

ETHYLENE DIMERIZATION ON NICKEL 4,4'-BIPYRIDINE COMPLEX SUPPORTED ON FAUJASITE TYPE ZEOLITES

E. Angelescu*, Rodica Zăvoianu*, O.D. Pavel*, Anca Angelescu**

abstract: This paper presents the activity and selectivity of a catalyst based on Ni(4,4'-bipyridine)Cl₂ complex co-activated with AlCl(C₂H₅)₂ and supported on faujasite-type zeolite Y utilised in the dimerization of ethylene at 298K in continuous flow of reactant. Chemo- and stereo-selectivity effects expressed as selectivity for dimers and oligomers, and respectively, the concentration of 1-C₄H₈ in C₄H₈ fraction and the molar ratios 2-trans-C₄H₈/2-cis-C₄H₈ are discussed. The results are correlated with the steric and diffusion hindrances induced by the microporous structure of the porous solid matrix.

keywords: ethylene dimerization, Ni(4,4'-bipyridine)Cl₂-AlCl(C₂H₅)₂, Y zeolite supported complex catalysts

Introduction

Heterogeneous complexes on zeolite supports are known to be catalysts [1-5] or electrocatalysts [6-8] with high activity and selectivity. Metal chelate complexes, such as Fe, Cu, Co, Ni – phthalocyanines 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 [1-5].

Nickel complexes with phosphine and acetylacetonate ligands co-activated with aluminium alkyls solved in hydrocarbons [9-14] or supported on SiO₂, Al₂O₃, SiO₂-Al₂O₃ carriers [15-17] were mainly utilised for reactions involving chain growth such as dimerization and oligomerization. The role of the co-activator is to generate Ni(I) or Ni(0) complex species with active bonds Ni-H or Ni-C which favour the insertion of the monomer previously activated by its coordination on Ni reduced sites [9-17]. In homogeneous catalysis, the oligomerization of olefins on Ni-complex catalysts has been already industrially applied in DIMERSOL (IFP) [18-21], and SHOP (Shell) processes [22]. However, these homogeneous processes present some disadvantages concerning the separation and the recovery of the catalyst from the reaction products.

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Recently, coordination polymers formed by open supramolecular coordination networks from molecular blocks of $\text{Me}(4,4'\text{-bipyridine})\text{X}_2$ ($\text{Me}=\text{Fe, Co, Ni, Cu}$; $\text{X}=\text{Cl, NO}_3, \text{ClO}_4, \text{N}_3, \text{O}_2\text{CCF}_3$) were reported as being crystalline materials with controlled pore size, shape and functions and high thermal stability. Their bidimensional structure contains transition metal centres octahedral coordinated by four bridging chlorine and two bipyridine ligands in trans positions [23-25].

In a recent work we reported that $\text{Ni}(4,4'\text{-bipyridine})\text{Cl}_2$ complex supported on Y zeolite and co-activated with $\text{AlCl}(\text{C}_2\text{H}_5)_2$ presented good activity in selective ethylene dimerization to n-butylenes when operated at 298K in static regime under an initial pressure of ethylene equal to 12 atm [26]. In this case after 5 hours reaction time the conversion of ethylene reached 50% while the selectivity to n-butylenes was higher than 90%. Since the discontinuous processes are less advantageous in industrial appliances, the present work was directed towards the study of the catalytic performances of these catalysts operated under continuous flow of reactant.

Experimental

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ p.a. (Merck), 4,4'-bipyridine p.a. (LOBA FEINCHEMIE), $\text{AlCl}(\text{C}_2\text{H}_5)_2$ 98% (Merck-Suchardt) and zeolite Y ($\text{Si}/\text{Al} = 2.31$) (synthesised by the Institute of Research for Petroleum Refining and Petrochemistry (INCERP) – Ploiești – Romania) were the raw materials utilised for the preparation of the complex catalysts. Before the preparation of the supported complex catalyst, the support was calcined at 460°C during 4 hours.

The pure complex $\text{Ni}(4,4'\text{-bipyridine})\text{Cl}_2$ (K) and the supported complex catalyst K/Y were prepared according to the methods described in detail in our previous work [26]. Briefly, the precipitation of the pure complex is performed by drop wise addition of a methanolic solution of 4,4'-bipyridine to an aqueous solution of NiCl_2 under stirring. K/Y was prepared by adding the support powder in the NiCl_2 solution at the beginning of the preparation and further addition of the methanolic solution of 4,4'-bipyridine. The content of Ni in the resulting solid was 3.5 wt.%. 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. Coactivation was realised in situ using the appropriate amounts of $\text{AlCl}(\text{C}_2\text{H}_5)_2$ in order to yield a molar ratio $\text{Al}/\text{Ni}=5/1$ in the catalyst.

