Effect of Introduction of Lanthanum Cations in ZSM-5 Crystallization Step on Ethanol Conversion to Hydrocarbons

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In this study, HZSM-5 and La-HZSM-5 catalysts were synthesized and experienced in ethanol conversion process to hydrocarbons. The physicochemical properties of catalysts were characterized by X-Ray diffraction (XRD), Fourrier Transformed-Infra Red (FT-IR), thermogravimetric and acidity measurements. Two sets of catalytic tests with unmodified and La modified HZSM-5 have been performed aiming at distinguishing the effect of lanthanum cation addition in zeolite synthesis mixture on the catalyst selectivity. The experimental result demonstrated that the addition of lanthanum results in modifying the catalytic performance as compared to unmodified HZSM-5 zeolite. The two catalysts prepared from unmodified and lanthanum modified ZSM-5 zeolite samples showed a remarkable difference in their selectivity. It was found that in the ethanol to hydrocarbons conversion process the La-HZSM-5 catalyst had a high selectivity in ethylene as compared to unmodified HZSM-5, the later leading to the formation of a wide range of gaseous and liquid hydrocarbons.

Keywords: La-ZSM-5, ethanol, conversion, hydrocarbons

The production of hydrocarbons such as ethylene, gasoline and aromatics from ethanol using zeolites like solid acid catalysts has been reported by many researchers [1-3]. Zeolites are very attractive due to their unique properties such as large surface area, adsorption capacity, ion-exchange capacity, defined channel systems, high hydrothermal stabilities and controllable densities of the active sites [2-7]. Using a ZSM-5 based catalyst the selectivity of the products in the bioethanol conversion can be changed by known methods such as direct-synthesis and post-synthesis procedures as ion exchange and impregnation, respectively. Incorporation of a heteroatom in the network structure of zeolite is an important modification method to be applied in order to reach a specific catalytic activity and selectivity. Catalytic behaviour is strongly influenced by different factors such as cation type, stability and positioning of inserted cation. It has been shown that rare earth ions, mainly lanthanum cations can inhibit the dealumination of zeolite framework, thus enhance the hydrothermal stability and consequently, impact on unit cell size stabilization and improve catalytic activity and selectivity of ZSM-5 zeolite to a large extent [8].

In this study we investigated the effect of introduction of lanthanum cations in ZSM-5 zeolite by direct-synthesis on catalytic performance in ethanol conversion to hydrocarbons.

Experimental part

Catalyst preparation

ZSM-5 zeolite was synthesized from an amorphous sodium aluminosilicate dry gel using a known hydrothermal method, in the presence of hexamethylene-diamine (HDA - $(CH_2)_6$ $(NH_2)_2$, 75 wt.%, Borzesti) as a structure-directing agent [9]. The molar composition of the original synthesis mixture was: 90 SiO_2 . 1 Al_2O_3 7.07 Na_2O . 21.6 HDA . 2230 H_2O. To prepare lanthanum containing ZSM-5 sample, an appropriate amount of lanthanum aqueous solution nitrate (La $(NO_3)_3$. $6H_2O$, Merk) was added to the original synthesis mixture to yield the La/Al atomic ratio of 0.25. The resulting synthesis mixture had the following molar composition: 90 SiO_2 . 1 Al_2O_3 . 0.25 La_2O_3 '. 7.07 Na_2O . 21.6 HDA . 2267 H_2O. In both cases, the hydrothermal synthesis has been carried out into a stainless steel autoclave in the following conditions: temperature 170^{0}C, pressure 6 bar and time 48 h under continuous stirring (150 rpm). The solid product was recovered by filtration, washed with distilled water, dried at 80^{0}C for 8 h and calcined in air at 580^{0}C for 8 h to decompose and remove organic cations occluded in the zeolite framework during the hydrothermal crystallization step. Then, the calcined Na-ZSM-5 zeolite powder was converted to ammonium form by ion exchange with ammonium nitrate (1M NH_4NO_3, Chimopar) and the resulting NH_4-ZSM-5 zeolite powder (unmodified or La modified samples) was formulated by extrusion using a pseudoboehmite type hydrated alumina (65 wt.% Al_2O_3, Vega Ploiesti) as binder and nitric acid (12 wt.% HNO_3, Chimopar) as peptizing agent, according to the procedure in a previous article [9]. The final composition of the calcined H-ZSM-5 extrudates consisted of 60 wt.% of HZSM-5 (or La-HZSM-5) zeolite and 40 wt.% of γ-Al_2O_3.

