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Abatement of hydrocarbons by acid ZSM-5 and BETA zeolites under cold-start conditions

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Abstract Simulated cold-start tests have been carried out to evaluate the performance of H-ZSM-5 and H-BETA zeolites as hydrocarbon traps under simulated gasoline car exhaust gases, paying special attention to the effect of water on their behaviour. It is concluded that the hydrothermal treatment of the zeolites in the acidic form contributes to the better performance of these materials as hydrocarbon traps since the stabilization of the zeolites takes place. Moreover, the decrease of the surface acidity of the zeolites results in an increase of the Si/Al ratio, which contributes to the decrease of the water affinity for adsorption sites. Thus, the competition with hydrocarbon molecules in the exhaust for the adsorption sites is reduced which increases their trap efficiency. The stabilized H-ZSM-5 is the zeolite that showed the best performance with a propene offset temperature of 240 °C, which should be high enough for the three-way catalyst to carry out its role as catalytic converter.

Keywords Cold-start · Vehicle emissions · Zeolites · Hydrocarbon trap · Stability

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1 Introduction

The growing social interest in environmental pollution, together with more stringent legal restrictions, have driven the researcher community to study new palliative measures to reduce pollution in every emission source. In this sense, an important environmental problem arises from the lack of treatment capacity of hydrocarbons (HC) under cold-start conditions by three-way catalysts (TWC). Fresh catalysts start to operate at ca. 170 °C, but aged catalysts light-off at ca. 200–225 °C (Lox and Engler 1997). These catalysts need between 60 and 120 s to reach these temperatures and during this time up to around 70 % of pollutants in a driving cycle are emitted (Heck and Farrauto 2001). The emission control during this cold-start period is essential to reduce the environmental impact of gasoline vehicles. As a result, attention has focussed on trying to adsorb these HC emissions during the cold-start period and desorbing them once the TWC has reached the operation temperature (Park et al. 2009). Zeolites have been found to be the preferred adsorbents for this application, mainly due to their thermodynamic affinity to adsorb HC. Moreover, in some cases, their catalytic properties to carry out the catalytic combustion of HC make them very interesting to control the HC emissions during the cold-start. However, it has been reported that the presence of water leads to a significant decrease in the performance of these materials as HC traps, thus, the effect of steam must be studied in detail. The presence of water in the vehicle exhaust can produce the extraction of aluminum from the zeolite framework ("dealumination"), thus producing the migration of aluminum species to crystal surfaces and modifying the activity of these sites (Chambellan et al. 1992). This effect increases the Si/Al ratio of the zeolite, and can also modify the zeolite crystallinity and/or its adsorption capacity (Burke et al. 2003). A high hydrothermal stability is of great importance for zeolites used as HC traps, since both high temperatures and water contents up to 10 % v/v are reached in gasoline engine exhausts. In this application, if a zeolite is not stable enough, the framework structure can collapse by the reaction with steam, and fast deactivation occurs.

Therefore, a stabilized zeolite is required, which can be obtained by different dealumination (stabilization) processes. The hydrothermal treatment consists of a thermochemical treatment of the zeolite in steam (steaming), while the chemical treatments involve the acid extraction or the isomorphous substitution of AlO_4^{5-} for SiO_4^{4-} inside the zeolite crystal lattice by means of a zeolite treatment with $SiCl_4$ (Charistos et al. 1997). Among them, hydrothermal treatment is one of the most important and frequently used methods for dealumination. It can effectively modify the acidity, tune the porosity and improve the stability of zeolites. There are several studies in the literature related to the hydrothermal stability of zeolites. Most of them take into account the effect of steam pressure, temperature and duration of the hydrothermal treatment on the stability of zeolites (Ding et al. 2007; Dimitrijevic et al. 2006; Li et al. 2008). Ding et al. (2007) concluded that the particle size is the factor that influences the most on the hydrothermal stability of BETA zeolite, followed by the steam pressure. The effect of temperatures up to a value of 550 °C and duration of the hydrothermal treatment had lower impact on the loss of stability of this zeolite (Ding et al. 2007). However, Dimitrijevic et al. (2006) concluded that BETA zeolite remained stable up to 750 °C after 3 h of sample steaming treatment under atmospheric pressure. On the other hand, for ZSM-5 zeolites, Li et al.(2008) studied the hydrothermal stability of H-ZSM-5 and alkali-treated ZSM-5 zeolites in 100 % steam at 600 °C for 8 h concluding that the steaming treatment significantly reduced the acid density of the zeolite, including weak and strong sites, and also induced the formation of mesopores.

In this work, the different behaviour of H-ZSM-5 and H-BETA zeolites under simulated cold-start conditions has been studied. These zeolites have been selected since they are those that, in the sodium form, present the highest HC adsorption capacity for the control of HC emissions during the cold start (López et al. 2010). These zeolites have been stabilized by steaming in order to compare their performance with that of fresh zeolites in their as-synthesized form. Thus, the differences in surface acidity as well as in pore texture and crystallinity of the stabilized zeolites have been studied in the application of these solids as HC traps.

2 Experimental

2.1 Synthesis of zeolites

Four samples have been used in this study, which are referred to as H-ZSM-5 fresh, and stabilized and H-BETA fresh and stabilized. Acidic forms of ZSM-5 and BETA zeolites were obtained from their sodium counterparts prepared by the authors as previously reported elsewhere (López et al. 2010). The sodium zeolites were treated with a 1 M aqueous solution of NH_4NO_3 (12 ml NH_4NO_3 solution/g sample) at 80 °C for 24 h in order to exchange the Na^+ cations by NH_4^+. After the ion-exchange, the samples were filtered, washed, and subsequently dried at 80 °C for 12 h. The exchange, washing, and drying procedures were repeated twice. The obtained NH_4-ZSM-5 and NH_4-BETA samples were calcined at 450 °C for 6 h (heating rate 5 °C/min) to obtain H-ZSM-5 and H-BETA samples.

2.2 Zeolite stabilization

Once the zeolites were synthesized, a hydrothermal treatment in the presence of steam was carried out to stabilize the samples. To do this, the adsorbents were treated at 500 °C for 1 h under an argon flow, and then, the zeolites were treated under a gas flow of 30 ml/min which contained 10 % v/v water and 90 % v/v argon by increasing the reactor temperature from 30 to 500 °C at 50 °C/min and keeping the maximum temperature for 10 h.

2.3 Characterization of zeolites

Powder X-ray diffraction (XRD) was used to identify the crystalline phases present in the zeolites. A Bruker D8 Advance diffractometer with monochromatic Cu K_α source operated at 40 kV and 40 mA was used. Scanning measurements from 2° up to 40° were done with a scanning rate of 2°/min.

The morphology and crystal sizes were examined by a scanning electron microscope (SEM) in a HITACHI microscope (model S-3400N). Micro-chemical characterization was made by energy-dispersive X-ray analysis (EDX) for Si/Al atomic ratio determination. An EDX analyser coupled to the SEM microscope, with electron beam energies from 3 to 30 keV was used. Before EDX analysis of the stabilized samples, these samples were washed with 4 M hydrochloric acid at 70 °C and dried at 110 °C to eliminate the extra-framework aluminum.

The textural characterization of the zeolites was carried out by N_2 adsorption at −196 °C, using a Micromeritics ASAP 2020 apparatus. Prior to the adsorption measurements, the zeolites were outgassed in situ in vacuum at 250 °C for 4 h to remove adsorbed gases. Surface area was calculated from N_2 adsorption isotherms using the BET equation (S_{BET}) and the total micropore volume (V_{DR} (N_2)) was calculated applying the Dubinin-Radushkevich (DR) equation.

NH_3-Temperature Programmed Desorption (NH_3-TPD) profiles were obtained using a conventional flow-through reactor connected to a thermal conductivity detector. 100 mg of each zeolite were cleaned in flowing argon at 500 °C for 6 h, and cooled down to 125 °C. The samples were treated for 4 h with 5 % v/v NH_3 and argon balance under a total flow of 30 ml/min, and the weakly adsorbed NH_3 was removed afterwards by 1 h evacuation at 125 °C. The NH_3–TPD profiles were finally obtained by heating the reactor at 5 °C/min up to 600 °C in 30 ml/min helium flow.

Thermogravimetric analysis (TGA) were used to determine the amount of coke formed during the experiments. Thus, the weight change of the zeolites during the oxidation was measured. The sample was heated to 900 °C at a rate of 80 °C/min under air flow (250 ml/min). The weight loss between 200 and 900 °C was attributed to coke burning. Measurements for each sample were repeated three times.

2.4 Cold-start tests (CST)

The zeolite performance as HC trap was tested under simulated cold-start conditions by means of adsorption–desorption tests. The inlet gas composition used in the experiments was 100 ppmv propene, 87 ppmv toluene, 1 % v/v oxygen, 10 % v/v steam and argon balance under a total flow of 30 ml/min. Flow rates of all gases were controlled by mass flow controllers. Steam was generated in an auxiliary reactor with temperature control, and was introduced into the main stream. The experiments were run in a fixed bed reactor (diameter = 0.457 cm; 0.15 g of stabilized sample) externally heated and coupled to a Mass Spectrometer. Under these conditions, the reactor temperature was increased from 30 °C up to 500 °C at 50 °C/min, keeping the maximum temperature for 30 min and the following signals were monitored: m/z 40 for Argon, 42 for Propene, 91 for Toluene, 32 for Oxygen, 44 for Carbon Dioxide and 18 for Water. The m/z 56 was also followed due to polymerization of propene molecules over the zeolite surface.