The catalysts were characterized by elemental analysis, XRD, Diffuse Reflectance UV-VIS (DR-UV-VIS), and FTIR spectroscopy.

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

The DR-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 BioRad FTS 135 spectrometer.

Samples were prepared using the technique with KBr discs. Resolutions of 8 cm^{-1} and 16 scans were used.

The tests performed in continuous flow of reactant were realised at 298 K under atmospheric pressure in a glass microreactor with a fixed bed of catalyst. The contact time varied in the range 1 – 8 s. Analysis of the reaction products was performed at 15 minutes intervals until steady state was reached. Ethylene (99% purity) produced at PETROBRAZI – Ploiești Romania was used as reactant. The reaction products were analysed with a Thermoquest chromatograph equipped with FID detector and a capillary column Al_2O_3 -PLOT (30 m length).

Results and Discussion

The elemental analysis of the synthesized complex $\text{Ni}(4,4'\text{-bipyridine})\text{Cl}_2$ gave the following results: 41.3 wt.% C, 3.15 wt. % H, 8.96 wt.% N and 20.42 wt. % Ni. The slight discrepancy between these values and the values calculated considering the chemical formula (e.g. 42 wt.% C, 2.8 wt. % H, 9.8 wt.% N and 20.55 wt. % Ni) is likely caused by the presence of water molecules in the crystal lattice. In agreement with the published data [25], the results of the XRD analysis of the neat complex show that the complex has an orthorhombic symmetry, belonging to space group C_{mmm} (N° 65) ($a = 11.974$; $b=11.335$; $c=3.584$).

The electronic spectrum of the complex (fig. 1) presents the most intense bands due to Ni cation in octahedral coordination at 298 nm (charge transfer from ligand to metal), 409 nm and 713 nm (d-d spin allowed transitions) and the other bands corresponding to $\pi\text{-}\pi^*$ transitions characteristic to the ligand [27,28]. The same bands are also noticed in the spectra of the supported complex catalyst. Their intensity is lower due to the low concentration of complex in the catalyst.

The FTIR spectra are presented in fig. 2. The main bands of the parent zeolite corresponding to Si-O vibrations (1000 and 1100 cm^{-1}), Al-O (700 and 780 cm^{-1}), D6R and D4R (570 , 440 and 460 cm^{-1}) are not significantly modified following the deposition of the complex indicating that the structure of the zeolite is not destroyed [29]. Several new bands appear in the regions where the neat complex presents its highest intensity bands, e.g. 637 cm^{-1} , 809 cm^{-1} , 1420 cm^{-1} , 1609 cm^{-1} 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 $1000\text{-}1223\text{ cm}^{-1}$ are overlapped by the bands corresponding to the support at $440\text{-}570\text{ cm}^{-1}$ and $1000\text{-}1100\text{ cm}^{-1}$, respectively. Due to this overlapping, in the spectrum of K/Y, the bands at 484 cm^{-1} and respectively 1028 cm^{-1} are broader and more intense than those of the parent zeolite. The most significant difference between the spectrum of Y zeolite and K/Y is noticed in the region where the vibrations corresponding to the hydroxyl groups appear. Thus, K/Y spectrum presents a very low intensity of these bands, which are also shifted to higher wavenumbers, e.g. 3555

cm^{-1} and 3627 cm^{-1} compared to 3140 cm^{-1} and respectively 3446 cm^{-1} in the spectrum of the parent zeolite.

This could be an effect of the screening of the hydroxyl groups by the complex supported on the zeolite surface.

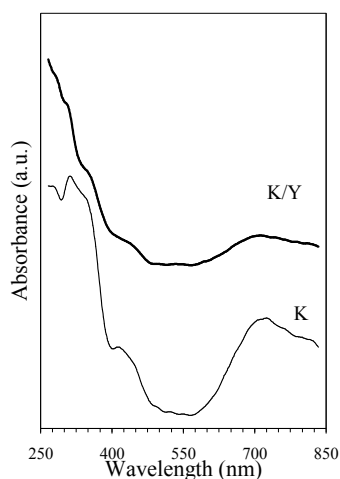


Fig. 1. DR-UV VIS spectra of K, and K/Y

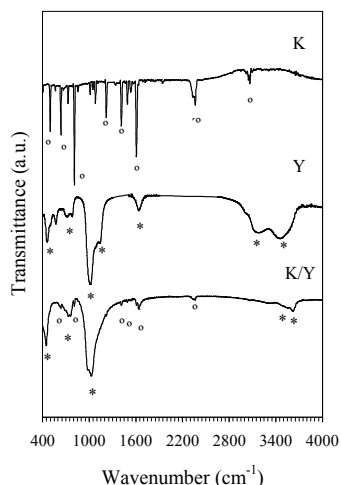


Fig. 2. FTIR spectra of 4,4'-bipyridine, K, Y, and K/Y (most intense bands: complex - # ; Y zeolite - *)