Characterization techniques

X-ray diffraction (XRD) patterns of the zeolite samples were recorded on a Bruker Discovery 8 powder diffraction system (0,154 nm, 40 kV, 40 mA) using Cu$K\alpha$ radiation in the 2θ range of 5-50^0. The infrared spectra (FT-IR) of the HZSM-5 and La-HZSM-5 zeolite samples were recorded using a Bruker (ATR) transform infrared spectrometer with germanium crystal at 4000-375 cm^{-1} intensity, with 4 cm^{-1} resolution, 16 scans. Thermogravimetric analysis (TGA) was performed with a DuPont Instruments device "Thermal Analyst 2000/2100" coupled to a module "951 Thermogravimetric Analizer". The procedure was as follows: before the adsorption operation of the base zeolite samples were subject to a heat treatment at 160^{0}C in vacuum for 24 h in order to remove impurities. After cooling the samples to the room temperature, the amine was introduced with the syringe until the saturation of the sample has occurred. Desorption of base was carried out by heating the sample from room temperature to 600^{0}C.

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Catalytic test

The catalytic tests were carried out in an electrically heated fixed bed reactor, operating at continuous flow rate. Each extruded catalyst sample (10 g) was loaded into reactor, in the center of the device between two layers of the inert material. The catalysts were activated under nitrogen flow (40 mL/min) at 350-500 ^{0}C for 5 h. Ethanol conversion runs were performed at the temperatures of 350-500^{0}C, pressure of 5 atm and WHSV = 2.5, 5 and 10 h^{-1}. The experimental planning was designed to study the effects of addition of lanthanum ions, temperature and WHSV over the variation of the gas fraction. The reaction was performed diluting ethanol vapors (96 wt.%, Chemical Company) with a carrier gas (hydrogen, Linde, 5.0) under constant flow rate. The gaseous products were analyzed using gas chromatography with hydrogen as carrier gas.

Results and discussions

Characterization

Figure 1 displays the XRD patterns of samples synthesized by using HDA as template exhibiting the crystalline structure of ZSM-5 zeolite. The XRD profiles of the two ZSM-5 samples, namely: the unmodified HZSM-5 zeolite and the modified La-HZSM-5 zeolite exhibit the crystalline MFI phase with characteristic diffraction peaks at 2θ values = 7.9; 8.8; 23; 23.9 degrees, representing (011), (020), (051) and (033) planes of crystal structure that are in agreement with published literature [10]. As figure 1 shown, neither La_2O_3, nor other crystalline phases and lanthanum species are formed during the synthesis of lanthanum containing ZSM-5 zeolite. It is to be noted the well-crystallized MFI structure resulted from original synthesis (without a heteroatom addition), but a lower crystalline ZSM-5 zeolite was obtained in the presence of La^{3+} addition in the synthesis mixture. This result can be related to the composition of the synthesis mixture defined by the initial Si/T atomic ratio, where T includes Al and La. It can observed that an additional amount of La^{3+} (having a big ion radius of 0.103 nm as compared to 0.04 nm for Si^{4+} and 0.0535 nm for Al^{3+}, respectively) in aluminosilicate (Si/Al = 45) synthesis mixture has a significant effect on the ZSM-5 zeolite crystallization. Thus, using a La/Al atomic ratio of 0.25 results in an initial Si/Al+La atomic ratio of 36. Starting with this composition MFI type phase formed, but the crystallization was not complete. The presence of amorphous material in XRD pattern of lanthanum containing ZSM-5 zeolite can be clearly seen in figure 1. The relative crystallinity of synthesized samples was determined in comparison with a ZSM-5 reference sample synthesized with the same template (HDA). XRD analysis evidenced relative crystallinity values of 100% for unmodified zeolite and of 88% for lanthanum modified zeolite, respectively.

