Application of Zeolitic Additives in the Fluid Catalytic Cracking (FCC)

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Abstract

Current article describes application of zeolites in fluid catalytic cracking (FCC). The use of several zeolitic additives for the production light olefins and reduction of pollutants is described. Application of zeolites as fluid catalytic cracking (FCC) catalysts and additives due to the presence of active acid sites in the zeolite framework increase the formation of desired cracking products (i.e., olefin and branched products) in the FCC unit.

1. Introduction

1.1. Description of FCC unit

Crystalline nanoporous materials like zeolites have numerous industrial applications. They have determinant features, such as high surface area, uniform porosity, accessible pore volume, high adsorption capacity, ion-exchange ability, enhanced catalytic activity, selectivity based on shape and size and etc. Fluid catalytic cracking (FCC) is a central technology in modern refining. The FCC unit is used to upgrade heavy gas oils and residue to high-octane gasoline, diesel fuel, and light gases [1]. This is accomplished by cracking the vaporized feed over a solid acid catalyst, e.g. zeolite. The catalyst promotes a reaction mechanism which can be explained by carbonium ion theory. A fluid catalytic cracking (FCC) process or apparatus employs a catalyst in the form of fine catalyst particles which act as a fluid when aerated with a vapor. The fluidized catalyst is circulated continuously between a reactor and a regenerator and acts as a vehicle to transfer heat from the regenerator to the hydrocarbon feed and reactor (schem. 1) [2]. The fluid catalytic cracking process or apparatus is valuable to convert heavy hydrocarbons into more valuable distillate gasoline and lighter products.

1. 2. Zeolite catalyst in FCC

The introduction of zeolite in commercial FCC catalysts in the early 1960s was one of the most significant advances in the history of cat cracking (FCC). Zeolite catalysts provided a greater profit with little capital investment. Zeolite catalysts were

and still are the biggest bargain of all time for the refiner. Compared to amorphous silica-alumina catalysts, the zeolite catalysts are more active and more selective. The higher activity and selectivity translate to more profitable liquid product yields and additional cracking capacity [3].
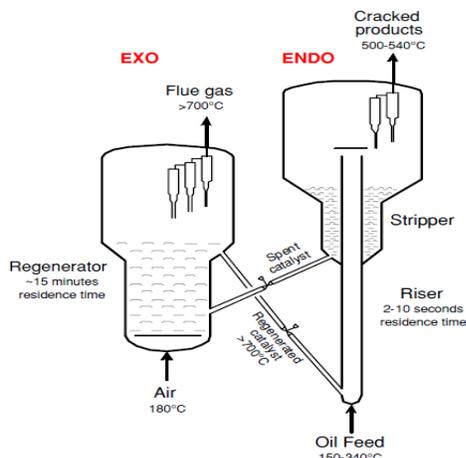
Scheme. 1. schematic representation of a modern FCC(fluid catalytic cracking) unit.

Basically, the FCC catalysts are divided into three main categories, based on the refiners objectives: (i) maximization of valuable products, (ii) improvement of gasoline quality and (iii) minimization of residues. In order to achieve those goals, the FCC catalyst used during the last decades was consisted of two major components, the zeolite and the matrix. Besides, those catalysts can also have other functional ingredients and/or additives for specific functions like enhancement of gasoline octane, increasing of the conversion of residual feedstocks, enhancement of the resistance to metallic poisons, promotion of the CO combustion, reduction of the NO_x and SO_x emissions, etc [4].

Zeolite FCC catalysts must have the following characteristics:

-catalytic (controlled acidity) properties which allow the cracking of feedstocks into the desired product,

- attrition resistance in the circulating environment,
- fluidizability,
- hydrothermal stability at the partial temperatures and steam pressures in the regenerator,
- minimized coking tendency at a high cracking activity when processing resids,
- metals tolerance when using heavy feedstocks.