The results of the catalytic tests for ethylene dimerization at 298K and continuous flow of reactant using K and K/Y catalysts co-activated with $\text{AlCl}(\text{C}_2\text{H}_5)_2$ are presented in figs. 3-6. The data presented in Fig. 3 show that for both catalysts ethylene conversion increases with the contact time and the supported complex is always more active than the unsupported complex catalyst, probably due to the higher dispersion of the active sites in K/Y. There is a significant increase of conversion up to a contact time of 5 s. Once rising above this value of the contact time the conversions does not increase significantly, the values being around 15% for the unsupported complex and respectively 30% for K/Y.

Fig. 4 shows that both catalysts are more selective for dimerization than for oligomerization since the selectivity for n-butylenes is higher than 80%. The increase of the contact time leads to a decrease of the selectivity to n-butylenes accompanied by an increase of the selectivity to oligomers. This fact suggests that the production of oligomers is a slower process, which requires in a first stage the obtaining of n-butylenes [10-20, 26]. Probably, the lower selectivity to oligomers obtained for K/Y could be related to the diffusion hindrances that appear subsequently to the encapsulation of the complex in the porous carrier.

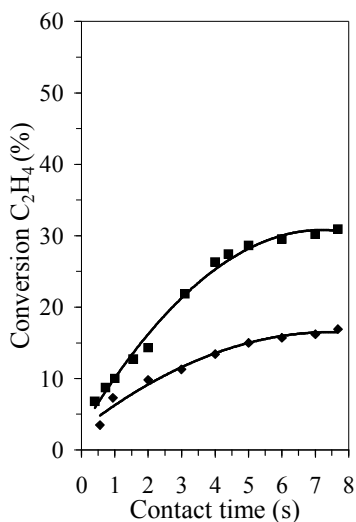


Fig. 3. Variation of ethylene conversion as a function of the contact time on K (◆), and K/Y (■) catalysts co-activated with $AlCl(C_2H_5)_2$ (Al:Ni=5:1)

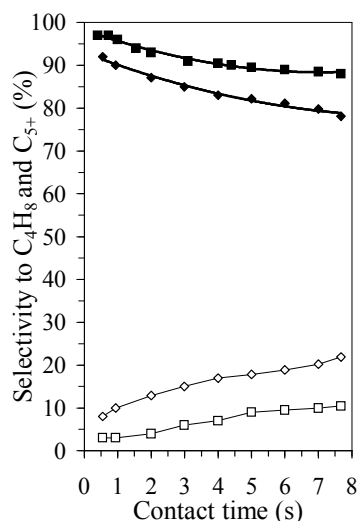


Fig. 4. Variation of the selectivities to $n-C_4H_8$ (◆, ■) and C_5 (◇, □) as a function of the contact time on K (diamond symbols) and K/Y (square symbols)

As it may be seen from Fig. 5, the prevailing isomer present in *n*-butylenes fraction is 1-butylene which represents more than 78%, value much higher than the one corresponds to thermodynamic equilibrium, e.g. 2.5% [10-13].

The decrease of the concentration of 1-C₄H₈ with the contact time indicates that 2-C₄H₈ is formed by subsequent isomerization of 1-C₄H₈ [15-20]. This behaviour is more significant for K than for K/Y (e.g. almost 10% for K and only 5% for K/Y). However K/Y is less selective for 1-C₄H₈ than the neat complex suggesting that in this case there is likely a slight contribution of the residual acid sites of the support. The data from Fig. 6 show that the increase of the contact time above 2 s does not influence the ratio between *trans* and *cis* isomers of 2-C₄H₈. For both catalysts the formation of *cis* isomer is increased since the value of the ratio *trans*-2-C₄H₈/*cis*-2-C₄H₈ is less than half of the value corresponding to thermodynamic equilibrium (e.g. 3.22).

A comparison between the results obtained with K and K/Y catalysts when operated in continuous flow of reactant and in static regime is presented in Table 1.

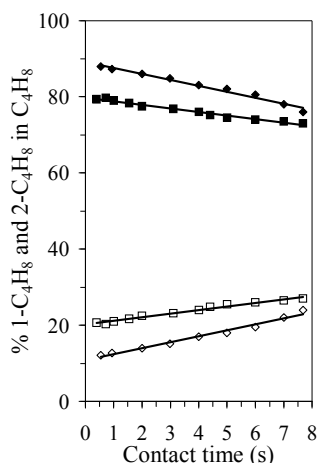


Fig. 5. Variation of the concentrations of 1- C_4H_8 (\blacklozenge , \blacksquare) and 2- C_4H_8 (\blacklozenge , \square) in $n-C_4H_8$ fraction+ as a function of the contact time K (diamonds) and K/Y (squares)

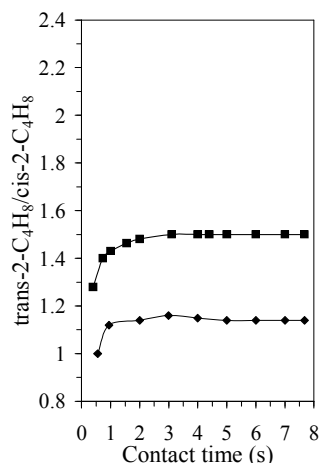


Fig. 6. Variation of the ratio $trans-2-C_4H_8/cis-2-C_4H_8$ as a function of the contact time on K (\blacklozenge), and K/Y (\blacksquare) catalysts

*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.

Table 1. Comparison of the results obtained at ethylene dimerization on complex catalysts K and K/Y co-activated with $AlCl(C_2H_5)_2$; Molar ratio Al/Ni = 5/1, T = 298 K

Operating conditions	Continuous flow, p = 1atm., 0.2 grams of catalyst, contact time 5 s, steady state conditions		Static regime, $p_{C_2H_4} = 12$ atm., 5 h reaction time, 0.2 grams catalyst	
Catalyst	K	K/Y	K	K/Y
Intrinsic activity *				
$\left[\frac{\text{moles of } C_2H_4 \text{ transformed}}{\text{moles of Ni} \cdot h} \right]$	3.2	8.0	4.1	29.5
Selectivity to C_4H_8 (%)	82.2	89.5	91.6	93.4
% 1- C_4H_8 in $n-C_4H_8$ fraction	82.0	74.5	71.6	38.7
$\left[\frac{trans-2-C_4H_8}{cis-2-C_4H_8} \right]$	1.1	1.5	1.33	1.3
Selectivity to oligomers C_{5+} (%)	17.8	10.5	8.4	6.6

Equilibrium composition at 298 K: %1- C_4H_8 in $n-C_4H_8$ fraction = 2.5%; $Trans-2-C_4H_8/Cis-2-C_4H_8 = 3.22$

The data presented in table 1 show that both the intrinsic activity and the selectivity for dimerization are higher for the supported catalyst than for the neat complex. This fact may be related to the more uniform dispersion of Ni complex active sites on the support. Both the intrinsic activities and the selectivity for dimerization are enhanced in the tests performed in static regime. The higher activity for oligomerization in tests carried out in continuous flow of reactant may be a consequence of a more facile desorption of the reaction products under these operating conditions. The lower selectivity for 1- C_4H_8 in tests carried out under static regime may be a consequence of an increased isomerization to 2-

C₄H₈ at long contact time. However, the ratio between *trans* and *cis* isomers of 2-C₄H₈ is not influenced significantly by the operating conditions.

Aiming to study the leaching possibility under continuous flow of ethylene at atmospheric pressure, catalytic tests using 20 cm³ of catalyst at a contact time 1.5 s were performed during 4 hours. In the colourless oligomer fraction collected after this reaction time only traces of Al not exceeding 13 ppm and no traces of Ni could be detected. Therefore it may be concluded that during the catalytic tests the complex Ni(4,4'-bipyridine)Cl₂ was not washed out by the reagent flow.

Conclusion

Ni(4,4'-bipyridine)Cl₂ complex co-activated with AlCl(C₂H₅)₂ and dispersed on Y zeolite is an active and selective catalyst for ethylene dimerization to n-butylenes under normal conditions of temperature and pressure. The higher activity compared to that of the neat complex might be a consequence of a more uniform dispersion of Ni active sites.

When this catalyst is operated under dynamic regime, at low contact time, high concentrations of 1-butylene may be produced as a consequence of the steric hindrances imposed to the molecular traffic by the supported complex.

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