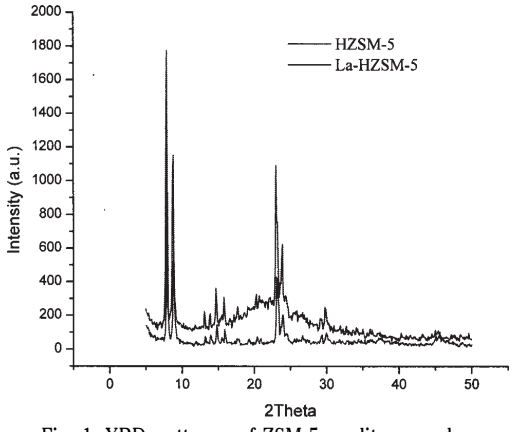

Fig. 1. XRD patterns of ZSM-5 zeolite samples

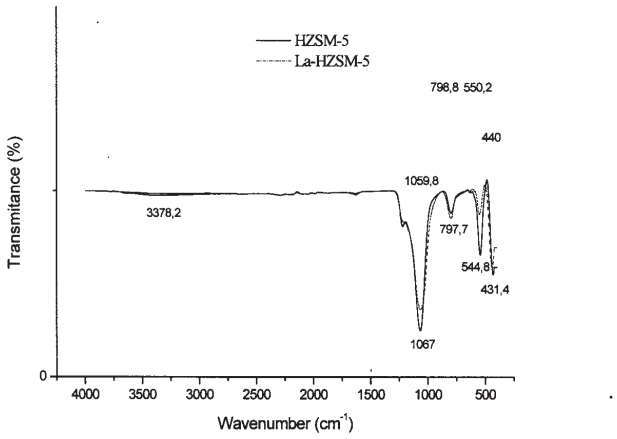

Fig. 2. FT-IR spectra of ZSM-5 zeolite samples

The IR spectra for unmodified ZSM-5 zeolite and La^{3+} modified zeolite by direct-synthesis, are shown in figure 2. The characteristic band of five – member ring of pentasil structure (double ring vibration) at 550 or 545 cm^{-1} and bending vibration of T-O-T bend at 440 or 431 cm^{-1} could be seen in the spectra of HZSM-5 and La-HZSM-5 samples. The bands around 1067 cm^{-1} and 798 cm^{-1} were related to the zeolite framework, i.e. the asymmetric and symmetric flexural vibrating of T-O-T (T=Si, Al) groups. The bands shifted from 1067 to 1059.8 cm^{-1} after La ion addition indicated the La ions being incorporated into ZSM-5 zeolite channels [12]. Asymmetric vibrations of T-O bond at 1221 cm^{-1} could be assigned to external links between TO_4 tetrahedral [11-13]. The presence of absorption bands around 3400 cm^{-1} corresponds to the stretching vibration of Si-O terminal groups, water molecules adsorbed in the structure of the zeolite [14].

The acidity of ZSM-5 zeolite samples was investigated by diethylamine desorption coupled with thermogravimetric analysis (DEA-TGA). Table 1 summarizes the acidity of H-ZSM-5 and La-HZSM-5 samples. The main difference between unmodified and modified zeolite consists of a significant decrease of the total acidity as a result of La introduction in synthesis mixture. Thus, the total amount of acid sites was of 0.763 mmol/g and 0.371 mmol/g for unmodified HZSM-5 and modified La-HZSM-5, respectively. In fact, in comparison with unmodified HZSM-5, a lower amount of each acid site type is observed for lanthanum containing zeolite. Taking into account XRD results, it may be assumed that the decrease of the La-HZSM-5 acidity can be due to its lower crystallinity as compared to unmodified HZSM-5 sample. Also, the low amount of strong acid sites ascribed to the framework aluminum can be the effect of the presence of amorphous phase in lanthanum containing crystallization product, which can be associated with a lower aluminum content in crystalline phase. However, the presence of hydroxy-lanthanum cations species in ZSM-5 channels can play a role in reducing of amount of strong acid sites. The decrease of the acidity of ZSM-5 zeolite by lanthanum addition is in accordance with reported data [8, 13].

