

Metal impregnated catalysts for bioethanol conversion tested by n-hexane cracking

Raluca PROSCANU*^a, Vasile MATEI^a, Rodica GANEA^b, George PROSCANU^a and Chol Ryong JANG^c

^a*Department of Petroleum Processing Engineering and Environmental Protection, Faculty of Petroleum Technology and Petrochemistry, Petroleum-Gas University of Ploiești, Bd. București 39, 100680, Ploiești, Romania*

^b*Zecasin S.A. Bucuresti, Romania*

^c*Department of Petroleum Processing Engineering, Faculty of Petroleum Technology, Hamhung University of Chemical Industry, Str. Jongsong, Hamhung, D. P. R. of Korea*

Abstract The catalytic activity of catalysts for bioethanol conversion to hydrocarbons was tested by cracking n-hexane in a glass microreactor in the temperature range of 623 to 823K. The microreactor is a tubular one with axial thermocouple measurements in flow, initially for some experiments in nitrogen and for others by hydrogen. Reaction products were collected and analyzed as gaseous samples by Gas Chromatography. The samples of Me-ZSM-5 zeolites (Me=Fe, La, Ce) were prepared by impregnation method. All the prepared samples had a metal content of approximate to 3 % wt. ZSM-5 zeolite was synthesized by using a structure direct agent, namely tetrapropylammonium hydroxide (TPAOH) and hydrothermal crystallisation method under alkaline conditions according to reported procedures.

Keywords: ZSM-5, metal impregnated, n-hexane, cracking

1. Introduction

Steam cracking of various hydrocarbons has been the major source of lower C₂-C₄ olefins and one of the core process in the petrochemical industry. This process requires high reaction temperatures (800-850°C) that accounts for 40% of the total energy consuming every year in the entire petrochemical industry [1]. The catalytic cracking of hydrocarbons allows preparation of olefins at lower temperature and with higher selectivity. The search for catalysts that promote hydrocarbons cracking started in the late 1960s [2]. Different types of catalysts namely acidic catalysts, basic catalysts, transition metals and oxide catalysts have been studied and found active in this process. Use of catalysts in cracking process leads to a higher yields of olefins [3, 4, 5]. The most studied and active catalysts for hydrocarbons cracking are solid proton-donor acids, including zeolites [1].

Zeolites are widely utilized catalysts in major areas of catalytic reactions: industrial petrochemical processes and pollution control. Zeolites are the key for the petroleum industry in a variety of reactions like fluid catalytic cracking, hydrocracking, paraffin isomerisations, aromatic alkylation, xylene isomerisation and toluene disproportionation [6]. There are three properties of zeolites that make them technologically important: they are selective and strong adsorbants, they are selective ion exchangers and they are catalytically active [7]. The properties of zeolites essentially originate from their structure. Cations are then required to preserve aluminosilicate framework neutrality. The presence of cations or a hydroxyl proton to balance the negative charge allows zeolite crystals to be used in ion-exchange processes but it creates an acid site (a weak Lewis acid site or a strong Brønsted acid site). The Brønsted acidity can be created by changing the original cations with a proton acid or better with

NH_4^+ cation which decomposes then by calcination generating protons bonded to the oxygen atoms of the zeolite network. Replacement of sodium ions with hydrogen leads to increased acidity zeolite surface. The notion of acidity may explain the carbocationic reaction mechanism, accelerated by zeolites as isomerization, cracking and polymerization. The carbocationic mechanism of these reactions is the formation of intermediates reaction due to the interaction between reactant molecules and acid centers on the surface of zeolite. Under the influence of a Brønsted acid site, a hydrocarbon reactant may be transformed into a carbocation [7, 8]. The acidity of zeolites is very strong, about 1000 times stronger than that of amorphous aluminosilicates. In catalytic applications, high-silica zeolites are preferred because of the thermal stability of their crystalline network [9].

The catalytic cracking of various types of hydrocarbons have been investigating over the metal impregnated ZSM-5 in order to enhance light olefins productions [1]. The effect of ZSM-5 modification on the selectivity of favorable products can be studied considering various approaches.

Maia *et al.* [10] studied ZSM-5 catalyst modified with Ni in the reaction of n-hexane cracking. Nickel was introduced in ZSM-5 zeolite by two different methods: dry impregnation and ionic exchange. Calcinated nickel ZSM-5 zeolite catalyst improves the selectivity toward light olefins in cracking reaction when compared to pristine zeolite. A careful examination of nickel supported on silica catalyst (mixed or not with ZSM-5) and ZSM-5 confirmed that the bi-functional catalysis occurred on calcinated Ni-ZSM-5 samples. This bifunctional catalysis can be optimized by the use of a proper methodology for metal impregnation.