2. Experimental procedure
2.1. Catalyst components

The current FCC catalysts consisted of a complicated combination of different materials, which have different functions: acidic functions in amorphous and crystalline matrices, metal impurities traps, combustion promoters, SO_x traps, octane boosters, and olefins promoter additives. The acidic functions in FCC catalysts are due to the local structure of aluminosilicates either crystalline or amorphous. Acid sites in the crystalline framework of zeolites have a lower tendency to form coke because of the shape selectiveity. In addition, the aluminum concentration in the crystalline framework can affect the properties of the acid site: high Si/Al ratios tend to depress the hydrogen transfer attitude and therefore to reduce the olefins saturation, the aromatic formation, and the coke formation. The size of the zeolite pores limits the activity to the molecules that can access the active sites. The porosity of the silica–alumina matrix can be tuned by the preparation procedure and pore size can span from micro-, to meso- to macropores. In the last 40 years, the zeolite phase has been optimized in to reach the maximum conversion and the optimum product quality. From

this point of view, the best product is still the modified Y-type zeolite [5].

A fresh FCC catalyst is composed of spray-dried spherical, fluidizable, attrition-resistant particles, typically containing 20–40% ultrastable Y (USY) zeolite, a binder, and optionally a catalytically active, acidic matrix, as well as various additives that serve different functions. FCC catalysts are in the form of fine powders with an average particle size in the range of 75 microns. A modern cat cracking catalyst has four major components: zeolite, matrix, binder, and filler [6].

2.1.1. Zeolite

Zeolite is the key ingredient of the FCC catalyst which increases product selectivity and catalytic activity. The catalyst activity is highly depended on the nature and quality of the zeolite. To reach the desired yields, understanding of the zeolite structure, types, cracking mechanism, and properties is necessary.

2.1.2. Matrix

The matrix i.e. the non-zeolitic catalyst component contributes significantly to the overall performance of the FCC catalyst. An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not as selective as the zeolite sites, but are able to crack larger molecules that are hindered from entering to the small pores of zeolite. The active matrix precracks heavy feed molecules for further cracking at the internal zeolite sites [7]. The result is a consequence of the interaction between matrix and zeolite, in which the activity attained by their combined effects can be greater than the sum of their individual effects. One of the advantages of an active matrix is that it guards the zeolite from becoming deactivated

prematurely by impurities, e.g. the vanadium and basic nitrogen [8].

2.1.3. Filler and Binder

The filler is a clay incorporated into the catalyst to dilute its activity. Kaoline is the most common clay used in the FCC catalyst. The binder serves as a glue to hold the zeolite, matrix, and filler together. Binder may or may not have catalytic activity.

2.1.4. Additives

For many years, cat cracker (FCC) operators have used additive compounds for enhancing cracking performance of the catalyst. The main benefits of these additives (catalyst and feed additives) are to alter the FCC yields and reduce the amount of pollutants emitted from the regenerator.

3. Results and discussion
3.1. Production of light olefins

Higher yields of light olefins (C_3 and C_4) in the FCC process are desirable since they can be used for the production of polypropylene, high-octane gasoline additives, such as methyltertiarybutyl ether (MTBE) and alkylation gasoline. Utilization of the Ultra-Stable Y (USY) zeolite as the main active component of the FCC catalyst and addition of the shape-selective ZSM-5 zeolite enhance the production of light alkenes and increases the gasoline research octan number (RON) [9].

The LPG produced in the FCC is an important source of C_3-C_4 olefins. An effective way to increase the propylene yield from the FCC unit is the use of specialized catalysts containing ZSM-5 zeolite [10]. ZSM-5 has shown a very good ability to strongly increase the produced propylene when it is used as a zeolitic FCC additive. Generally, to maximize propylene yield, the content of ZSM-5 in FCC catalysts should be increased, but the costs to

