# THE ROLE OF ZEOLITES IN THE DEACTIVATION OF MULTIFUNCTIONAL FISCHER-TROPSCH SYNTHESIS CATALYSTS: THE INTERACTION BETWEEN HZSM-5 AND Fe-BASED FT-CATALYSTS

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**Abstract -** In order to produce gasoline directly from syngas, HZSM-5 can be added to the Fischer-Tropsch catalyst. However, this catalytic system shows an important deactivation rate. Aiming at describing this phenomenon, Fe-based catalysts and physical mixtures containing these catalysts and HZSM-5 were employed in this reaction. All these systems were characterized using the following techniques: XRD, XPS, TPR and TPD of CO. This work shows that HZSM-5 interacts with the Fe-based Fischer-Tropsch catalyst during the reduction step, decreasing the Fe concentration on the catalytic surface and thus lowering the activity of the catalytic system in the Fischer-Tropsch Synthesis.
*Keywords*: Fischer-Tropsch Synthesis; HZSM-5; Fe; Deactivation.

## INTRODUCTION

The production of bio-fuels is one of the most important subjects being researched nowadays as governments and societies from all over world are increasingly becoming aware of how global warming is adversely affecting the environment. Moreover, the local production of bio-fuels is also very relevant nowadays because it can ensure a continuous supply, especially in countries where the demand for fuel is high. For both purposes, the Fischer-Tropsch Synthesis (FTS) is one of the most important chemical processes as it can produce clean fuels from biomass.

As well known, the FTS produces large amounts of n-paraffin, which generates diesel. However, in order to produce gasoline, linear hydrocarbons need to be further processed (Yoneyama *et al.*, 2005). Aiming to generate isoparaffin during the FTS, many groups have proposed the addition of zeolites to the Fischer-Tropsch catalyst (FT catalyst) (Botes, 2005), (Botes and Bohringer, 2004), (Pour *et al.*, 2008), (Martínez *et al.*, 2008).

Botes *et al.* (2005) added HZSM-5 to the Fe-based FT catalyst. The main product was gasoline, although a high deactivation rate was observed. These authors proposed that the migration of the

alkali metal from the Fe-based catalyst towards the zeolite surface was the main deactivation reason.

The deactivation of a bi-functional Fe-HZSM-5 catalyst during the FTS was also studied by Pour *et al*. (2008). These researchers proposed that the formation of coke together with the alkali migration were the main contributing factors to the deactivation process.

Martínez *et al*. (2008) generated high quality gasoline employing mixtures which were comprised of 20%Co/SiO$_2$ and zeolites. By doing so, they also observed a severe deactivation process, and thus suggested that the structural properties of the zeolites determine the amount and location of the coke.

It can be inferred that, until now, it is not clear which is the main cause of the deactivation process mentioned above. Therefore, this contribution aims at further studying this phenomenon when a physical mixture of a zeolite and a Fe-based FT catalyst is employed in the FTS.

## EXPERIMENTAL

### Catalyst Syntheses

The Fe-based catalysts were prepared by co-precipitation using Ca, Al, K or Ru as promoters. Calcium and Al were added during the precipitation procedure, whereas K was included later by impregnation of the solid previously obtained. Ruthenium was also employed as a promoter, replacing K. Firstly, an ammonium hydroxide solution (5 M) was added to the Fe, Ca and Al nitrates solutions (1.2 M, 0.045 M and 0.049 M, respectively). The materials obtained were aged for 24 h. Then they were filtered, washed with hot water and dried (100 ºC for 24 h). After that, the solids were calcined in a muffle furnace at 450 ºC for 5 h at a heating rate of 10 ºCmin$^{-1}$. The promoters K or Ru were added afterwards by impregnation employing K$_2$CO$_3$ and [Ru(NO)(NO$_3$)x(OH)y] (x+y=3) as precursors, respectively. The resulting materials were calcined at 450 ºC during 5 h and the final samples were labeled as FT-K (FT catalyst prepared by K impregnation) and FT-Ru (FT catalyst prepared by Ru impregnation). The nominal concentrations of CaO, Al$_2$O$_3$, K$_2$O and Ru were 2.5, 2.5, 0.65 and 3 wt. %, respectively.

### Characterization

### X- