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# Synthesis of cocrystallized USY/ZSM-5 zeolites from kaolin and its use as Fluid Catalytic Cracking catalysts

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A series of samples with a cogrowth of USY/ZSM-5 zeolites have been synthesized from kaolin and silica following a sequential two-step procedure with a content of ZSM-5 from 5 to 25wt%. The presence of the ZSM-5 phases have been confirmed by XRD and 29Si-NMR. The samples were stabilized by steaming and tested as FCC catalyst in the cracking of vacuum gasoil. The results obtained show that the effect of ZSM-5 as propylene booster is enhanced when zeolites USY and ZSM-5 were synthesized in the same kaolin particles instead of conforming physical mixtures of the two zeolites. This enhancement is attributed to a higher ability of ZSM-5 to crack the larger olefins suppressing their hydrogen transfer to the gasoline fraction, when the zeolites are grown together.

## Introduction

Since its development in the 40's, Fluid catalytic cracking is one of the most important petrochemical process due to its flexibility for converting different lower-value feedstocks to highly demanded middle distillates, gasoline and diesel, and light olefins, especially propylene and butenes. This flexibility is due to the design of the catalysts able to offer a suitable pore arquitecture for converting the large molecules of feed and to drive the selectivity to the desired products.[1-4] Nowadays, in the current scenario of low oil price and increasing environmental regulations, the role of the FCC catalyst is even more important to include if required, renewable feeds coming from biomass as part of the feed.[5, 6]

The demand of propylene is continuously increasing and the FCC unit is one of the principal producers, together with steam cracking and propane dehydrogenation. ZSM-5, initially used for increasing the octane number of gasoline is currently added to FCC catalysts containing ultraestable Y zeolite to produce C3-C4 olefins from the cracking of heavier olefins yielded by a primary cracking on the matrix and on zeolite USY, that otherwise would be saturated by hydrogen transfer reactions.[7] However, there is a limit for the amount of ZSM-5 that can be added to the catalyst formulation for having a positive effect on propene yield[8].

The need to provide processes for the synthesis of zeolites in a more economic and sustainable way has promoted the use of clays as raw material instead of synthetic silica and alumina compounds. Two different methods to obtain zeolite Y from kaolin were developed. One involves dissolving kaolin completely as source of silicon and aluminum, and a second method in where the clay is partially transformed to zeolite Y while the rest of the clay acts as a matrix of the catalyst[9]. By means of the first method involving complete conversion of the Al-rich kaolin, the Si/Al ratio of the material must be adjusted to the expected Si/Al ratio of the final zeolite Y. Thus, Howell et al. synthesized zeolite Y from metakaolin (obtained by calcination of kaolin at high temperature) digested in a NaOH solution by adding additional silica during the synthesis[10] or by doing previous leaching in acid to remove aluminum[11]. The method based on the partial conversion of kaolin and other clays was first developed by Haden et al., which spay-dried kaolin to form fluidizable microspheres that in a solution of NaOH partially crystallized to zeolite Y[12, 13]. Later, Brown and Speronello et al. improved the method by increasing the amount of crystallized zeolite Y on the kaolin clay while the rest acts as active binder[14-16], being this technology commercially adopted. Since then, other authors have introduced modifications to this methodology. Xu et al. showed how ultrafine zeolite Y crystals can be grown on kaolin microspheres[17], Tan et al. assembled preformed Y nanoclusters on kaolin, obtaining composites of improved porosity[18] and Li et al.[19] synthesized zeolite Y from kaolin activated with a highly concentrated alkali solution method in the presence of diatomite.

Recently other zeolites have also been synthesized from clays. Then, Wei et al.[20] using rectorite instead of kaolin, obtained ZSM-5 with good selectivity to light olefins when used as additive of FCC catalyst. Ding et al.[21] obtained hierarchical ZSM-5 in which the unreacted rectorite clay acted as seed and mesoporosity conformer, while Yue et al.[22] have followed the

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Table 1. Chemical Composition of the raw kaolinite.

| Component | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | MgO | $TiO_2$ | LOI | $SiO_2/Al_2O_3$ (mol/mol) |
|---|---|---|---|---|---|---|---|---|
| wt (%) | 57.12 | 28.81 | 1.53 | 0.17 | 0.50 | 0.55 | 11.43 | 3.36 |

high-concentration alkali solution method to obtain ZSM-5 samples, and others[23]. However, there is no report on the combined growth of zeolites Y/ZSM-5 from kaolin.

We thought that the performance of ZSM-5 for cracking the heavy olefin intermediates before being saturated on zeolite Y, would be enhanced if zeolites Y and ZSM-5 were intimately intergrowth in the same catalyst particle. In this way, olefin recracking may favorably compete with secondary reactions such as oligomerization-cracking and hydrogen transfer, allowing to surpass the ceiling of propylene. Nevertheless, in-situ synthesis of additives as ZSM-5 or others on kaolin by following the way of the partial conversion of kaolin microspheres will compete with zeolite Y crystallization[9]. Moreover, the co-synthesis of Y and ZSM-5 by the route of total conversion of kaolin is impeded by their different crystallization kinetics: zeolite ZSM-5 is crystallized at temperatures above 150˚C[24] while the synthesis of zeolite Y is performed at lower temperatures (ca. 100˚C) [9] and is metastable being transformed into zeolite P.

We will show here that it is possible to synthesize joint USY/ZSM-5 samples from kaolin at different ratios of the two zeolites by following one pot-two step procedure. The potential advantage of this type of catalysts for FCC is presented.

## Experimental

### Synthesis of USY/Kaolin sample

The A sample of Y-based zeolite was synthesized following the route of partial conversion of kaolin clay. A batch of kaolin (Tunisian Kaolinite from the region of Tabarka, see composition in Table 1) was transformed in its metastable phase metakaolin by calcination at 700ºC 2h. Then, 1 gram of metakaolin was dispersed in 25 ml of NaOH solution (2.16 M), and 1.3 g of sodium silicate (Aldrich, $Na_2O$=10.24%; $SiO_2$=29.75%; $H_2O$=60.01%) was slowly added under constant stirring for 1 hour to get a homogeneous mixture. In order to direct the crystallization, a small amount of commercial zeolite YNa (CBV100 from Zeolyst) was added and the mixture was transferred into a Teflon-lined steel autoclave and aged at room temperature for 24 hours to form a gel slurry. Crystallization was done in static at 100˚C for 24 hours. The obtained sample

was separated from the mother liquor by centrifugation, washed until a constant pH and dried overnight at 100°C being named Yk. Then, the sample was sodium-exchanged to about 80% twice in an aqueous solution of 2.5 M ammonium chloride (Aldrich) at 80° C for 1 h under reflux and stirring. Finally, the sample was treated with 100% steam at 550°C followed by two steps of ammonium-exchange and calcination at 500° C in air until the sodium content became lower than 2% of the original (sample Yk550). A further steaming was carried out at 750°C for 5 h to equilibrate the sample and the sample was named Yk750. For comparison, a similar stabilization procedure was done for a YNa commercial sample (CBV100 from Zeolyst) and the three samples obtained from the commercial YNa were named COM, COM550 and COM750 for the fresh, twice ammonium exchanged + steamed at 550 + twice ammonium exchange-calcination, and finally steamed at 750ºC respectively.