Wakui *et al.* investigated the effect of alkaline earth metal (i.e. Mg, Ca, Sr, Ba) modification on the performance of H-ZSM-5 in the catalytic cracking of n-butane. The favorable results ($\text{C}_2^- + \text{C}_3^-$) were obtained over Ba-ZSM-5 [11]. The ZSM-5 zeolites modified with transition metals, such as Cu, Zn and Ag increase the yield of aromatics and reduce $\text{C}_2^- + \text{C}_3^-$ yield in catalytic cracking of C_4 alkanes [3, 12].

The effect of rare earth metals on catalytic performance of H-ZSM-5 zeolite was investigated by Wang *et al.* The best total alkenes yield was

achieved over Ce/H-ZSM-5 at 600°C and Nd/H-ZSM-5 at 650°C. The loading of rare earth metal in H-ZSM-5 sample promotes the performance of H-ZSM-5 [13]. The use of tridimensional micropore structure ZSM-5 zeolite with large specific surface area, modified with alkaline and alkaline earth metals, transition metals, rare earth elements has led to promising results in the catalytic cracking of different types of hydrocarbons at 550-650°C that is about 200°C lower than the steam cracking [1].

In this work, we investigated the catalytic properties of modified ZSM-5 zeolite by metal impregnation for the cracking of n-hexane. The catalytic cracking of n-hexane over Me-HZSM-5 (Me = Fe, La, Ce) was studied as a test reaction of bioethanol conversion to hydrocarbons to find the performance of catalysts.

2. Experimental

2.1. Catalysts preparation

A series of H-ZSM-5 type zeolite supported catalysts has been prepared as follows. A sample of ZSM-5 zeolite has been synthesized in the presence of tetrapropylammonium hydroxide as structure directing agent according to reported procedures. The synthesized Na-ZSM-5 zeolite powder was calcinated in air at 550°C for 8 h to remove organic cations occluded in the zeolite network. Then, the calcinated Na-ZSM-5 zeolite powder was converted to ammonium form by ion exchange with 1M NH_4NO_3 solution for two times at 90°C followed by filtering, washing with distilled water and drying at 80°C overnight. The resulting NH_4 -ZSM-5 zeolite powder was formulated by extrusion using a pseudoboehmite type hydrated alumina (65% Al_2O_3) as binder and nitric acid (12 % wt. HNO_3) as peptising agent. The obtained extrudates were dried at room temperature for 24 h and at 80°C overnight and finally calcinated at 550°C for 4 h to convert the ammonium form to the hydrogen form of the ZSM-5 zeolite and to transform the hydrated alumina to the γ - Al_2O_3 phase. The final composition of the calcinated support (cylindrical extrudates having a diameter of 2 mm and a length of 3-5 mm) consisted of 60 % wt. of H-ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 90) and 40 % wt. of γ - Al_2O_3 . The catalyst samples containing different trivalent metallic cations ($\text{Me}^{3+} = \text{Fe}^{3+}$, La^{3+} and Ce^{3+} , respectively)

were obtained by incipient wetness impregnation of the H-ZSM-5 based extruded support using aqueous nitrates solutions of iron, lanthanum and cerium, respectively of suitable concentrations to obtain a final concentration of metallic cation/support of 3 % wt. After drying at room temperature for 24 h, the impregnated support samples were dried at 80°C overnight and finally calcined at 550°C for 4 h. During calcination metal nitrates pass into corresponding metal oxides.

2.2. Catalytic reaction

The catalytic activity of catalysts was tested by cracking of n-hexane. The catalytic studies were performed at atmospheric pressure in a electrically heated fixed bed reactor (diameter 16,4 mm, length 620 mm) [10]. The quartz microreactor is a tubular one with axial thermocouple temperature measurements in flow. Prior to the reaction, the catalyst was activated at 450°C for two hours under a flow of dry nitrogen. The catalyst (1g) was loaded in a special temperature zone (the center of the microreactor) and the inert porcelain clay was packed in the rest of the microreactor. The reaction temperature was controlled with chromel-alumel thermocouple placed in the center of the catalyst bed. The temperature varied between 350°C and 550°C. The reaction was performed by diluting n-hexane vapors with a carrier gas under constant flow rate (approximately 900 h⁻¹). Two sets of experiments were conducted in different carrier gas: one in nitrogen flow and another in hydrogen flow. N-hexane (Merck, 99,8%) was pumped into microreactor and mixed with carrier gas. Under the given conditions n-hexane underwent cracking to C₁-C₄ paraffins and C₂-C₄ olefins. The reaction products were collected like gaseous samples and analyzed by Gas Chromatography with stationary phase ββ'- dioxipropionitril HWD with High Resolution Gas Chromatograph 5300 Series Carlo Erba Instruments. The chromatograph was operated under the following conditions: column temperature of 25°C, interface temperature of 25°C and injector temperature of 200°C, using hydrogen as mobil phase. The liquid reaction products were collected using a condensation device which was cooled in ice and then were measured.