This CST procedure allows the investigation of competitive adsorption and desorption from an initially empty zeolite, which is closer to the conditions that would be experienced by an in-line HC trap in an automobile. During a simulated CST, molecules first diffuse into an empty adsorbent at low temperatures. Thus, as the temperature increases the driving force for diffusion changes direction, causing molecules to diffuse back out of the solid and into the gas stream.

Initial CST were carried out with fresh samples (as-synthesized form) and stabilized zeolites (after steaming). Moreover, in order to study the stability of these materials, three consecutive CST were performed with each zeolite. The resulting materials from the stabilized zeolites have been referred to as aged samples.

3 Results

3.1 Zeolite characterization

3.1.1 *Fresh samples*

The phase purity and crystallinity of the samples prepared in this study were confirmed by XRD as it can be seen from Fig. 1. The ZSM-5 XRD pattern showed peaks at ~8° and 24°, which corresponds to the characteristic peaks of ZSM-5 zeolite (MFI structure) whereas BETA zeolite showed the BEA morphology type peaks. BETA zeolite was a combination of two polymorphs of different lattice type: tetragonal and monoclinic-B as it can be seen from the first peak in the XRD pattern (2θ ≈ 8°) (Tesche et al. 2007).

Figure 2 contains the nitrogen adsorption–desorption isotherms at −196 °C. The isotherms for the fresh zeolites (ZSM-5 and BETA zeolites) correspond to a type I

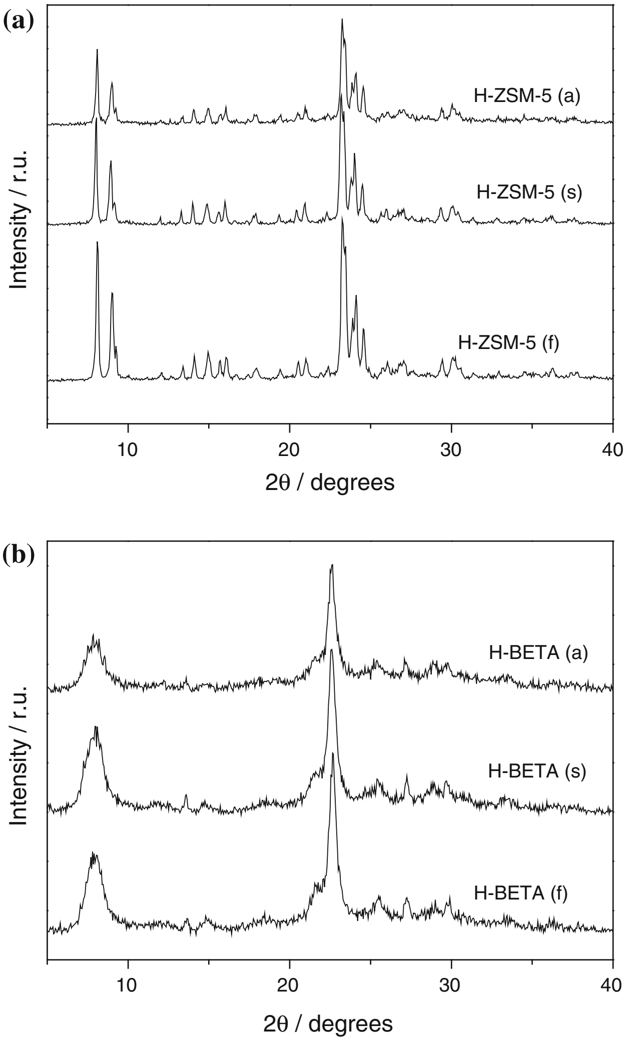


Fig. 1 XRD patterns corresponding to **a** H-ZSM-5 and **b** H-BETA zeolites. *f* fresh, *s* stabilized, *a* aged