### Synthesis of ZSM-5 from kaolin

Zeolite ZSM-5 was synthesized following the route of total conversion of kaolin. 1 g of metakaolin powder was dispersed under stirring in 20 ml of distilled water containing 1 g of NaOH. After 1h of stirring at room temperature 6 g of colloidal silica (Ludox HS-40 from Aldrich) was added and maintained 1 h under stirring. Final pH was adjusted to 9-11 by HCl addition. Then, 0.5g of Tetrapropylammonium bromide (TPABr) was added under an additional hour of stirring. The resultant gel was transferred to a Teflon-lined steel autoclave and heated in agitation at 175ºC for 24h. The product was washed, calcined, ammonium exchanged and calcined again.

### Synthesis of the cogrowth USY/ZSM-5 samples from kaolin

Different USY/ZSM-5 samples were synthesized by the route of total conversion of kaolin (Figure 1) 1 g of metakaolin powder was dispersed under stirring in 20 ml of distilled water containing 1 g of NaOH. After 1h of stirring at room temperature 6 g of colloidal silica (Ludox HS-40 from Aldrich) was added and maintained 1 h under stirring. Final pH was adjusted to 9-11 by HCl addition. Then, different amounts of tetrapropylammonium bromide (TPABr) (0.1, 0.2, 0.3, 0.4 and 0.5g) were added under an additional hour of stirring. The resultant gel was transferred

to Teflon-lined steel autoclaves and heated in agitation at 175ºC for 24h. Then, 1 g of ZSM-5 precursor obtained above was mixed in 25 ml of NaOH solution (2.16 M) and 1.3 g of sodium silicate solution (Aldrich, 10.6% $Na_2O$; 27,21% $SiO_2$; 62.18% $H_2O$) was slowly added under constant stirring for 1 hour to get a homogeneous mixture. Then, seeds (5% wt. of a NaY zeolite with respect to the initial mixture) were added to the synthesis and the gel was transferred to the teflon-lined autoclaves and aged at room temperature while stirring for 24h. Crystallization was carried out at 100˚C for 24 h. The obtained samples were separated from the mother liquor by centrifugation, washed until a constant pH and dried overnight at 100°C. Samples were submitted to ammonium exchange twice in an aqueous solution of 2.5 M ammonium chloride (from Aldrich) at 80° C for 1 h under reflux and stirring conditions followed by steaming at 550ºC for 3h. Then two steps of ammonium exchange and calcination at 500ºC for 3h were performed to decrease the sodium content below 2% of the original amount. Finally, the samples were ultrastabilized by steaming at 750ºC for 5h. obtaining the USY/ZSM-5 samples of different ratios. A picture of the sequential steps of the procedure is shown in Figure 1.

## Characterization

XRD was performed using a PANalytical Cubix X'Pert Pro diffractometer, with Cu Kα radiation, k = 1.5418 Å in the 2Θ angle range of 2-40. The specific surface area and pore volume of the selected zeolites were determined by $N_2$ adsorption on a Micromeritics ASAP 2420 at 77 K. The pore size distribution was determined using BJH methods. The micropore volume and micropore surface area were calculated using a t-plot method. A ZEISS Ultra-55 microscope was used for field emission scanning electron microscopy (FESEM). Transmission Electron Microscopy has been performed in a 200kV Field Emission Electron Microscope JEOL 2100F. The MAS NMR spectra were recorded using a a Bruker AV400 spectrometer. $^{29}Si$ MAS NMR spectra were recorded at 79.46 MHz with a 60° pulse length of 4µs and 60s repetition time, spinning the sample at 5kHz. $^{27}Al$ MAS NMR spectra were recorded at 104.22 MHz with a spinning rate of 10 kHz at a 90° pulse length of 0.5 µs with 1 s repetition time. $^{27}Al$ and $^{29}Si$ chemical shifts are reported to $Al(H_2O)_6$ and tetramethylsilane, respectively.

## Catalytic cracking tests

The cracking reactions of vacuum gas-oil[27] were performed in an automatic cracking unit type MAT (Micro Activity Test) unit described previously[25, 26], and able to operate several cycles of reaction-stripping-regeneration cycles. 500 mg of catalyst was diluted in 2.5 g of inert silica and catalyst-to-oil ratio was varied between 1.5 and 3.5 g/g by changing the amount of the feed. Gases were analyzed by Gas Chromatography in a Rapid Refinery Gas Analyzer from Bruker (450-GC) and simulated distillation of liquids was performed in a Bruker SIMDIS.

