of K_iY the appropriate amounts of NiCl_2 and 2,2'-bpy allowing to obtain the same concentration of the complex on the support as in K_eY , were used. The zeolite was impregnated with NiCl_2 aqueous solution yielding a solid containing 3.5%wt Ni. After drying, the complexation of Ni species was performed in the manner previously described using the corresponding amount of ligand (ratio Ni:2,2'-bpy = 2:1). The obtained solid was washed with distilled water, ethanol and acetone to remove the weakly hold amounts of un-reacted NiCl_2 and 2,2'-bipyridine from the surface of the support and dried afterwards on P_2O_5 . Even if the results after analysing K_iY (%wt: Ni – 2.0%, N – 1.9, C – 8.1, and Cl – 2.4) were slightly smaller than those obtained for K_eY , the ratio Ni:N:C:Cl = 1:4:20:2 was identical, suggesting that the

same complex species are supported. The UV–Vis and FTIR spectral characteristics of the pure complexes $\text{Ni}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (green), $\text{Ni}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (light-blue) (K) and $\text{Ni}(\text{C}_2\text{H}_5)_3\text{Cl}_2$ (pink) [16–19] were compared to those of K_eY and K_iY in order to confirm the nature of the supported complex.

The co-activated catalysts were prepared “in situ”, using the Ni-containing solids previously prepared, and the appropriate quantities of $\text{AlCl}(\text{C}_2\text{H}_5)_2$ solved in toluene (ratio Ni:Al = 1:12 in the final products). In a sealed ampoule, the solid previously evacuated under 10^{-4} Torr was maintained in contact with $\text{AlCl}(\text{C}_2\text{H}_5)_2$ solution during 10 min. Afterwards, the solvent was eliminated under vacuum and the catalytic test was started.

2.2. Catalysts characterization

The catalysts were characterized by chemical and elemental analysis, diffuse reflectance UV–Vis (DR-UV–Vis), and FTIR spectroscopy. The determination of Ni content was performed by Atomic Absorption Spectrometry on Pye-Unicam AAS Spectrometer. N and C were determined by elemental analysis on Carlo Erba automatic analyser. Cl content was determined by volumetric analysis of the solution used for the absorption of the gases evolved during the combustion of the sample by Schöniger method. The DR-UV–Vis spectra were recorded in the range 200–1600 nm at room temperature with JASCO V570 spectrometer, using MgO as reference. Infrared spectra in the region 400–4000 cm^{-1} (resolution 4 cm^{-1} , 64 scans) were recorded on Perkin–Elmer 1600 FTIR spectrometer, using the KBr discs technique.

2.3. Catalytic testing

Catalytic tests were performed in a continuous flow reactor, in the 298–333 K temperature range, varying the molar contact times W/F from 7.5 up to 37 $\text{g}_{\text{cat}} \cdot \text{h} \cdot (\text{moles } \text{C}_2\text{H}_4)^{-1}$. For each test, 3 g of fresh catalyst were used.

3. Results and discussion

The electronic spectrum of Ni–Y (Fig. 1(a)) shows the specific features for octahedrally coordinated Ni^{2+} situated in the sites I' and II of Y-zeolite framework (Fig. 1(b)) [21,22]. The spectrum of K presents the electronic d–d transitions characteristic for a distorted-octahedral structure: $\nu_3(^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F}))$ – 608 nm, $\nu_2(^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F}))$ – 966 nm and $\nu_1(^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P}))$ – 1450 nm. The band for ν_1 transition presents a shoulder at 1380 nm suggesting that besides the prevailing *cis*-configuration of the complex, traces of *trans*-configuration are also present [20]. The prevailing *cis*-configuration is further confirmed by the presence of a well