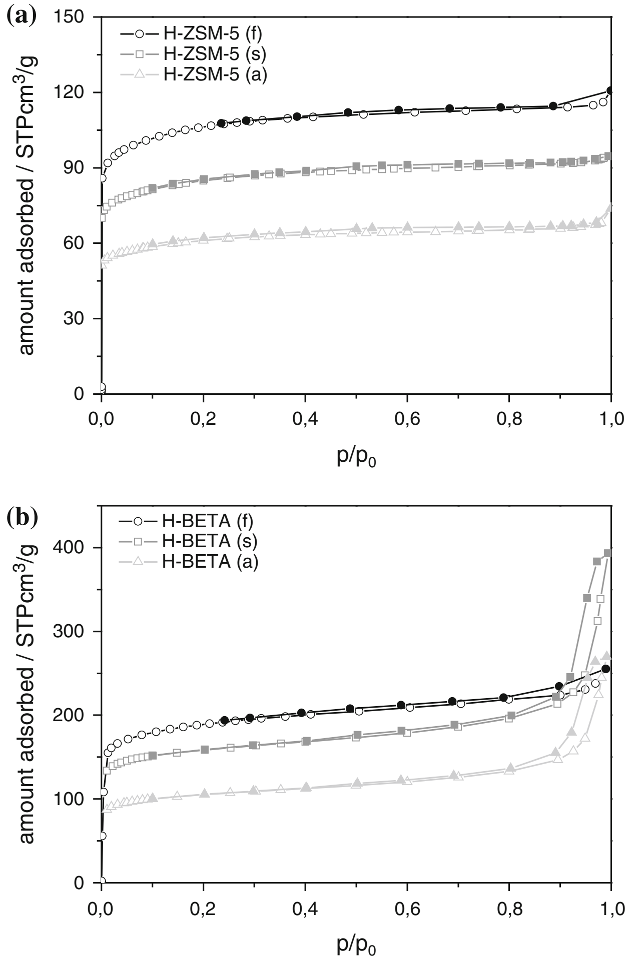


Fig. 2 N_2 adsorption–desorption isotherms at −196 °C corresponding to **a** H-ZSM-5 and **b** H-BETA zeolites. *f* fresh, *s* stabilized, *a* aged

Table 1 Porous texture characterization and Si/Al atomic ratios

Sample	S_{BET} (m^2/g)		V_{DR} (N_2) (ml/g)		Si/Al
		Aged		Aged	
H-ZSM-5 fresh	373	–	0.17	–	11.5
H-ZSM-5 stabilized	288	210	0.14	0.10	26.5
H-BETA fresh	563	–	0.31	–	9.5
H-BETA stabilized	500	348	0.25	0.16	22.2

isotherm, showing a high uptake of nitrogen at very low relative pressures, which is characteristic of microporous materials, and a light hysteresis loop related to the presence of mesopores. The specific surface areas estimated from the BET equation (S_{BET}), the total micropore volume (V_{DR} (N_2)) and the Si/Al atomic ratios for the different zeolites are reported in Table 1. BETA zeolite showed the highest surface area and pore volume.

NH_3-TPD characterisation was used to analyse the nature of surface acid sites on the different zeolites. The

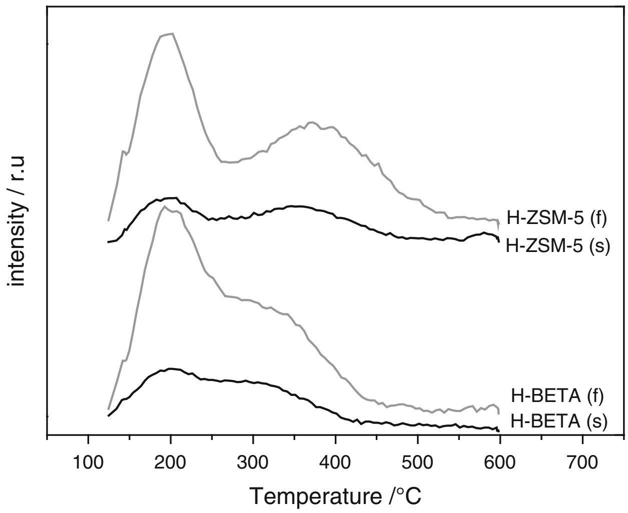


Fig. 3 NH_3-TPD profiles. *f* fresh, *s* stabilized

NH_3-TPD profiles of the zeolites prepared in this study are compiled in Fig. 3. The H-BETA zeolite presented an intense band in the temperature range from 120 to 280 °C and a weaker second band up to 440 °C. The presence of these two bands is in accordance with Wang and Xin (2001), who observed the predominance of weak acid sites for low Si/Al ratios. In the case of H-ZSM-5, two ammonia desorption peaks were observed, which is in accordance with previous studies (Katada et al. 1997; Lónyi and Valyon 2001). The first one was found between 120 and 280 °C and was attributed to desorption of weakly adsorbed ammonia retained via hydrogen bonds on zeolite hydroxyl groups. The high temperature peak was observed in the temperature region between 300 and 500 °C, and was attributed to the ammonia desorption from strong Brönsted acid sites and/or Lewis acid sites composed of aluminum with low coordination or $\equiv Si^+$ ions formed from dehydroxilation at temperatures higher than 500 °C that act as an electron pair acceptor in charge transfer processes (Katada et al. 1997).

3.1.2 Stabilized samples

XRD patterns (Fig. 1) showed that stabilized H-BETA and H-ZSM-5 zeolites exhibited similar XRD patterns as fresh samples, except for slight differences in the intensities of the peaks, indicating no changes in the basic structure of ZSM-5 and BETA. Thus, the samples maintained almost the same crystallinity after the stabilization treatment (500 °C for 10 h with 10 % v/v water).