## Results and discussion

### Characterization

**Synthesis of USY/Kaolin.** The transformation of kaolin by thermal treatment at 700ºC into the more active phase metakaolin is shown by PXRD in Fig 2. Kaolinite (K) is identified by its characteristic X-ray diffraction peaks at 7.18 Å and 3,58 Å [27]. This
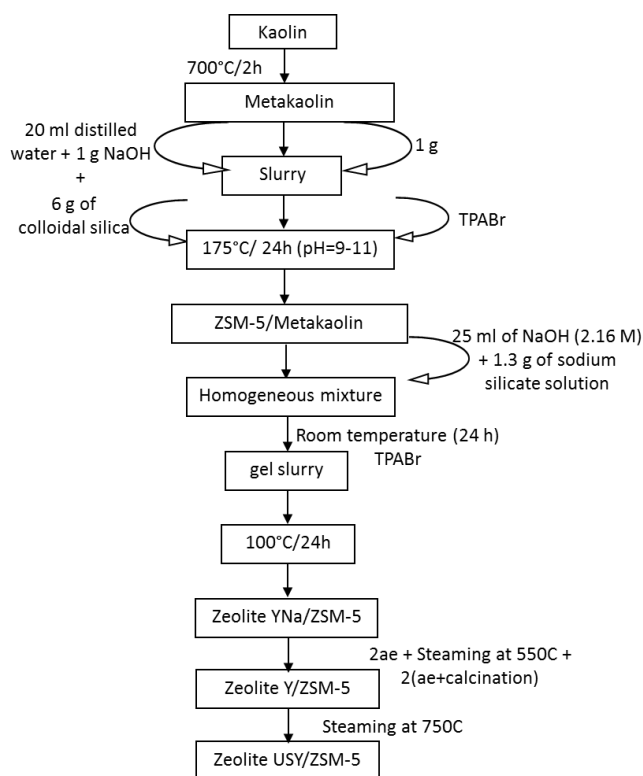
**Fig.1** Procedure of synthesis of USY/ZSM5 samples from Kaolin. ae: ammonium exchange.
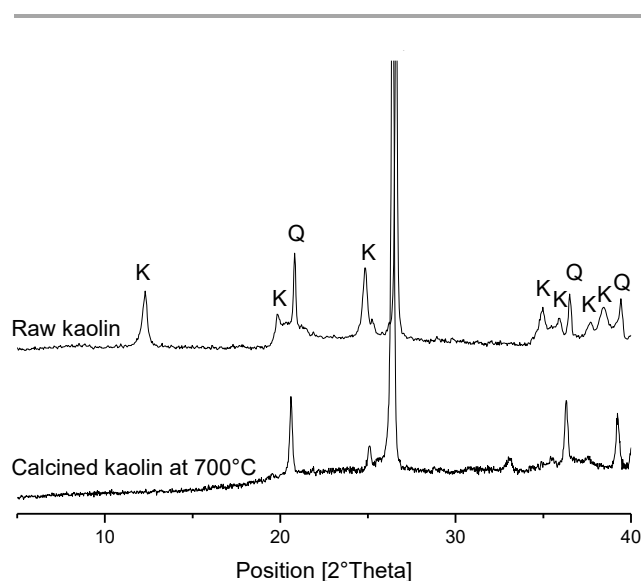
**Fig. 2** Powder X-Ray Diffraction pattern of Raw Kaolin and after calcination in air at 700ºC. K labels peaks characteristic of Kaolin and Q of Quartz.

transformation causes the disappearance of kaolin diffraction peaks and the growing of an amorphous phase from 20 to 30° 2Ɵ which will be more reactive at the reaction conditions for the synthesis of zeolites. Strong signals at 3.37 and 4.30 Å are assigned to well crystallized quartz[28] and persisted after thermal treatment. The PXRD of zeolite Y synthesized on kaolin and after steaming at 550°C and after equilibration at 750°C are compared with similar samples synthesized starting from commercial zeolite YNa in Fig. 3. It is shown that sample Yk presents characteristic peaks of zeolite YNa with the additional presence of Quartz as impurity and an amorphous background due to Kaolin. After steaming, the intensity of the peaks is reduced for both Yk and YNa and the bands shifted indicating a

shrinkage of the unit cells which in turn indicates that, as expected for the low Si/Al ratios of zeolite YNa, an important dealumination of the structure is accompanied by a decrease in its crystallinity. In addition, the intensity of the signals of sample Yk is always lower than those of commercial YNa because not all the kaolin has been transformed to zeolite Y.

The amount of zeolitic phase crystallized on kaolin can be more accurately calculated from the micropore volume measured by adsorption of nitrogen and calculated by the t-plot method (ASTM D4365)[29,30]. Thus, Fig. 4 shows the adsorption–desorption nitrogen isotherms of the prepared and the commercial Faujasite materials before and after ammonium exchange and steaming treatments. The descriptions of the
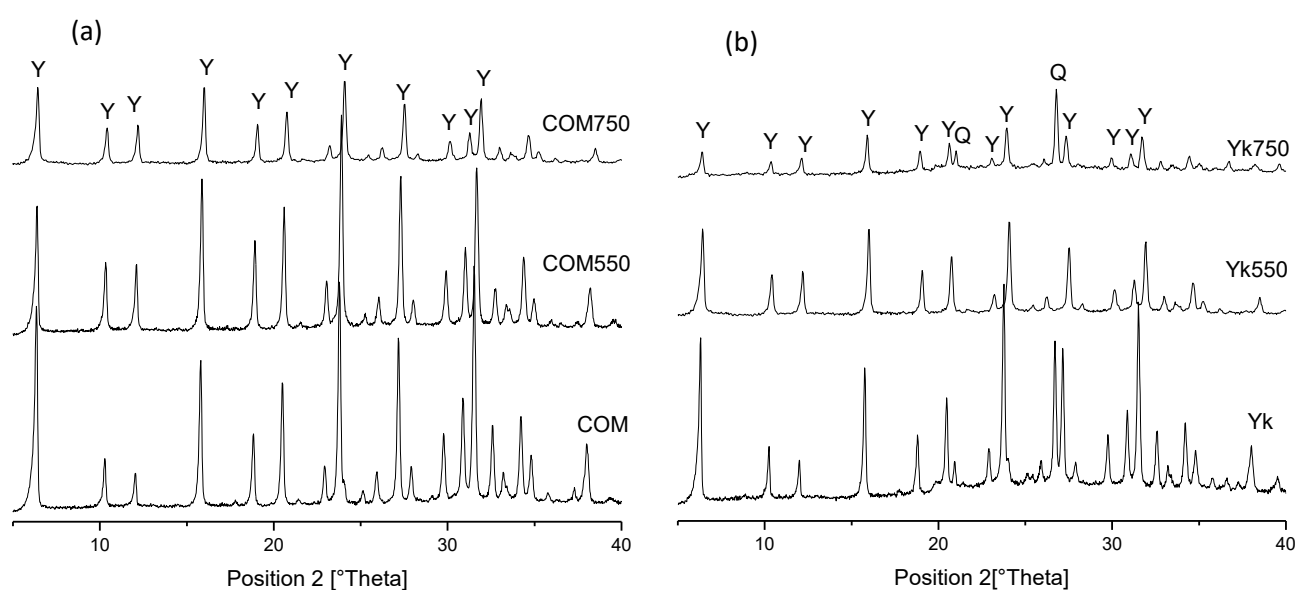