3. Results and Discussions

The results obtained with experimental planning showed that the gaseous products of the catalytic cracking of n-hexane are CH₄, C₂ (ethane, ethylene), C₃ (propane, propene), C₄ (butanes, butenes,). The **figures 1-3** show the catalytic performances over Fe/H-ZSM-5, La/H-ZSM-5, Ce/H-ZSM-5 catalysts in n-hexane cracking under different reaction conditions.

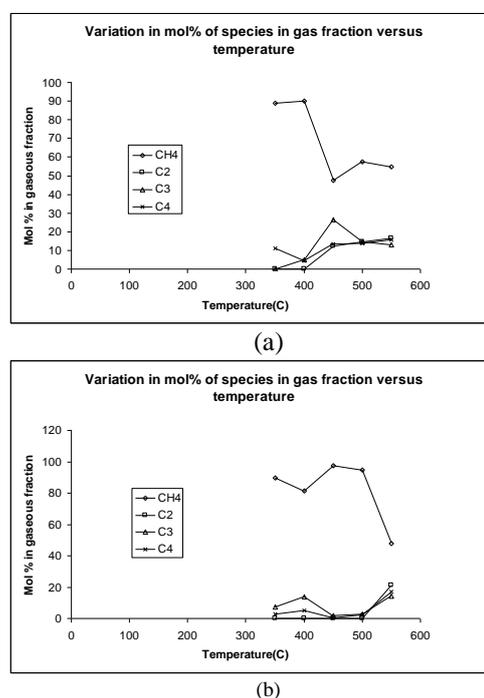


Fig.1 Variation of compounds concentration in gas fraction versus temperature for Fe/H-ZSM-5 catalyst in (a) nitrogen or (b) hydrogen carrier gas, % mol

The results indicate that the products distribution was directly affected by the temperature and the type of the carrier gas. It can be seen that the decreasing/increasing of the molar percentage of methane leads to increasing/decreasing of the molar percentage of the C₂, C₃, C₄ species. High temperatures are favorable to obtain a low molar percentage of methane in the gas fraction.

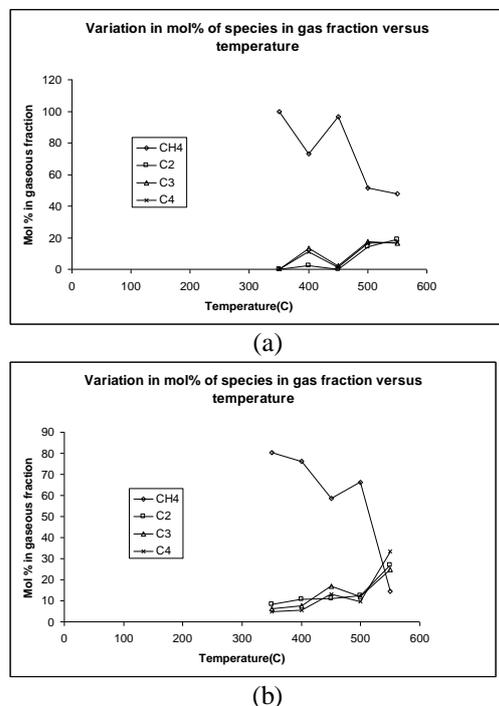
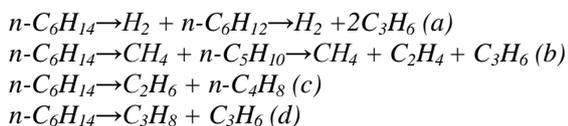


Fig.2. Variation of compounds concentration in gas fraction versus temperature for La/H-ZSM-5 catalyst in (a) nitrogen or (b) hydrogen carrier gas, % mol

The authors believe that this large amount of methane established by chromatographic analysis of gaseous products is confirmed by the fact that coke is formed on the catalyst surface. For testing of La/H-ZSM-5 catalyst it has been observed a lower coke deposition. Therefore it is found that the H-ZSM-5 impregnation with lanthanum nitrate reduces the molar percentage of methane which could prevent the coke deposition and improve its stability. The result is in good agreement with literature [14].