be paid are consisted of the loss of catalyst activity and other desirable products. The shape selectivity of ZSM-5 allows preferential cracking of long-chain, low-octane normal paraffins, as well as some olefins, in the gasoline fraction. ZSM-5 accomplishes this by upgrading low-octane components in the gasoline boiling range (C_7 to C_{1O}) into light olefins (C_3, C_4, C_5), as well as isomerizing low-octane linear olefins to high-octane branched olefins, ZSM-5 inhibits paraffin hydrogenation by cracking the C_7^+ olefins [11]. The higher increase in the formation of gaseous alkenes was achieved by the H/Cu-ZSM-5 additive [12]. The catalytic activity of metal-modified H-ZSM-5 zeolite as FCC catalyst-additive depends both on the number and strength of its acid sites and on the nature and the amount of the metal species within the zeolite sample. However, the modification of H-ZSM-5 with different metal ions, such as transition metal ions that exhibit high dehydrogenation activity, can promote the formation of light alkenes in the FCC process. Partially ion-exchanged H-ZSM-5 zeolite with copper provides an effective catalyst-additive for maximizing light alkenes yield (propylene and butylenes) without increasing coke formation.

A novel FCC catalyst NaY/kaolin composite microspheres with additive microspheres containing HZSM-5 was applied for maximizing propylene production. The catalytic cracking results confirmed that compared to the commercial catalyst, the propylene yield of the novel catalyst was increased and propylene selectivity and the coke yield was decreased (Table1) [13].

Medium pore-size zeolites other than ZSM-5 were investigated as an FCC additive include MCM-22 and ITQ-13. MCM-22 gives a similar increase in propene yield at lower loss in gasoline yield compared to ZSM-5, mainly because it forms less

propane at the same time. ITQ-13, behaves similarly.

Table 1. Product distributions of the two propylene maximizing FCC catalysts

Produt	The commercial catalyst	The novel catalyst
Propylene yield (Wt%)	8.08	9.35
Propylene selectivity (Wt%)	30.56	33.49
Coke (Wt%)	7.71	5.72

Beta zeolite was successfully applied for increasing the C_4 and C_5 olefinic products and more specifically the yields of isobutylene and isopentene. Possible application of zeolite beta as a cracking component has been studied quite extensively, with the aim of increasing isobutane or isobutene yields, or overall butene yields .Hydrothermal stability is poor compared to zeolite USY, which is why phosphorus stabilization would be in all likelihood necessary [14]. Dual zeolite additives containing MFI and MOR (or BEA) are effective to improve the production of light olefins in the FCC reactions. Both MOR and BEA zeolites are more effective after a treatment with phosphoric acid. The use of MFI-based additives in the fluid catalytic cracking (FCC) process in order to increase both the production of light olefins and gasoline octane number has been commercially proven [15]. It is well known that impregnation by phosphorus increases the stability of aluminum atoms of H-MFI zeolite framework, resulting in higher yields of desired products. Phosphorus treatment has an impact on both MOR and BEA zeolites. H-MOR and H-BEA zeolites both treated with P improved the catalytic activity and selectivity of the catalysts as already observed for H-MFI. Propene yield at iso-conversion for the

samples that underwent hydrothermal treatment is presented on (Fig.1). Although the presence of phosphorus reduced the surface area, propene yield was increased in the presence of either MOR or BEA samples when compared to the base case [16]. It was observed that the steamed samples containing phosphorus presented a similar activity compared to the phosphorus free steamed.
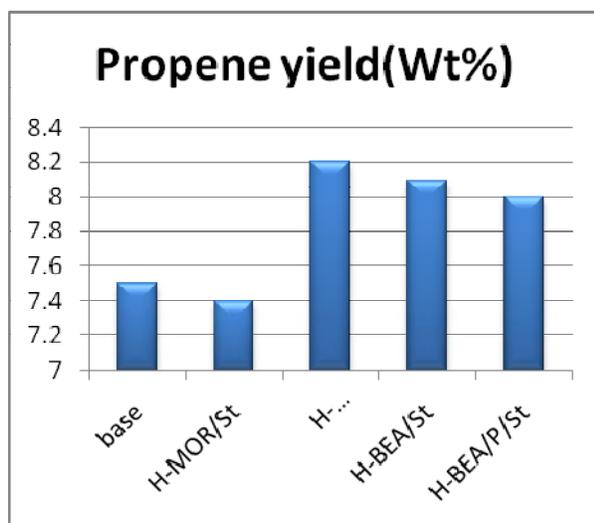

Fig. 1. Propene yield at iso-conversion of 68 wt.%.