Fig. 3. XRD Patterns of (a) Commercial zeolite YNa fresh (COM), after steaming at 550°C (COM550) and 750°C (COM750). (b) Prepared zeolite Yk from metakaolin fresh, after steaming at 550°C (Yk550) and 750°C (Yk750).
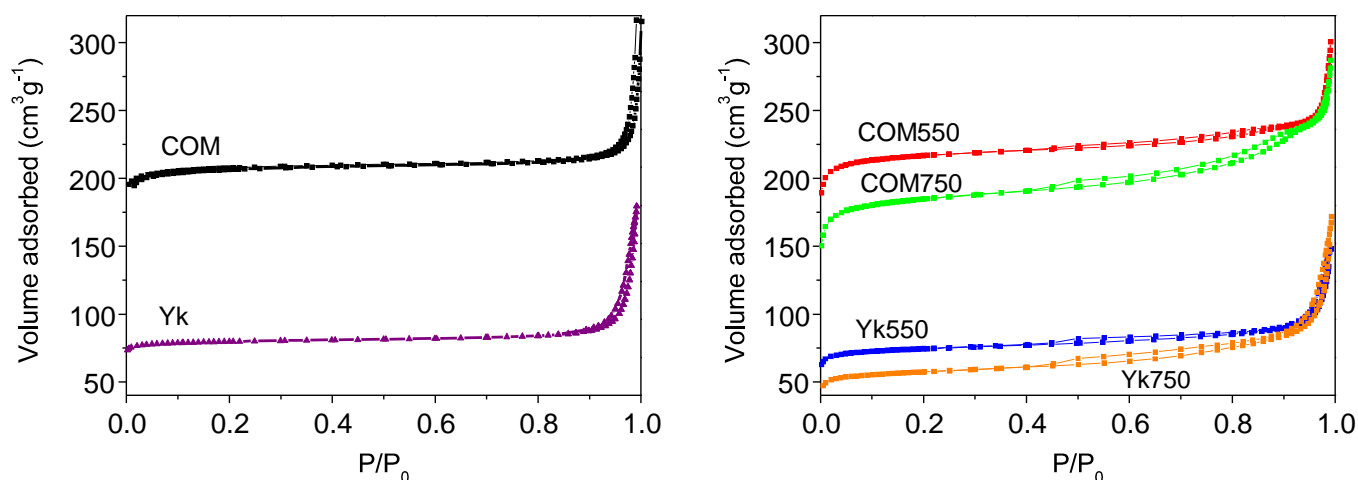


Fig. 4. Nitrogen adsorption-desorption isotherms of COM commercial zeolite YNa fresh and after steaming at 550°C and 750°C; and sample Yk from metakaolin fresh and after steaming at 550°C and 750°C..
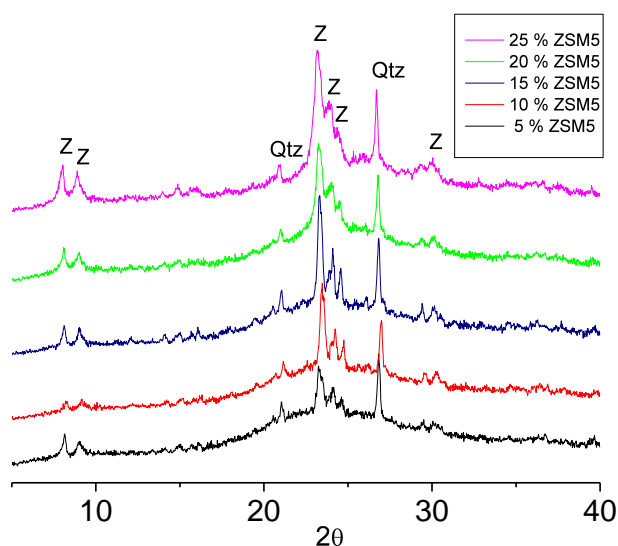
Fig 5. Powder X-Ray Diffraction pattern of original ZSM-5 obtained with different amount of TPABr. Z designs peaks of ZSM-5 and Qtz of Quartz from Kaolin.

samples and the corresponding textural parameters derived from the nitrogen adsorption isotherms are summarized in Table 2. For original Yk and COM samples, a type I isotherm was observed which is typical of microporous materials [30]. After postsynthesis modifications, hysteresis loops appear indicating the formation of mesopores being the isotherm a mixture of type I and IV. From Table 2, it can be seen that during the dealumination process, the mesopore volumes increase gradually when increasing the treatment temperature at the expense of their micropore volume reaching their maximum mesopore volumes after steaming at 750°C. From comparison of micropore volumes for Yk and the commercial YNa zeolite, it can be deduced that the sample synthesized on kaolin presents a content of 37% of zeolite Y. This amount of zeolite Y on kaolin is higher than amount reported by the method of Haden et al.[13] (lower than 30%) and lower than that reported by Speronello et al. (close to 60%) in which a solution of preformed seeds is added to the synthesis mixture.[16]

**Synthesis of the combined Y and ZSM-5 Kaolin catalyst.** The combined synthesis of zeolites Y and ZSM-5 presents the problem of the different conditions and kinetics of crystallization of the two zeolites. In fact, while the synthesis of
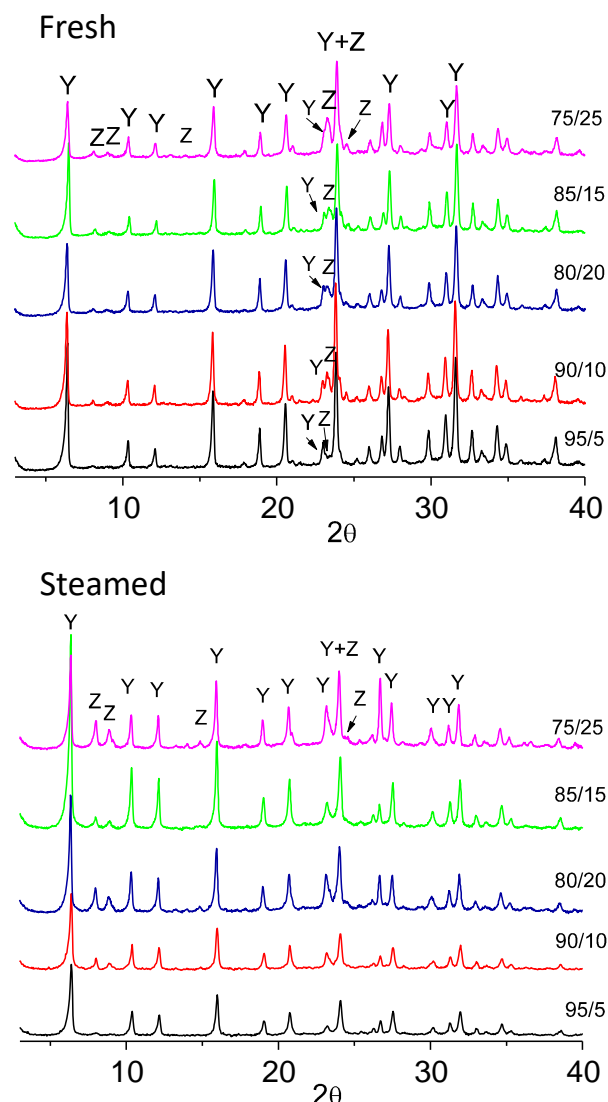