The reaction products can be accounted for by the following monomolecular cracking for n-hexane:



Although several additional reactions (e) and (f) are possible:

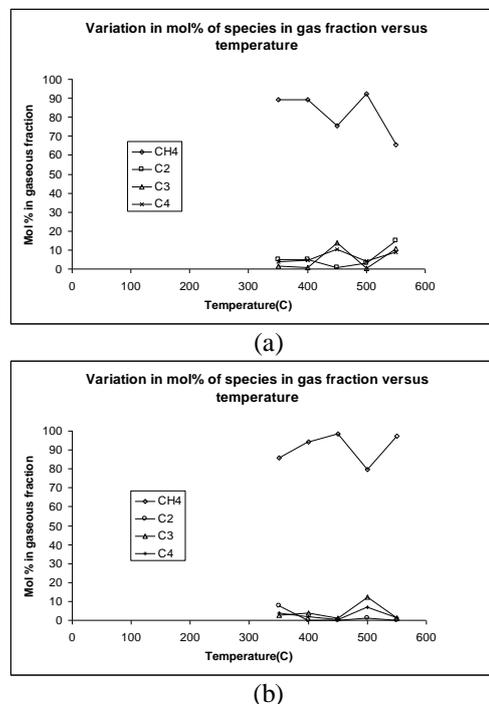
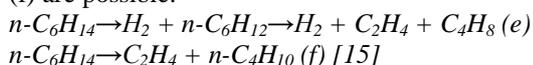


Fig.3 Variation of compounds concentration in gas fraction versus temperature for Ce/H-ZSM-5 catalyst in (a) nitrogen or (b) hydrogen carrier gas, % mol

As expected for a selective cracking reaction, low molecular weight hydrocarbons, such as ethane are favored by higher temperature. At a high temperature, part of the butane molecules produced by cracking of n-hexane begins to be consumed by forming propane or ethane [16].

The hydrogen resulting from different reactions may be used up in the saturation of olefins through hydrogen transfer reactions or it may be released as hydrogen. **Figures 4-6** (the set of experiments in the presence of nitrogen as carrier gas) show by increasing the reaction temperature, the propane/propene ratio or butane/butenes ratio increased gradually, indicating progressive saturation of propene or butenes.

For comparison, the level of saturation of other olefins (ethylene) was far less pronounced. These results suggest that the catalysts have H-transfer abilities. This H-transfer ability of the catalysts might be helping in desorbing the strongly adsorbed olefins as saturates and aromatics [17].

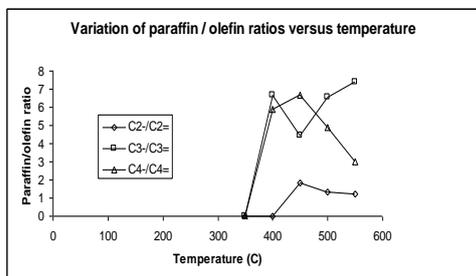


Fig.4. Variation of paraffin/olefin ratios versus temperature for Fe/H-ZSM-5 catalyst

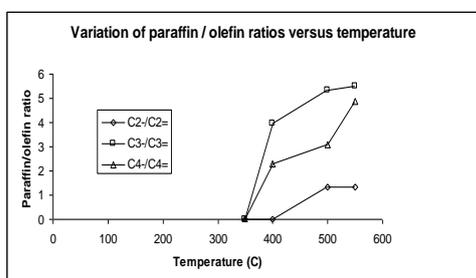


Fig.5. Variation of paraffin/olefin ratios versus temperature for La/H-ZSM-5 catalyst

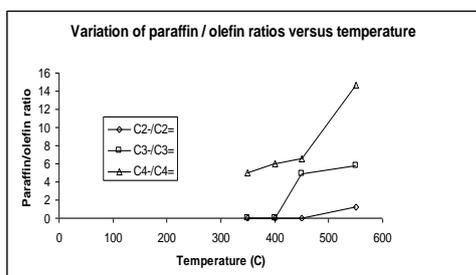


Fig.6. Variation of paraffin/olefin ratios versus temperature for Ce/H-ZSM-5 catalyst

Because there are different reactions that may take place in the presence of the studied catalyst such as n-hexane cracking, hydrogenation of the olefins, isomerisations, we explain these results to be caused by the competitive reactions occurring on different active sites of the catalysts.