ITQ-7, yields more gasoline of a higher alkene and lower aromatics content, by virtue of a reduced extent of hydrogen transfer. In the catalytic cracking of gasoil, when comparing with beta zeolite, ITQ-7 produces higher gasoline yield, with lower content of aromatics, more isoamylenes, and higher olefinicity in the LPG fraction. ITQ-7 gives higher ratios of propylene/propane, butenes/butanes and isobutene/isobutane than beta. This indicates that a lower ratio of hydrogen transfer to cracking is taking place in the pores of Al-ITQ-7. Results indicate that the lower content in aromatics for ITQ-7 gasoline should produce a decrease of the research octane number (RON) of the gasoline produced; that is, however, compensated by the increase in isoparaffins and isoolefins obtained when using

ITQ-7. The use of ITQ-7 of lower Si/Al ratio produces a gasoline with higher aromatic content and a decrease in isoparaffins with similar levels of olefins and naphthenes. RON and MON are also increased when using ITQ-7 with more framework aluminum. It seems that the benefit in the octane numbers comes mainly from the increase in the aromatic content. Thus high Si/Al ratios would be preferred to obtain gasoline with less aromatics and higher isoamylene yields [17].

La-P/ZSM-5- and $MgAl_2O_4$-based bifunctional additives are for enhancing the production of propene and removal of SO_2 in the FCC process. Results obtained with the addition of bifunctional additives (HZSM-5/$MgAl_2O_4$ and LaPZSM-5/$MgAl_2O_4$) and the commercial additive ZSM-5/kaolin to the base are shown in Table 2 [18].

Table 2. Product distributions with 10 Wt% propene additive.

Additives	HZSM-5/$MgAl_2O_4$	LaPZSM-5/$MgAl_2O_4$	ZSM-5/kaolin
Conversion (Wt%)	82.77	83.48	82.22
Gasoline (Wt%)	42.91	38.66	38.61
Coke (Wt%)	8.23	8.79	8.77
$C_3^=$/LPG (Wt%)	0.3405	0.3615	0.354

It is clear that HZSM-5/$MgAl_2O_4$ was the least active of the three aged additives. The addition of LaPZSM-5/$MgAl_2O_4$ and ZSM-5/kaolin resulted in approximately similar shifts in LPG and gasoline yields. With respect to the propene selectivity in LPG, the introduction of LaPZSM-5/$MgAl_2O_4$ and ZSM-5/kaolin also brought evidently larger increases than HZSM-5/$MgAl_2O_4$. Besides, the slightly lower conversion with the insertion of the additives was due to the dilution effect of the propene additive, and the little influence on the coke

yield arisen from the low acid density and small pore diameter of MFI zeolite. However, greater differences in LPG and propene yields were observed between LaPZSM-5/MgAl$_2$O$_4$ and ZSM-5/kaolin. It appeared that LaPZSM-5/MgAl$_2$O$_4$ was somewhat superior to ZSM-5/kaolin for improving yields of light olefins, especially for the propene yield.The added MCM-41 to FCC catalyst is positively capable to crack heavy oil feedstock, in which the yields of the diesel and lighter oil increased and coke yield decreased [19]. Gao reported that mesoporous MCM-41 co-promoted REUSY FCC catalyst were positive to improve the selectivities for gasoline, diesel and propylene and negative to coke deposition [20].

3.2. Reduction of gasoline olefin

In order to reduce the contents of sulfur compounds and olefins of FCC gasoline as well as preserve its RON, because of the high olefin content of gasoline causes the terrible automobile emissions, researchers have proposed various hydro-upgrading processes that combine hydrodesulfurization (HDS) with hydrocracking and hydroisomerization. Zeolite ZSM-5 has excellent activity for both HDS and light alkane and alkene aromatization. Moreover, silicoaluminophosphate zeolite SAPO-11 has been widely applied to the isomerization of C$_4$–C$_7$ hydrocarbons for producing gasoline with high RON [21]. SEM pictures of samples are shown in Fig 2. It was confirmed by these images that the composite had more mesopores favorable for the diffusion of substances and suitable acidity distribution advantageous to enhancing the synergism effect between Bronsted and Lewis acids.