Fig 6. Powder X-Ray Diffraction pattern of Y/ZSM-5 samples fresh (top) and after steaming at 750ºC (bottom)

zeolite Y can be obtained without OSDA at 100°C, the synthesis of zeolite ZSM-5 is easily obtained using TPABr as OSDA at 175°C. Thus, we have followed a one pot two step synthesis procedure. In a first step, precursors of ZSM-5 were obtained by the route of total conversion of kaolin adding different amounts of TPABr. The PXRD of the ZSM-5 precursors obtained are shown in Fig. 5. It can be seen there that the intensity of the

Table 2. Textural properties of COM commercial zeolite YNa fresh and after steaming at 550°C and 750°C; and sample Yk from metakaolin fresh and after steaming at 550°C and 750°C.

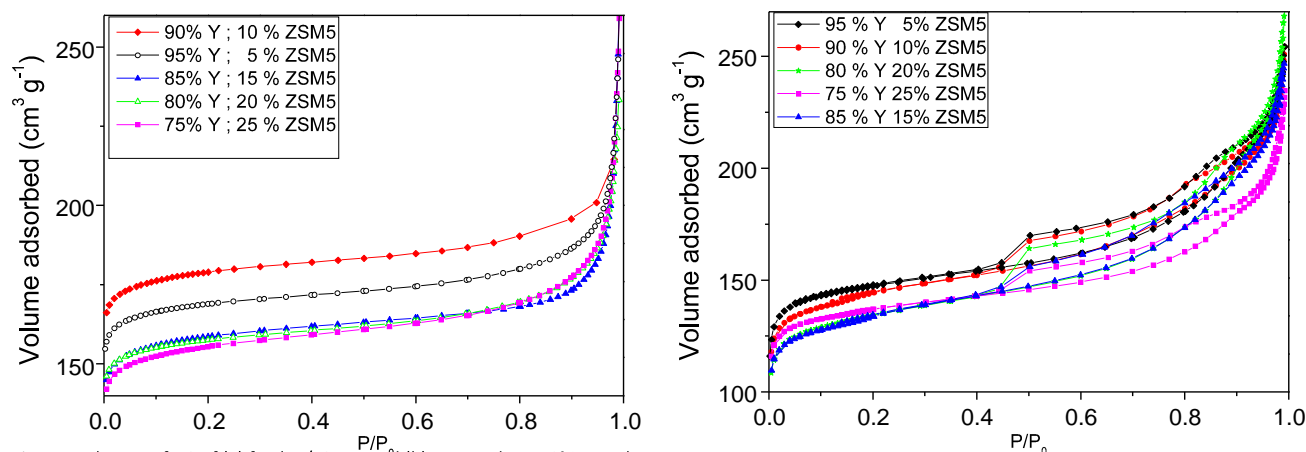| Samples | $S_{BET}$ $(m^2g^{-1})$ | $S_{micro}$ $(m^2g^{-1})$ | $S_{meso}$ $(m^2g^{-1})$ | $V^a_{micro}$ $(cm g^{-1})$ | $V^b_{meso}$ $(cm^3g^{-1})$ | UCS(Å) | Si/Al (UCS) |
|---|---|---|---|---|---|---|---|
| COM | 658 | 647 | 11 | 0.31 | 0.01 | 24.66 | 2.6 |
| COM550 | 690 | 659 | 31 | 0.32 | 0.04 | 24.53 | 4,8 |
| COM750 | 592 | 531 | 55 | 0.26 | 0.10 | 24.37 | 11.5 |
| YK | 253 | 244 | 5 | 0.12 | 0.01 | 24.66 | 2.6 |
| YK550 | 238 | 210 | 22 | 0.10 | 0.03 | 24.53 | 4.8 |
| YK750 | 185 | 143 | 40 | 0.07 | 0.06 | 24.34 | 15.0 |

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Fig. 7. Isotherms of N2 of (a) fresh Y/ZSM-5 and (b) steamed at 750°C samples.

ZSM-5 peaks on the amorphous material correlates with the amount of OSDA introduced in the synthesis. The amount of OSDA added will be that required for obtaining the targeted amount of ZSM-5 in the final catalyst. Then, the Y zeolite component was synthesized in a second step following the conditions described in the experimental part. The PXRD patterns of the final Y/ZSM-5 samples fresh and after steaming are shown in Fig. 6. A characteristic pattern of zeolite Y and small peaks corresponding to ZSM-5 are observed, being the peaks of ZSM-5 more intense when increasing the amount of TPABr in the synthesis. A relative amount of ZSM-5 (5, 10, 15, 20, and 25%) with respect to the total Y zeolite was estimated and corresponds to relative areas of peak at 18.85° for zeolite Y and 14.1° and 24.6° for zeolite ZSM-5. After the steaming treatment, the samples preserve good crystallinity (Fig. 6 bottom) and the unit cell parameters of the fresh Y zeolite samples give a value of 24.66 nm which is similar to the values reported for NaY in the literature. After ion exchange and steaming, the unit cell equilibrates around 24.28 nm (Table 3).

Interestingly enough, it seems that at increasing amounts of ZSM-5 the zeolite Y stabilizes at higher values of unit cell (24.33 nm). This is an important observation that may have industrial relevance.