Table 1
ACIDIC SITES DISTRIBUTION OF THE ZEOLITE SAMPLES

Zeolite samples	Acidic sites distribution (mmol/g)			Total acidity (mmol/g)
	Weak sites	Medium sites	Strong sites	
HZSM-5	0,3348	0,2857	0,1428	0,7633
La-HZSM-5	0,1713	0,1339	0,0664	0,3716

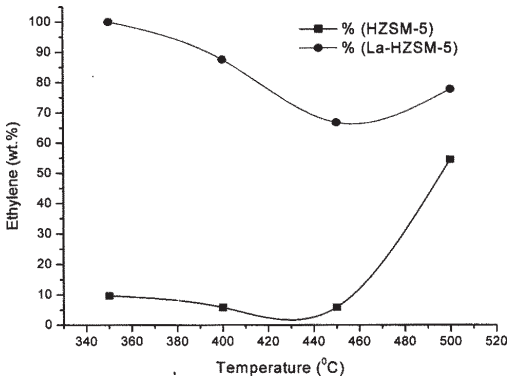

Fig. 3. Influence of reaction temperature on the conversion of ethanol to ethylene over HZSM-5 and La-HZSM-5 at 5 atm pressure and 2.5 h^{-1} WHSV.

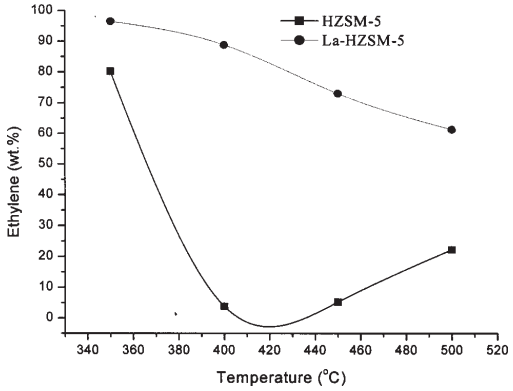

Fig. 4. Influence of reaction temperature on the conversion of ethanol to ethylene over HZSM-5 and La-HZSM-5 at 5 atm pressure and 5 h^{-1} WHSV.

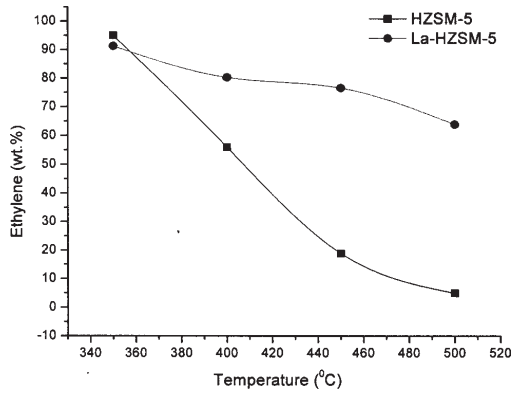

Fig. 5. Influence of reaction temperature on the conversion of ethanol to ethylene over HZSM-5 and La-HZSM-5 at 5 atm pressure and 10 h^{-1} WHSV

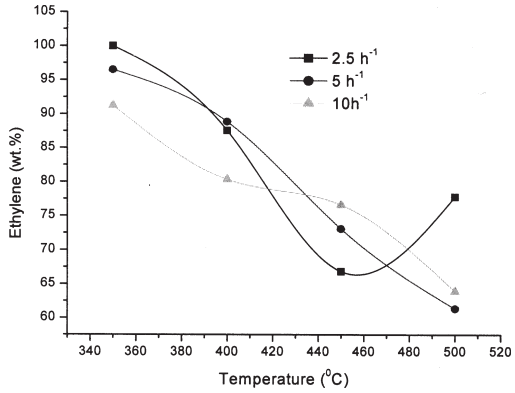

Fig. 6. Influence of reaction temperature on the conversion of ethanol to ethylene over La-HZSM-5 at 5 atm pressure and different WHSV.

In this study we investigated the effect of lanthanum addition on the activity of ZSM-5 catalyst for ethanol conversion. The main difference between unmodified and La modified zeolite catalysts appears in ethylene selectivity. Thus, ethylene was the main product that has been obtained by using La-HZSM-5 catalyst, while a variety of gaseous and liquid products were produced with unmodified HZSM-5 catalyst.