To develop a novel catalyst system that has excellent olefin reduction capability for FCC gasoline without loss in octane number, the SAPO-

11/HMOR/β/ZSM- 5 quadruple composite zeolite supported catalyst led to higher liquid yield, improved gasoline RON, and lower coke deposit amount for the hydro-upgrading of FCC gasoline and thus can be considered as a potential catalyst system [22]. Acid strength and acid type were two important factors influencing hydroisomerization and aromatization activities, a novel technique that can preserve gasoline octane number while reducing the olefin content of gasoline. A FCC gasoline upgrading process with balanced hydroisomerization and aromatization performance is necessitated. The loss of gasoline octane number due to olefin reduction can be compensated by the increase of i-paraffins and aromatics that have higher octane number. A catalyst system based on composite carriers consisting of silicoaluminophosphate and aluminosilicate zeolites should provide a balanced isomerization and aromatization performance and thus benefit the upgrading of FCC gasoline. HMOR, Hβ and SAPO-11 are advantageous in hydroisomerization and HZSM-5 is predominant in aromatization.Modified nanoscale ZSM-5 zeolite was used for the olefins reduction in FCC gasoline. When the crystal size of HZSM-5 zeolite was reduced to the nanoscale, it showed stronger ability and better stability for olefins reduction than the microscale ones, and found that olefins were greatly transformed into aromatics with a high RON [23].TEM image of ZSM-5 (Fig 3) shows that the crystal size of ZSM-5 is about 20–50 nm. The crystal size of zeolites has a great effect on catalytic activity and selectivity.
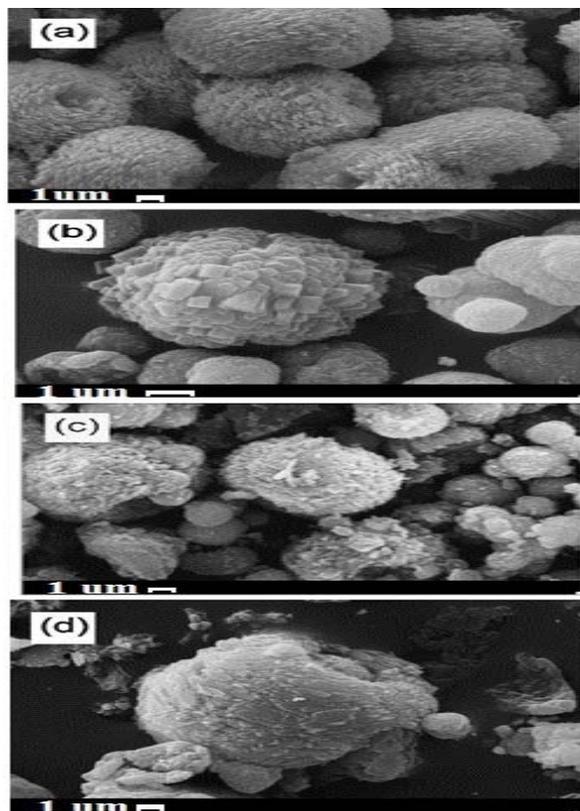
Fig 2. SEM images of the as-synthesized samples (a) SAPO-11 (pseudo-spherical aggregates of the size ranging from 7 to 8 mm consisting of uniform cubic plate monocrystals), (b) ZSM-5 (spherical aggregates of the size ranging from 3 to 5 mm), (c) mechanical mixture (the large pseudo-spherical particles assigned to SAPO-11 are separate from the small spherical ones assigned to ZSM-5) (d) composite crystallized (the ZSM-5 phase in the composite is covered by a film of SAPO-11).
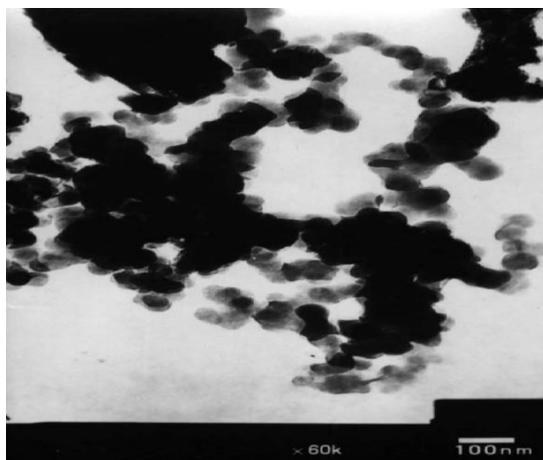