The textural properties presented in Table 3 show that the fresh samples present high surface areas, as corresponds to zeolite YNa, which slightly decrease when the amount of ZSM-5 increases due to the lower BET area of the later. The micropore volumes shows a similar behavior. After the steaming treatment, the BET surface area of all samples decrease while the mesoporosity strongly increases due to the dealumination process, as typically occurs for zeolites USY. This mesoporosity is also shown in the hysteresis loop of the isotherms of nitrogen adsorption (Fig. 7). FESEM pictures (Fig. 8) show that the samples are formed by crystallites of faujasites, and the presence of ZSM-5 is more difficult to see due to the very small size of ZSM-5 crystallites as indicated by the broad peaks in the XRD pattern (Fig. 2). TEM pictures of steamed samples (Fig. 8)

Table 3. Textural properties of Y/ZSM-5 samples fresh and after steaming at 750ºC

| Fresh Samples Y/ZSM-5 | %Y | %ZSM-5 | $S_{BET}$ (m²g⁻¹) | $S_{micro}$ (m²g⁻¹) | $S_{meso}$ (m²g⁻¹) | $V^a_{micro}$ (cm g⁻¹) | $V^b_{meso}$ (cm³g⁻¹) | UCS(Å) |
|---|---|---|---|---|---|---|---|---|
| 95/5 | 95 | 5 | 538 | 512 | 21 | 0.25 | 0.03 | 24.66 |
| 90/10 | 90 | 10 | 568 | 543 | 38 | 0.27 | 0.05 | 24.66 |
| 85/15 | 85 | 15 | 506 | 483 | 21 | 0.24 | 0.03 | 24.65 |
| 80/20 | 80 | 20 | 502 | 474 | 23 | 0.23 | 0.04 | 24.66 |
| 75/25 | 75 | 25 | 448 | 420 | 38 | 0.21 | 0.06 | 24.65 |
| Steamed Samples Y/ZSM-5 | | | | | | | | |
| 95/5 | 95 | 5 | 475 | 401 | 64 | 0.19 | 0.12 | 24.28 |
| 90/10 | 90 | 10 | 468 | 379 | 113 | 0.18 | 0.15 | 24.28 |
| 85/15 | 85 | 15 | 445 | 349 | 118 | 0.17 | 0.16 | 24.33 |
| 80/20 | 80 | 20 | 435 | 349 | 104 | 0.17 | 0.16 | 24.30 |
| 75/25 | 75 | 25 | 402 | 353 | 82 | 0.17 | 0.11 | 24.31 |

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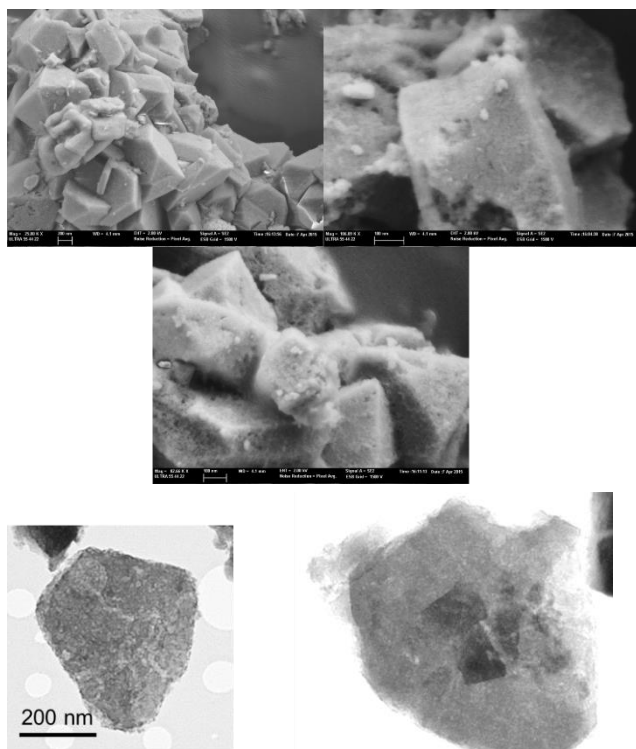


Fig. 8. FESEM (top) and TEM (bottom) pictures of USY/ZSM-5 80/20 sample after steaming at 750ºC



Fig. 9. $^{29}$Si and $^{27}$Al NMR analysis of sample USY/ZSM-5 80/20 fresh and steamed at 750ºC.

shows the presence of mesoporosity into the crystallites of zeolite Y and possibly the presence of smaller crystals of ZSM-5. The mesoporosity is also seen by FESEM as a rugosity and cracks on the surface of the particles.

The presence of ZSM-5 was also confirmed by $^{29}$Si-NMR analysis of fresh Y/ZSM5 80/20 (Fig. 9). In fact, the resonance at -113 ppm is characteristic of ZSM-5 and it is assigned to Si(0Al) species.[31] The band at -106 ppm is also typical of ZSM-5 (Si(1Al) but overlaps with the resonance at -108 ppm corresponding to Si(0Al) of zeolite Y.[32-34] The other signals at -101, -95, and -90 correspond to Si(1Al), Si(2Al), and Si(3Al) in zeolite Y. After steaming, two signals are clearly the majority and correspond at -113 and -108 ppm corresponding to Si(0Al) in ZSM-5 and zeolite Y respectively. The $^{27}$Al-NMR spectrum of the fresh sample shows a single signal at -60 ppm, which means that all the aluminum is occupying tetrahedral positions. After the steaming treatment the spectrum is less intense, as it occurs for steamed zeolite Y[32], showing signals at 60, 29 and -1 ppm, which are assigned to Al(IV), distorted tetrahedral Al or Al(V), and extraframework Al(VI).

In summary, from the characterization results it has been confirmed the synthesis of Y/ZSM-5 samples following a one
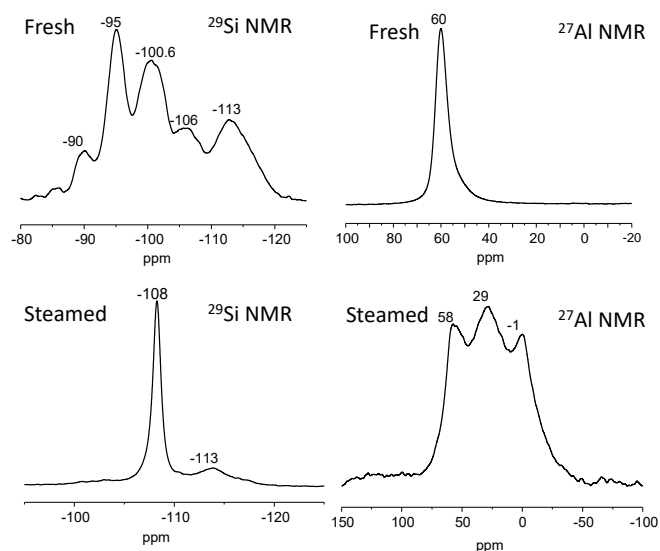
pot - two stages procedure. In this way, samples were obtained that contain amounts of ZSM-5 from 5 to 25% respect to Y zeolite. These samples present good textural properties that are preserved after the stabilization treatment with steam and, in principle, should present good properties as catalyst for the cracking of vacuum gasoil.