4. Conclusions

A wide range of products can be obtained by using metal impregnated ZSM-5 zeolite in the n-hexane cracking. Me/H-ZSM-5 catalysts are suitable for the formation of small olefins and paraffins. Among the impregnated metal oxides from the best results were obtained by lanthanum at temperatures of 550°C in the presence of the hydrogen gas carrier. The authors believe that this metal can be used as promoter in catalytic cracking process due to its ability to lower the coke content. C₃, C₄ species are formed in significant amount over Fe/La/H-ZSM-5 catalysts, at a high temperature. As a result of a parallel formation of propene or butenes, a significant hydrogen transfer activity takes place between them resulting in the saturation of propene or butenes while ethylene played a less significant role. Ingram *et al.* studied the conversion of bioethanol to C₃ hydrocarbons and observed the formation of C₄ species; as the reaction temperature was increased, C₄ was further polymerized to higher olefins, some of which were cracked into C₃ species [18]. Behind theoretical and experimental studies, the authors are going to test this set of catalysts in the conversion of bioethanol to hydrocarbons.

5. Acknowledgments

The authors thank scientific committee of international conference CHIMIA 2012 "New trends in applied chemistry" for the useful discussions.

6. References

- * E-mail address: rproscanu@yahoo.com
- [1].N. Rahimi and R. Karimzadeh, *Applied Catalysis: General* **398** 1-17 (2011)
 - [2].J. Zheng, J. Dong, W. Zhang, Q. Xu and C. Song, *Fuel Chemistry Division Preprints*, **47**(1), 181 (2002)
 - [3].Y. Yoshimura, N. Kijima, T. Hayakawa, K. Murata, K. Suzuki, F. Mizukami, K. Matano, T. Konishi, T. Oikawa, M. Saito, T. Shiojima, K. Sheozawa, K. Wakui, C. Sawada, K. Satof, S. Matsuto and N. Yamaoka, *Catal. Surv. Jpn.* **4** 157-167 (2000)
 - [4].J. Feigl, G. Schmidt, *Hydrocarbon Process*, **86** 45-54 (2007)

- [5].Y. Wei, Z. Liu, G. Wang, Y. Qi, L. Xu, P. Xie and Y. He, *Stud. Surf. Sci. Catal.* **158** 1223–1230 (2005).
- [6].F.C.Jentof and B.C.Gales, *Top.Catal.* **4**, 1-13 (1997)
- [7]. J. Cejka, H. van Bekkum, A. Corma, F. Schüth (Eds), *Introduction to Zeolite Science and Practice*, 3rd Revised Edition, **168** 1-105 (2007)
- [8]. M.Crueceanu, *Zeolitic molecular sieves (in Romanian)*, ed. Stiintifica si Enciclopedica, Bucuresti 1986, pp.257-264
- [9].C.J.Y. Houssin, *Nanoparticles in Zeolite Synthesis*, Technische Universiteit Eindhoven, 2-12 (2003)
- [10].A.J. Maia, B. Louis, Y.L. Lam and M.M. Pereira, *Journal of Catalysis* **269** 103–109 (2010)
- [11].K. Wakui, K. Satoh, G. Sawada, K. Shiozawa, K. Matano, K. Suzuki, T. Hayakawa, Y. Yoshimura, K. Murata and F. Mizukami, *Catal. Lett.* **81** 83-88 (2002)
- [12].J. Schultz and F. Bandermann, *Chem. Eng. Technol* **15** 413-418 (1992)
- [13].X. Wang, Z. Zhao, C.Xu.A. Duan, L. Zhang and G. Jiang, *J. Rare Earth* **25** 321-328 (2007)
- [14].X. Zhao, X. Guo and X. Wang, *Energy Fuels* **20** 1388 (2006)
- [15].E. Rojasov, A. Smiekov, P. Hudec and Z. Zidek, *React. Kinet. Catal. Lett.* **66**(1), 91-96 (1999)
- [16].M.J.B. Souza, F.A.N. Fernandes, A.M.G. Pedrosa and A.S. Araujo, *Fuel Processing Technology* **89** 819 -827 (2008)
- [17].S.K. Saha and S. Sivasanker, *Catal. Lett.* **15** 413-418 (1992)
- [18].C.W. Ingram, R.J. Lancashire, *Catal. Lett.* **31** 395-403 (1995)

Submitted: September 28th 2012

Accepted in revised form: October, 25th 2012