Fig. 3. TEM picture of nanoscale ZSM-5.

One effective approach to the reduction of gasoline olefins is the use of extremely high hydrogen transfer catalysts (the beneficial effects of increasing hydrogen-transfer activity are the reduction in gasoline olefinicity and increasing gasoline yields).

3.3. Reduce the amount of pollutants emitted from the regenerator and gasoline sulfur control

Sulfur oxides (SO_x) are a major atmospheric pollutant and precursors for acid rain. The majority of SOx produced from the FCC unit comes from the sulfur in coke that is burned off during hydrothermal regeneration of the catalyst in the FCC regenerator [24].

The main source of sulfur in gasoline is the FCC gasoline and desulphurization has to be executed with care so as not to reduce octane quality. Sulfur in gasoline increases SO_x emissions in combustion gases, reduces the activity of vehicle catalytic converters, and promotes corrosion of engine parts [25]. The Ga/alumina additive was able to reduce sulfur content of FCC gasoline fraction. La-P/ZSM-5- and $MgAl_2O_4$-based bifunctional additives adsorb SO_x and then transfer sulfur back into the riser, where it is released as H_2S, which is removed in the usual way (Claus process) [26].

The synergistic effects of Bronsted acid and Lewis acid in catalyst are also an important factor for sulfur reduction. Therefore, one of the key objectives in FCC catalyst development is to modify zeolite to achieve a suitable acidity to effectively remove sulfur. The USY modified with the combination of rare earth elements and V yielded the superior catalyst that showed both high sulfur reduction performance and desirable product selectivity [27].

The use of MCM-36 as catalytic additives for the reduction of NO from FCC regenerator flue gas

streams. The results demonstrate the high catalytic activity of MCM-36-type materials containing mixed alkaline earth aluminum oxide pillars in the reduction of NO with CO to N_2 and CO_2, in the presence of oxygen [28].

3.4. Potential Use of Other Zeolites in FCC

New types of zeolite materials with large (12-MR) or extra-large (14-MR) micropores have been synthesized and tested as FCC catalysts or as their additives, i.e. MCM-22 (MWW) [29], CIT-1 (CON) [30], SSZ-24 (AFI) [31], ITQ-7 (ISV), NU-86 (no FTC), NU-87 (NES), IM-5 (IMF) [32], ITQ-21 [33] and ITQ-33 [34].

The main requirement of the FCC catalyst components is their cost because FCC units may be fed up to several tons per day of fresh catalyst. Many of the newer structures require relatively expensive organics and/or long hydrothermal synthesis times, and although it is not inconceivable that low-cost synthesis routes may be developed for alternative materials, cost is likely to remain a significant hurdle.

4. Conclusion

Fluid catalytic cracking (FCC) is a central technology in modern refining that upgrade heavy gas oils and resid fuels to high-octane gasoline, diesel fuel, and light gases by solid acid catalyst, e.g. zeolite. The use of several zeolitic additives for the production light olefins and reduction pollutants is described. Hydrothermal stability and metals tolerance are the main advantages of zeolites.

References

[1] X. Zhao, T.G. Roberie, K. Rajagopalan, Appl. Catal. A. 145 (1996)
407–418.

[2] D.W. Kraemer, H. I. de Lasa, Ind. Eng. Chem. Res. 27 (1988) 2002–2008.

[3] H. Harding, A.W. Peters, J. R. D. Nee. Appl. Catal. A 221 (2001) 389–396

[4] W.H.J. Stork, I. E.Maxwell, Stud, Surf. Sci. Catal. 137 (2001) 747–819.