## Catalytic results

The samples USY/ZSM-5 have been tested in the cracking of vacuum gasoil and the results are presented in Fig. 10. It can be seen that the conversion of gasoil decreases at increasing content of ZSM-5 due to the dilution of the zeolite Y content. When comparing at constant conversion, increasing contents of ZSM-5 strongly decrease the yield of gasoline while, accordingly, gases C1-C4 increases. These results are characteristic of FCC catalysts containing ZSM-5 as additive of zeolite USY[8, 35]. Among gases, propylene increases with the content of ZSM-5 until a maximum at 15wt% of ZSM-5. The olefinicity increases as measured by the hydrogen transfer ratios C4=/C4 and C3=/C3 (Fig. 10). The results agree with the reported role of ZSM-5 that is to crack the heavier olefins from the gasoline yielded by zeolite Y that, instead of being transformed on gasoline isoalkanes by hydrogen transfer, are cracked to light olefins. There is an optimum between 15-25% in the ratio ZSM-5/Y of the synthesized samples and above that, olefins precursors seems depleted and the maximum of propylene is attained.
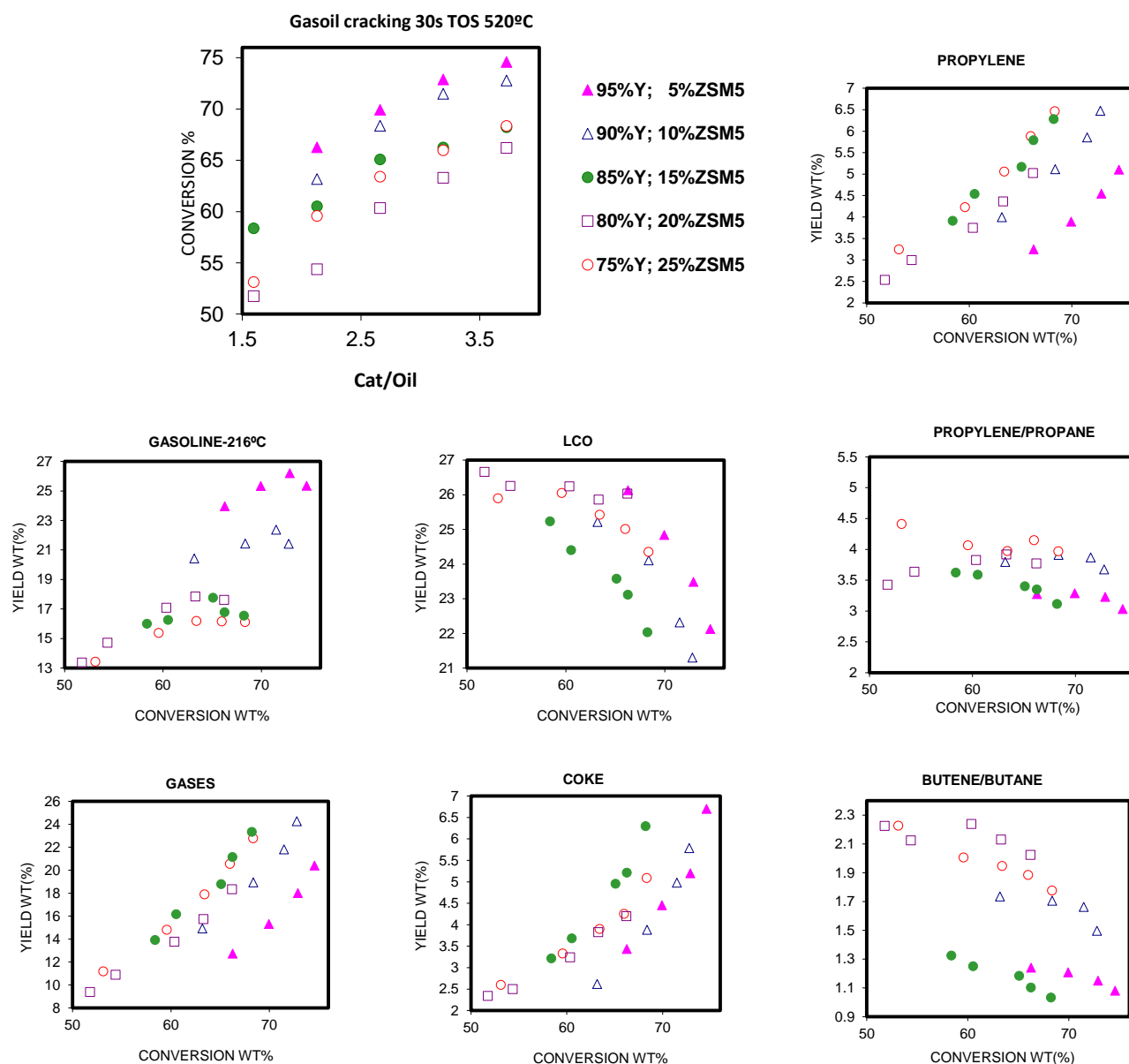
Fig. 10. Conversion and selectivities in the cracking of gasoil of USY/ZSM-5 zeolites grown on kaolin at 520ºC and 30s TOS.

The results obtained with the samples Y/ZSM-5 have been compared in Table 4 with those achieved with pure zeolite Y and also with a physical mixture of zeolite Y and 20% of ZSM-5 obtained from kaolin. It is shown there that the samples with Y and ZSM-5 synthesized in the same catalyst particle yield much more gases C1-C4 with a stronger decrease in gasoline comparing with zeolite Y alone. Among gases, the increment in the yield of butenes and specially propylene is much more important in the case of samples Y/ZSM-5 than with the physical mixture of the separately synthesized Y and ZSM-5 zeolites. The olefinicity ratios also indicate that the samples Y/ZSM-5 are much more effective for the cracking of heavy olefins from gasoline and therefore are more effective for suppressing its hydrogen transfer to isoalkanes. Thus, their butene/butane and propene/propane ratios are higuer than those obtained with the physical mixture (Table 4). In addition, the C1+C2/isobutane ratio, also called "cracking mechanism ratio"[36], is much lower for the physical mixture, indicating that hydrogen transfer reactions (leading to isobutane) dominates vs. protolytic cracking (C1+C2). Moreover, the C3/C4 ratio, which can be used to monitor the activity of ZSM-5 in the catalyst inventory[7, 37], is higher for the samples USY/ZSM-5 than for the physical mixture of USY and ZSM-5. All these results indicate that the joint synthesis of zeolite USY/ZSM5 enhances the effect of the additive within the FCC catalyst and offer further possibilities to increase propylene, while further improving octane number of the gasoline. Notice that both, Research and Motor Octane Numbers of the gasoline obtained are higher when vacuum gasoil was cracked on the cosynthesized Y and ZSM-5 samples form Kaolin. All the increments on the above parameters are