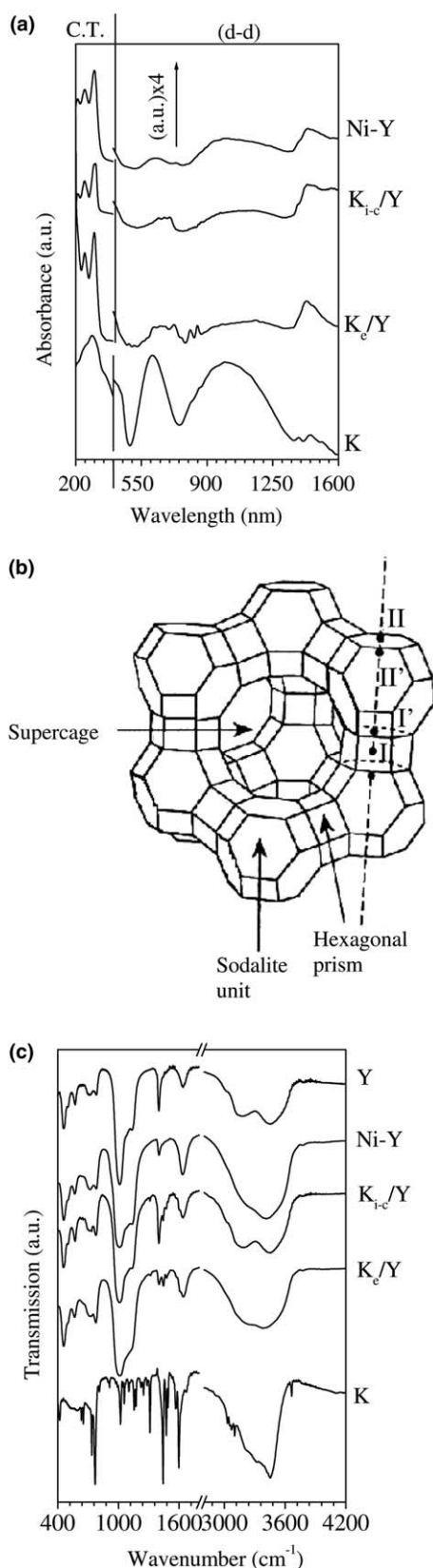


Fig. 1. Spectroscopic characterization of catalysts: (a) DR-UV-Vis spectra – (absorbance in the range 400–1600 nm is four times amplified); CT = domain for charge transfer bands, (d-d) = domain for d-d transitions; (b) Localization of Ni^{2+} ions in Y zeolite; (c) FTIR spectra.

defined band at 280 nm assigned to ligand to metal charge transitions [16]. The spectrum of K_{i-c}/Y presents all the above-mentioned bands suggesting the existence of both *cis* and *trans* complex-configurations while K_e/Y presented more intense lines corresponding to the *cis*-structure. The splitting of the band at 608 nm in the spectrum of K_e/Y could be a consequence of an intense spin-orbit coupling effect due to electrostatic interactions with the zeolite framework [21]. These strong interactions in Ni-Y , K_{i-c}/Y and K_e/Y are also suggested by the increased intensity of the bands corresponding to charge transfer in the region 200–400 nm. In the spectrum of K_e/Y , the shift of these bands to higher wavelengths indicates a decrease of the bonds strength. The absorption maxima of $\text{Ni}(\text{bpy})_3\text{Cl}_2$ and $\text{Ni}(\text{bpy})\text{Cl}_2$ (542, 876, 1468 nm and 520, 600, 940 nm, respectively) [16] were not found in the spectra of K_{i-c}/Y and K_e/Y .

The FTIR spectra (Fig. 1(c)) show that the ionic exchange with Ni^{2+} cations leads to slight modifications in the spectrum of Y zeolite, which presents the characteristic bands at: 440, 460, 570, 700, 780, 1000, and 1100 cm^{-1} . These bands are not significantly modified following ionic exchange or by supporting the complexes, proving that the structure of the zeolite is preserved [23,24]. The bands for Ni–O stretching vibrations ($400\text{--}587\text{ cm}^{-1}$ [25]), are covered by the bands of Y. The main effects noticed in the spectra of Ni-Y , and K_e/Y are the intensity decrease of the band corresponding to NH_4^+ groups (1400 cm^{-1}) due to their replacement with Ni^{2+} and the intensity increase of the bands at 1600 cm^{-1} and $3100\text{--}3600\text{ cm}^{-1}$ (deformation vibrations of H–O–H bonds). The modifications of the latter bands were associated with an enhancement of the superficial Lewis acidity [26,27]. The absence of the first effect in the spectrum of K_{i-c}/Y suggests that in this case the formation of the complex does not imply the severe removal of NH_4^+ ions following an ionic exchange.

The spectrum of K presents the bands corresponding to the ligand at: $630\text{--}650$, $730\text{--}740$, $760\text{--}770$, 1015, 1245, 1317, 1420, 1440, and $1500\text{--}1580\text{ cm}^{-1}$ [28]. The bands for Ni–Cl vibrations in the near infrared region were not determined in our analysis [17]. The main bands for Ni–N stretching vibrations, ($420\text{--}482\text{ cm}^{-1}$ [17,25]) have low intensity due to the small concentration of Ni in the complex. The FTIR spectra of K_e/Y and K_{i-c}/Y presented the characteristic spectral lines of K only in the region where these are not overlapped by the bands of the support. The major differences in the spectra of supported complexes when compared to the support appear at $1200\text{--}1600\text{ cm}^{-1}$. Since K_e/Y spectrum does not show the ligand bands at $630\text{--}650\text{ cm}^{-1}$ it seems that the encapsulation technique eliminates the traces of uncomplexed ligand while preserving the structure of the complex.