[5] J.E. Otterstedt , S.B. Gevert, P.G. Menon, Appl. Catal. 22 (1986) 159–179.

[6] V. P. Doronin, T. P. Sorokina, J. Gen. Chem. 77 (2007) 2224–2231

[7] P. Gamero, C. Maldonado, J. C. Moreno, O. Guzman, Stud. Surf. Sci. Catal. 111 (1997) 375–382

 [8] S. Jen Yang, Yu-Wen Chen, C. Li. , Appl. Catal. A 116 (1994) 59–68.

[9] J. S. Buchanan, Y. G. Adewuyi, Appl. Catal. 163 (1997) 15–29.

[10] J. Biswas, I. E. Maxwell. Appl. Catal. A 58 (1990) 19–27.

[11] J. S. Buchanan, Catal. Today 55 (2000) 207–212

[12] A. A. Lappas, C. S. Triantafillidis, Z. A. Tsagrasouli, V. A. Tsiatouras, Stud. Surf. Sci. Catal. 142 (2002) 807–814.

[13] H. Liu, H. Zhao, X. Gao, J. Ma, Catal. Today 125 (2007) 163–168

[14] N. Kubicek, F. Vaudry, B.H. Chiche, P. Hudec, Appl.Catal. A 175 (1998) 159–171.

[15] T. Blasco, A. Corma, J. Martinez-Triguero, J. Catal. 237 (2006) 267–277.

[16] F. Costa, . S .Henrique, M. M. Ferreira, M. S. Ruiz. Appl. Catal. A 319 (2007) 137–143

[17] A. Corma, J. Triguero, C. Martinez, J. Catal. 197 (2001) 151–159

[18] X. Xu, X. Ran, Q. Cui, Ch. Li, H. Shan. Energy Fuels 24 (2010) 3754–3759

[19] D. Jian-Wen, S. Chun-Min Q. Ling, S. Jian-Ming, X. Xing-Zhong, J .Porous Mater.15 (2008) 189–197

[20] R. G. Tailleur, J. B. Platin. J. Porous Mater. 106 (2005) 77-83

[21] Y. Fan, D. Lei, . Shi, X. Bao. Catal. Today. 114 (2006) 388–396.

[22] Y. Fan, X. Bao, D. Lei, G. Shi, Fuel 84 (2005) 435–442

[23] Z. H. Peiqing, W. Xiangsheng, G. Xinwen, G. Hongchen. Catal. Lett . 92 (2004) 1–2

[24] R. Maya-, E.F. Villafuerte R. Aguilar. Chem. Eng. J. 106 (2005) 145–152

[25] J. S Yoo, A. A. Radlowski. Ind. Eng. Chem. Res. 31(1992) 1252–1258

[26] K. Gwan, M. Olney. U.S. Patent 5,399,327, (1995).

[27] X. Pang, L. Zhang, Sh. Sun, T. Liu, X. Gao. Catal. Today 125 (2007) 173–177

[28] J.Olaf Barth, A. Jentys, E. F. Iliopoulou,A. Vasalos, J. A. Lercher. J. Catal. 227 (2004) 117–129.

[29] A. Corma, J. Martinez-Triguero, J. Catal. 165 (1997) 102–120.

[30] A. Corma, V. Gonza´ lez-Alfaro, A. V. Orchilles. Appl. Catal. A 187 (1999) 245–254.

[31] A. Corma, M. Davis, V. Forne, V. Gonz lez-Alfaro, R. Lobo, A. V. Orchille, J. Catal. 167 (1997) 438–446.

[32] A. Corma, J. Martıinez-Triguero, S. Valencia, E. Benazzi, S. Lacombe. J. Catal. 206 (2002) 125–133.

[33] A. Corma, M. J. Dıaz-Caban, J. Martınez-Triguero, F. Reyand J. Rius. Nature 418(2002) 514–517.

[34] A. Corma, M. J. Dıaz-Caban, J. L. Jorda, C. Martınez , M. Moliner, Nature 443(2006) 842–845.