After the steaming treatment of zeolites, the specific surface areas and the micropore volumes of the zeolites were importantly reduced, detecting the formation of some mesopores for H-BETA as it can be observed from the hysteresis appeared in the relative pressure range of 0.45-1 (see Table 1; Fig. 2). The steaming provoked a remarkable increase of Si/Al ratio (Table 1), revealing that dealumination took place. Considering that an amorphization of the framework was not observed after the treatment, it can be assumed that the aluminum released from the framework upon steaming remained in the samples as a component of extra-framework species. The formation, migration, and condensation of the extra-framework species seemed to be blocking a portion of the pore system resulting in the decrease of the micropore volume, as it was described to occur for H-BEA zeolites (Ribeiro-Carrott 2005). Moreover, these extra-framework Al (EFAl) species may block also acid sites and, therefore, reduce the acid site concentration of the material (Maier et al. 2011). This effect was observed after the hydrothermal treatment, when a decrease of the total amount of acid sites for H-ZSM-5 and H-BETA zeolites took place (Fig. 3). Moreover, for H-ZSM-5 zeolite, the peak intensity associated to strong acid sites shifted from 382 °C to 350 °C, indicating that the acid strength of the zeolite was weakened by the steaming treatment. In the case of H-BETA zeolites, it was observed that the proportion of strong acid compared to weak acid sites increased as a consequence of the hydrothermal treatment.

3.1.3 *Aged samples*

The resulting materials after the performance of three consecutive CST with the stabilized zeolites (referred to as aged samples) became grey, pointing out coke formation during CST. As explained in the experimental section, TGA was used to determine the amount of coke deposited over the zeolites. From these experiments, it can be stated that coke formation was higher for BETA zeolite (5.9 %) than for ZSM-5 zeolite (4.5 %). Coke formation is a shape selective reaction which depends mainly on the zeolite pore structure. Since the size of the intermediates and transition states involved in the formation of coke molecules is close to the size of the space available near the acid sites (cavities, channel intersections), steric constraints necessarily limit the formation of these intermediates. Thus, coke formation resistance of ZSM-5 is only attributed to its pore structure, which does not allow the creation of large coke clusters (Uguina et al. 2002). The acidity plays also an important role in coke formation: a higher density of acid sites leads to higher coke content (Magnoux et al. 2002), which explain, together with a wider channel structure, the fact that H-BETA zeolite showed the highest amount of coke.

XRD patterns of the aged samples were very similar to those of the stabilized samples (Fig. 1), except for slight differences in the intensities of the peaks, indicating that the structure of the stabilized zeolite was not importantly modified after three consecutive CST. The reduction of the peak intensities can be likely due to the formation of coke during CST in the materials.

Related to the porosity of the aged samples, it was observed a decrease in the nitrogen adsorption capacity (see Fig. 2), as a consequence of the coke deposition during the CST for all the zeolites. This fact could be due to the pore blockage associated to coke formation through the zeolite structure which also led to a decrease of the micropore volume as it can be seen from Table 1.

3.2 Cold-start tests

3.2.1 *Fresh samples*

The different zeolites in their as-synthesized form (fresh samples) were tested under experimental conditions that mimic the vehicle cold-start period by means of a CST. Figure 4 includes the results of CST (three cycles) corresponding to zeolites (a) H-ZSM-5 and (b) H-BETA. In all CST, it is worth commenting that initial HC signals before