The results of the catalytic tests (Table 1), show that ethylene conversion for K_e/Y , and K_{i-c}/Y is almost the double compared to the one obtained with $Ni-Y$. The complex catalysts present a higher selectivity to 1- C_4H_8 , since the value of 1- $C_4H_8/2-C_4H_8$ ratios are 14 and, respectively, 22 times higher than that corresponding to the thermodynamic equilibrium composition. This effect is less pronounced for $Ni-Y$ catalyst. The higher selectivity towards 1-butylene formation for Ni -complexes with basic ligands supported on different carriers was also shown by other authors [29–34]. The decrease of 2-*trans*- $C_4H_8/2-cis-C_4H_8$ ratio to values much lower than the one corresponding to the thermodynamic equilibrium shows that the embedding of the complex inside the zeolitic structure induces diffusion hindrances in K_e/Y and K_{i-c}/Y catalysts. This assumption is confirmed also by their higher selectivity for *n*-butylenes production and their lower selectivity to oligomers C_{5+} .

The addition of $AlCl(C_2H_5)_2$ to all catalysts increases almost five times their catalytic activity. The selectivity to 1- C_4H_8 is also increased significantly. This effect is most intense for $Ni-Y$ which presents a ratio 1- $C_4H_8/2-C_4H_8$ of 0.46 compared to 0.08, the ratio obtained without co-activation. The intensity of the diffusion hindrances increases while the selectivity to C_{5+} oligomers is severely decreased. It seems that different coordination of the ligands are obtained when adding $AlCl(C_2H_5)_2$ since the formation of 2-*cis*- C_4H_8 is favoured only in the case of $Ni-Y$ catalyst, while for K_{i-c}/Y , and K_e/Y the obtaining of 2-*trans*- C_4H_8 prevails.

In order to determine if leaching of the complex $Ni(2,2'-bpy)_2Cl_2 \cdot 12AlCl(C_2H_5)_2$ occurred, the liquid fraction obtained in the tests was submitted to UV-Vis spectroscopy analysis to investigate the presence of Ni and Al traces. For both supported complex 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.

Since the most active catalyst for ethylene dimerization was $K_e/Y + AlCl(C_2H_5)_2$, its activity was tested also under different operating conditions. As Fig. 2 shows, the increase of the contact time is always accompanied by an increase of ethylene conversion.

The increase of ethylene conversion goes along with an increase of the selectivity to oligomers and a decrease of dimers formation (Fig. 3(a)). Since higher conversions are obtained at longer contact times, it may be concluded that oligomers are formed in a slower process that takes place on behalf of the dimers that are produced in a previous stage [27]. Therefore, when the obtaining of a higher concentration of dimers is desired, lower contact times should be used.

The production of 1- C_4H_8 is enhanced at lower conversion levels. Meanwhile the formation of 2-*cis*- C_4H_8 is higher as the conversion increases (Fig. 3(b)). Thus, it

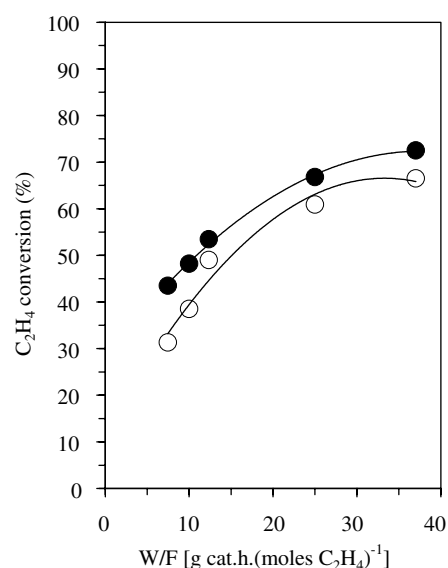


Fig. 2. Ethylene conversion on K_e/Y co-activated with $AlCl(C_2H_5)_2$ (ratio $Ni/Al = 1/12$) as a function of W/F ($g_{cat} \cdot h \cdot moles C_2H_4^{-1}$), $T = 298 K - \circ$, $T = 333 K - \bullet$.