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Table 4. Yields (wt%) and ratios interpolated at 70 wt% of total conversion in the cracking of gasoil on Y/ZSM-5 compared with a physical mixture of zeolite Y+20%ZSM-5 and the base catalyst. TOS: 30 s and Temp: 520ºC.

| | Zeolite USY 100% | 80%USY 20%ZSM-5 mixed | USY/ZSM-5 95/5 | USY/ZSM-5 90/10 | USY/ZSM-5 80/20 | USY/ZSM-5 75/25 |
|---|---|---|---|---|---|---|
| Yields (wt%) | | | | | | |
| Gasoline | 30.10 | 27.58 | 25.34 | 21.43 | 17.33 | 16.09 |
| LCO | 24.73 | 24.68 | 24.81 | 23.07 | 26.27 | 23.89 |
| Gases C1-C4 | 12.39 | 14.24 | 15.37 | 20.91 | 21.72 | 24.35 |
| Coke | 2.78 | 3.50 | 4.48 | 4.58 | 4.68 | 5.68 |
| | | | | | | |
| Hydrogen | 0.06 | 0.05 | 0.08 | 0.10 | 0.07 | 0.15 |
| Methane | 0.74 | 0.63 | 0.85 | 1.31 | 1.56 | 1.57 |
| Ethane | 0.69 | 0.56 | 0.76 | 1.13 | 1.45 | 1.38 |
| Ethylene | 0.94 | 0.92 | 1.08 | 1.64 | 1.93 | 1.97 |
| Propane | 0.84 | 0.77 | 1.19 | 1.47 | 1.62 | 1.78 |
| Propylene | 3.01 | 3.99 | 3.90 | 5.62 | 5.88 | 6.87 |
| Isobutane | 1.66 | 1.94 | 2.67 | 2.88 | 2.34 | 3.03 |
| n-Butane | 0.58 | 0.57 | 0.74 | 0.81 | 0.81 | 0.89 |
| Trans-2-butene | 1.06 | 1.26 | 1.15 | 1.62 | 1.60 | 1.79 |
| But-1-ene | 0.91 | 0.99 | 0.96 | 1.32 | 1.34 | 1.46 |
| Isobutylene | 1.11 | 1.64 | 1.15 | 1.82 | 1.94 | 2.13 |
| Cis-2-butene | 0.79 | 0.93 | 0.85 | 1.20 | 1.19 | 1.34 |
| | | | | | | |
| Ratios (wt/wt) | | | | | | |
| C4=/C4 | 1.72 | 1.92 | 1.21 | 1.61 | 1.93 | 1.71 |
| C3=/C3 | 3.58 | 5.19 | 3.29 | 3.81 | 3.64 | 3.87 |
| (C1+C2)/iC4 | 1.43 | 1.09 | 1.01 | 1.42 | 2.12 | 1.62 |
| C3/C4 | 0.63 | 0.65 | 0.68 | 0.74 | 0.81 | 0.81 |
| | | | | | | |
| Composition of gasoline fraction (wt%) | | | | | | |
| Aromatics | 47.13 | 51.46 | 48.56 | 48.66 | 54.26 | 60.84 |
| Isoparaffins | 16.15 | 22.06 | 22.39 | 19.64 | 15.64 | 16.82 |
| Naphthenes | 15.22 | 13.75 | 11.29 | 11.91 | 11.39 | 10.47 |
| Olefins | 19.58 | 10.85 | 15.32 | 17.47 | 16.33 | 11.53 |
| Paraffins | 1.92 | 1.88 | 2.45 | 2.33 | 2.36 | 1.66 |
| RON | 86.97 | 87.85 | 87.01 | 87.37 | 89.65 | 91.46 |
| MON | 83.53 | 84.54 | 83.66 | 83.89 | 86.10 | 87.83 |

clearly visible for the sample containing 20 and 25wt% ratio of ZSM-5 with respect to USY zeolite in the USY/ZSM-5 samples (Table 5).

## Conclusions

A series of Y/ZSM-5 samples have been synthesized from kaolin following a one pot-two step procedure with ZSM-5 contents ranging from 5 to 25wt%. The presence of ZSM-5 phases have been identified by XRD and $^{29}$Si-NMR. The samples have been stabilized by steaming and tested as FCC catalyst in the cracking of gasoil showing good stability and properties for increasing the yield of propylene. The effect of ZSM-5 as additive is enhanced by the synthesis procedure in which zeolites Y and ZSM-5 are synthesized in the same catalyst particle. These Y/ZSM-5 samples give higher yield of propylene when compared with a physical mixture of Y and ZSM-5.

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Table 5. Delta yields in the cracking of vacuum gasoil at 520ºC 30 s TOS on cosynthesized Y/ZSM-5 samples comparing to the physical mixture of 80%Y/20%ZSM-5.

|  | Y/ZSM-5 80/20 | Y/ZSM-5 75/25 |
|---|---|---|
| Delta Yields (wt%) | | |
| Gasoline | -10.3 | -11.5 |
| LCO | 1.6 | -0.8 |
| Gases C1-C4 | 7.5 | 10.1 |
| Coke | 1.2 | 2.2 |
|  |  |  |
| Hydrogen | 0.0 | 0.1 |
| Methane | 0.9 | 0.9 |
| Ethane | 0.9 | 0.8 |
| Ethylene | 1.0 | 1.1 |
| Propane | 0.9 | 1.0 |
| Propylene | 1.9 | 2.9 |
| Isobutane | 0.4 | 1.1 |
| n-Butane | 0.2 | 0.3 |
| Trans-2-butene | 0.3 | 0.5 |
| But-1-ene | 0.4 | 0.5 |
| Isobutylene | 0.3 | 0.5 |
| Cis-2-butene | 0.3 | 0.4 |
|  |  |  |
| Aromatics | 2.8 | 9.4 |
| Isoparaffins | -6.4 | -5.2 |
| Naphthenes | -2.4 | -3.3 |
| Olefins | 5.5 | 0.7 |
| Paraffins | 0.5 | -0.2 |
| RON | 1.8 | 3.6 |
| MON | 1.6 | 3.3 |

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