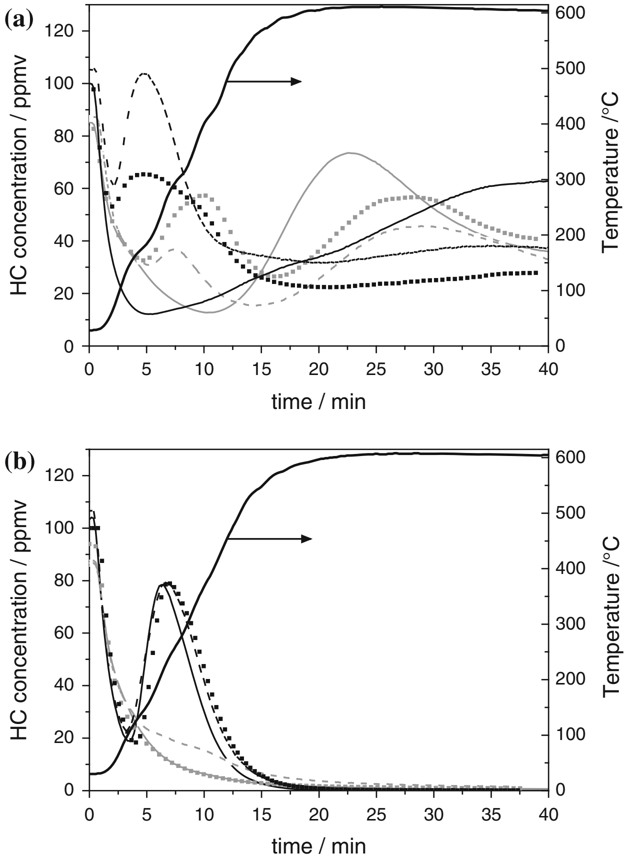
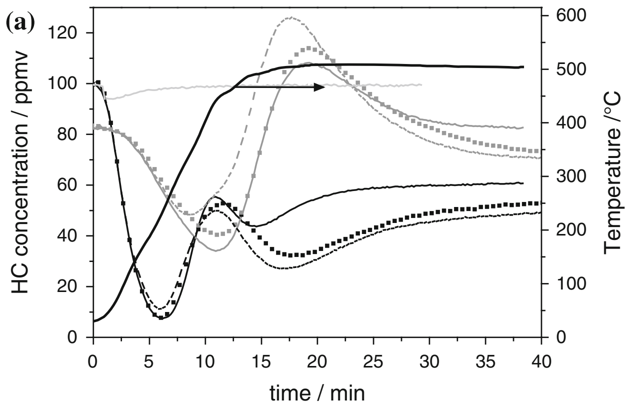


Fig. 4 CST performance (three cycles) corresponding to fresh **a** H-ZSM-5 and **b** H-BETA zeolites. *Black lines* represent propene concentration profiles and *grey lines* represent toluene. *Solid lines* represent the first cycle, *broken lines* represent the second cycle and *dotted lines* represent the third cycle



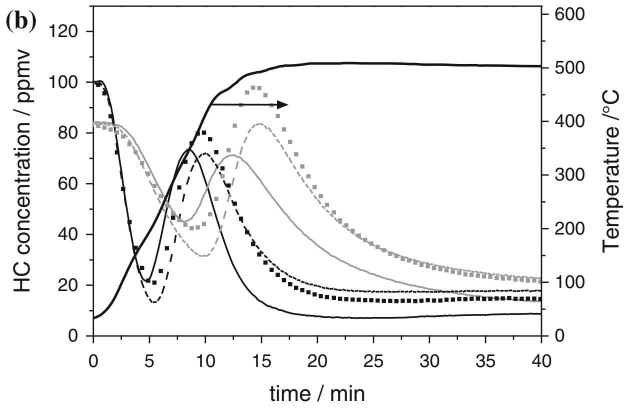


Fig. 5 CST performance (three cycles) corresponding to stabilized **a** H-ZSM-5 and **b** H-BETA zeolites. *Black lines* represent propene concentration profiles and *grey lines* represent toluene. *Solid lines* represent the first cycle, *broken lines* represent the second cycle and *dotted lines* represent the third cycle. *Light grey line* represents propene blank test

HC offset temperatures should not be accounted for HC emissions since these signals were due to HC molecules present in the void volume after the adsorption reactor, which slowly diffused to the detector as it was also observed for the propene signal for an empty tube (Fig. 5a). It can be seen that the toluene retention was higher than that of propene, even complete for H-BETA. In addition, although H-ZSM-5 had similar propene retention capacity than H-BETA zeolite in the first CST, it has a remarkable deactivation when increasing the number of cycles. It is worth commenting that although H-BETA deactivation was marginal, propene was released at very low temperature, thus it can be concluded that the use of this material as an HC trap was not appropriate.

3.2.2 *Stabilized samples*

Due to the severe deactivation of fresh H-ZSM-5 after several CST and the poor performance of H-BETA, the zeolites were stabilized by a steaming process which could avoid the negative effect of steam on the zeolite performance, both increasing the stability and decreasing the acidity of the zeolites. Once the zeolites were stabilized, their performances under CST conditions were analyzed. Figure 5 includes the propene and toluene profiles corresponding to these samples. It should be mentioned that CST experiments have also been carried out with zeolites in their parent (sodium) form but no relevant results have been obtained since the performance of the material is similar before and after the steaming treatment, which is in accordance to that observed by Ding et al. (2007).

Comparing the first cycles of fresh and stabilized samples (Figs. 4, 5), there is a clear improvement of the solid behaviour by increasing the offset temperature in around 50 °C for H-ZSM-5 and around 70 °C for H-BETA. In order to study the ageing effect on these hydrotreated materials, three consecutive CST were performed with each stabilized zeolite in the acidic form. Figure 5 reveals that both zeolites kept their trapping efficiency, even slightly improved, under three consecutive CST. In both cases, the propene desorption temperature of the stabilized samples was higher than 190 °C for the three cycles, and the toluene molecules were desorbed at temperatures higher than 300 °C. Moreover, comparing the performance of fresh and stabilized H-ZSM-5 zeolite after three cycles, the propene offset temperature increased from 55 to 240 °C, which was very close to the light-off temperature of the current TWC.