Table 1

Catalytic performances for ethylene dimerization $T = 333 K$; 3 g catalyst; $W/F = 12.4 g_{cat} h (moles C_2H_4)^{-1}$; 8 h reaction time

Catalyst	C_2H_4 conv. (%)	Selectivity (%)		TOF (h^{-1}) ^a	$\frac{1-C_4H_8}{2-C_4H_8}$ ^b	$\frac{2-trans-C_4H_8}{2-cis-C_4H_8}$ ^c
		C_4H_8	C_{5+}			
$Ni-Y$	4.1	32.1	67.9	0.5	0.08	2.36
$Ni-Y + AlCl(C_2H_5)_2^d$	26.4	51.2	48.8	4.9	0.46	1.88
K_{i-c}/Y	8.2	62.7	37.3	2.1	0.56	2.08
$K_{i-c}/Y + AlCl(C_2H_5)_2^d$	48.4	77.1	22.9	14.5	0.97	1.58
K_e/Y	10.1	70.6	29.4	2.6	0.87	1.94
$K_e/Y + AlCl(C_2H_5)_2^d$	53.5	82.4	17.6	16	2.16	0.47

^a TOF (turnover frequency) = moles C_2H_4 transformed/ Ni atom/h.

^b $\left[\frac{1-C_4H_8}{2-C_4H_8}\right]_{Thermodynamic\ equilibrium, 333\ K} = 0.0398$.

^c $\left[\frac{2-trans-C_4H_8}{2-cis-C_4H_8}\right]_{Thermodynamic\ equilibrium, 333\ K} = 2.75$.

^d Ratio $Ni/Al = 1/12$; C_{5+} – oligomers fraction.

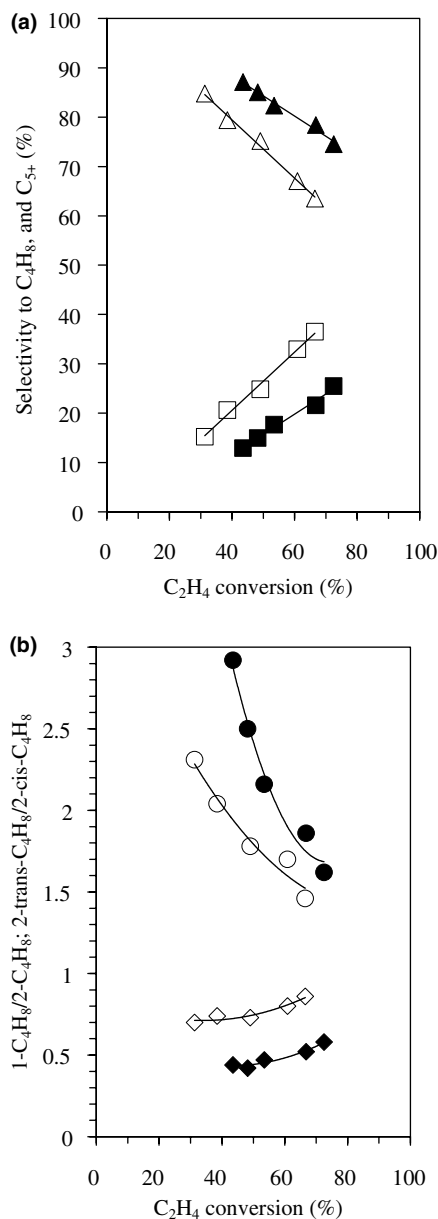


Fig. 3. Dependence of the selectivities as a function of ethylene conversion on K_6/Y co-activated with $AlCl(C_2H_5)_2$ (ratio $Ni/Al = 1/12$): (a) Selectivity to C_4H_8 \triangle ($T = 298$ K), \blacktriangle ($T = 333$ K); C_{5+} \square ($T = 298$ K), \blacksquare ($T = 333$ K); (b) $1-C_4H_8/2-C_4H_8$ ratio \circ ($T = 298$ K), \bullet ($T = 333$ K); $2-trans-C_4H_8/2-cis-C_4H_8$ ratio \diamond ($T = 298$ K), \blacklozenge ($T = 333$ K).

may be assumed that $1-C_4H_8$ is the primary product obtained during ethylene dimerization on $K_6/Y + AlCl(C_2H_5)_2$ catalyst. This fact was also reported in other works concerning ethylene oligomerization on supported Ni-complexes catalysts [15,27,30–34].

4. Conclusions

The complex $Ni(2,2'-bpy)_2Cl_2$ supported on Y zeolite and co-activated with $AlCl(C_2H_5)_2$ is a promising

catalyst for ethylene selective dimerization to *n*-butylenes under mild conditions of temperature (298–333 K) and atmospheric pressure. Such catalyst prepared using the “flexible ligand method” shows better activity than the one prepared by “impregnation–complexation” technique due to a more uniform distribution of the complex with *cis*-configuration inside the porous structure of the support.

Acknowledgement

The financial support of this work by CNCSIS Grant 34A-1117/2004 is gratefully acknowledged.

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