These results indicate that conversion of the alcohol to hydrocarbons is a complex process involving dehydration, oligomerization, hydrogen transfer, isomerization, aromatization and cracking reactions. It may be assumed that ethylene resulting in ethanol dehydration step becomes the raw material in oligomerization reactions and the catalytic process is followed by the other secondary reactions. Increasing temperature leads to a decrease in the concentration of ethylene due to its transformation into other products. At a temperature of 500^{0}C ethylene reappears in high concentrations in the gaseous fraction because of its potential of obtaining like product of cracking of process (figs. 3-4). According to Song et al, at low temperatures ethylene is primarily produced by dehydration of ethanol, whereas at high temperatures ethylene is a product of secondary cracking [15]. In figure 5 it can be observed that a small concentration of ethylene appears at a high temperature indicating a sharp increase in oligomerization activity.

It is accepted that for a HZSM-5 zeolite catalyst, Brönsted (protonic) acid sites are the active sites for the dehydration of ethanol and the subsequent reactions of hydrocarbons. Therefore, it is reasonable that any change of the Brönsted acid sites of catalyst could give rise to changes on the conversion of ethanol and the distribution of products [16]. Therefore the introduction of lanthanum in zeolite synthesis has led to decrease the acidity of the studied zeolite samples (modified La-HZSM-5 in comparison with unmodified HZSM-5). The lower acidity of the La-HZSM-5 zeolite could explain the formation of ethylene as the main reaction product.

It is to be noted that La-HZSM-5 is a high selective catalyst for the formation of ethylene by ethanol dehydration but it is not selective for the transformation to higher hydrocarbons, which is indicated by traces of liquid hydrocarbons in reaction products. Thus, the predominant reaction is the ethanol dehydration, while the subsequent reactions of hydrocarbon chain growth are not significantly. It may assume that charged hydroxy-metal cations species such as La $(OH)_2^+$ are stabilized in high silica ZSM-5 type zeolite. These lanthanum containing species can be located in the zeolite straight channel having a pore size narrowing effect and thus reducing the effective free pore volume, increasing the steric hindrance and finally improving the shape selectivity. Any modification in zeolite pore size determined by the presence of different metal cations in extra framework positions in zeolite channels results in significant changes in internal diffusion of the reactants, which leads to changes in the degree of transformation during the catalytic reaction steps. Therefore, the spatial properties of the channel system in lanthanum modified ZSM-5 zeolite prevent the formation of coke precursors due to the shape selectivity of the zeolite [8].

Our catalytic experiments show that on La-HZSM-5 catalyst, the amount of ethylene in the gaseous fraction decreases with increasing temperature (fig. 6). This can be explained by the fact that at higher temperatures the conversion of ethanol involves the oligomerization, hydrogen transfer, isomerization, aromatization and cracking reactions [8]. The presence of lanthanum cation

species in extra-framework positions in ZSM-5 structure can reduce the pore accessibility and only lead to ethylene oligomerization to C_4 species followed by C_4 species cracking to methane and propylene and this result has been confirmed by our experimental data, which are consistent with reported data. According to Ingram et al as the reaction temperature is increased, the gradual increase in the concentration of C_3 species and drastic decrease in the concentration of C_2 and C_4 products have occurred indicating that the process become more selective for C_3 species at higher temperatures. This suggests that C_3 species are not intermediate products between the formation of C_2 and C_4 species and propylene is produced by the cracking of higher olefins [17].

Conclusions

Introduction of lanthanum cations in the crystallization step of ZSM-5 zeolite generated modifications of crystallinity and acidity of the zeolite. Acidity played an important role on the product distribution for ethanol conversion over unmodified and lanthanum-modified HZSM-5. In comparison with unmodified ZSM-5 zeolite, lanthanum modified zeolite by direct-synthesis improved the catalytic performance for ethanol dehydration to ethylene at a low temperature, which could be ascribed to a decrease of the amount of acid sites and a partial blocking effect of channel system induced by the presence of extra framework lanthanum cations species. High performance of unmodified HZSM-5 in ethylene oligomerization was ascribed to the high crystallinity and high amount of acid sites of this zeolite sample synthesized at SiO_2/Al_2O_3 molar ratio of 90.

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