In the CST performed with the stabilized samples, it was also followed the oligomer formation due to the polymerization of propene molecules over the zeolite surface. As an example, the results obtained for the third CST are shown in Fig. 6. In the temperature range from 200 to 500 °C, a significant amount of these compounds was observed, especially in the case of H-ZSM-5 zeolite.

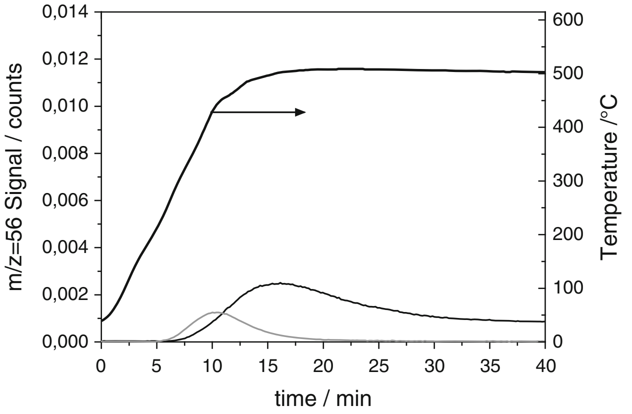


Fig. 6 Oligomer profiles of the third CST performed with stabilized samples: H-ZSM-5 (*black line*) and H-BETA (*grey line*)

4 Discussion

From the CST performed using fresh zeolite samples (H-ZSM-5 and H-BETA) as HC traps, the general finding is that while the heavier HC (e.g. toluene) are adequately trapped by the zeolites (even in the presence of 10 % steam), the lighter HC (e.g. propene) desorb from the HC trap at lower temperatures. The competition of steam and HC molecules for the adsorption sites of the zeolite is relevant. From the propene profiles obtained in this work, it can be observed that fresh zeolites present neither enough adsorption capacity (propene offset temperature of H-BETA is around 100 °C) nor stability (propene offset temperature of H-ZSM-5 varies from 190 to 55 °C). Both zeolites had a low Si/Al ratio which could favour the adsorption of water, leading to a poor HC retention. In addition, deactivation can be linked to the removal of some framework aluminum atoms by hydrothermal attack although it cannot be completely ruled out that coke formation was also taking place. However, since coke was also formed in the stabilised samples and these traps were not deactivating, coke was not expected to be the main deactivation pathway. These negative results made necessary a stabilization process.

It is established that pre-steaming of zeolites enhances the activity and the resistance against water vapor for selective reactions (Katada et al. 2004; Botella et al. 2002; Beyerlein and McVicker 2001). The steaming of the zeolites carried out in the present study (500 °C for 10 h with 10 % v/v water), did not change the basic structure of BETA and ZSM-5 (Fig. 1). However, this process changed considerably the acidity of the zeolites. It was measured a two fold increase in the Si/Al ratio for H-BETA and H-ZSM-5 after treatment. It is known that zeolites can be hydrothermally dealuminated in their hydrogen form or in cation forms convertible into the hydrogen forms upon thermal treatment. Consequently, the dealumination degree is limited by the efficiency of the ammonium or proton ion exchange generally preceding the dealumination procedure. For example, steaming of Na-ZSM-5 at 700 °C for 18 h resulted in the transformation into cristobalite, whereas under the same conditions the hydrogen form of that zeolite retained its crystal topology and the framework aluminum content decreased from 1.17 to 0.25 Al per unit cell (Anggoro and Amin 2011). Considering that an amorphization of the framework was not observed after the steaming carried out in the present study, it could be assumed that the aluminum released from the framework upon the treatment remained in the samples as a component of extra-framework species. The formation, conversion, and migration of EFAl species, may block acid sites and, therefore, reduce the acid sites concentration of the material. This EFAl species seemed to be blocking also a portion of the pore system which results in the decrease of the micropore volume (see Table 1).

CST carried out with the stabilized samples (Fig. 5) pointed out that the steaming process improved the trapping efficiency of zeolites from the first cycle. In this case, the decrease of the surface acidity as a consequence of the aluminum atoms migration and the resulting increase of the Si/Al ratio, contributed to a decrease of the water affinity for the adsorption sites in the zeolite surface, thus reducing the competition with HC for the adsorption sites in the adsorbent structure which, in turn, increased their trap efficiency. Contrary to that expected, the reduction of the micropore volume of the zeolites after steaming has led to a better performance of the HC traps, which could highlighted the role of the acid sites on the zeolite surface on the performance of these solids. Moreover, this reduction was consistent with the fact that during a CST experiment only a fraction of porosity was used to adsorb HC. This could be due to the fact that HC first diffused into an empty sample at low temperatures and thus were preferentially adsorbed in the most favourable sites. Then, as the temperature of the adsorbent increased, the adsorbed amount at equilibrium decreased and the less favourable sites were not significantly used (López et al. 2010). Therefore, it can be concluded that, in spite of the decrease of the micropore volume of the stabilized samples, the performance of the acidic zeolites through HC adsorption was improved.

Steaming was effective not only in improving the trap efficiency of H-ZSM-5 and H-BETA zeolites but also in their stabilization under cycling. Thus, it was observed that whilst fresh zeolite H-ZSM-5 accounted deactivation (see Fig. 4), the stabilized acid zeolites did not suffer an aging process after three consecutive cycles. Besides, the formation of coke by HC cracking did not imply a decrease of the performance of these materials after three cycles. Although the coke formation decreased the specific surface area, it can be stated that enough free adsorption sites were still available for HC adsorption. In the case of H-BETA zeolite, the amount of coke formed was higher than in H-ZSM-5 zeolite, although no deactivation was appreciated (see Fig. 5). As a consequence, a higher number of cycles should be performed in order to know if a higher potential formation of coke over the zeolite surfaces could reduce the trap efficiency of any of these adsorbents.

Related to the oligomer formation in the stabilized samples, it was observed that a significant amount of these compounds was formed especially in the case of H-ZSM-5 zeolite (Fig. 6), which can be also emitted to the atmosphere during a driving cycle. Oligomer formation is associated with hydroxyl groups attached to the surface of the zeolite that provide sites for aliphatic carbon adsorption that may ultimately lead to oligomerization (Stepanov et al. 1998). The oligomers were detected in the outlet stream at intermediate temperatures, in the range from 200 to 300 °C, in both acid zeolites. The propene molecules were

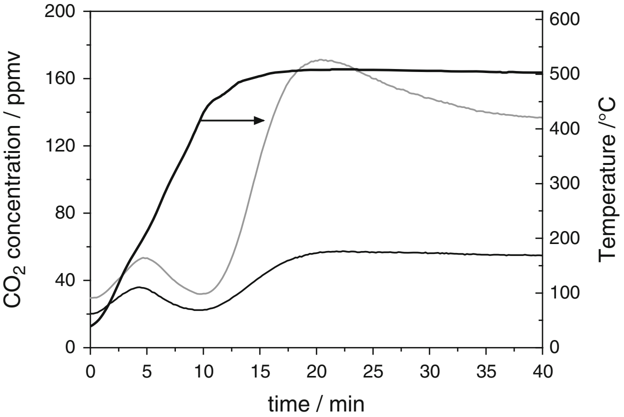


Fig. 7 CO$_2$ profiles of the third CST performed with stabilized samples: H-ZSM-5 (*black line*) and H-BETA (*grey line*)

adsorbed on the acidic sites of zeolites, and upon warming up, the propene molecules would form oligomer species in the zeolite pores. Such oligomer species were more strongly adsorbed on the zeolite than propene itself, hence they were released at higher temperatures as it can be seen from Fig. 6. The space in ZSM-5 channels was more confined than in BETA channels, thus propene was not allowed to form large oligomers and also less coking occurred as it has been observed previously through the TGA results. From an environmental point of view, the oligomer offset temperature was higher than 220 °C for both zeolites, which should be high enough for the TWC to be active and, therefore, oligomer emissions should be easily controlled, leading to another effective way to control the emissions of light HC.

An additional benefit of using zeolites as HC traps was that these solids can act as HC oxidation catalysts at temperatures higher than 400 °C (Botavina et al. 2000). To follow the activity as HC oxidation catalyst of the stabilized zeolites, CO$_2$ profiles were obtained and data of the third CST performed with these samples are plotted in Fig. 7. The higher concentration of CO$_2$ corresponded to H-BETA, which was the stabilised sample that reached the minimum concentration of HC at the end of the CST (see Fig. 5). In addition, this sample showed the highest amount of coke formed. Thus, total oxidation and cracking reaction were more favoured in H-BETA zeolite at high temperatures.

5 Conclusions

In this study, two zeolites (H-ZSM-5 and H-BETA) have been prepared, stabilized and tested as HC traps.The stabilized zeolites showed in all cases propene desorption temperatures higher than 190 °C and toluene offset temperatures higher than 300 °C. H-ZSM-5 was the zeolite that showed the best performance under simulated cold-start conditions. This was due to its lower acidity and its higher structure stability achieved after the steaming process. This treatment produced a stable zeolite structure where propene release was retarded up to 240 °C, which should be high enough for the TWC to carry out its role as catalytic converter.

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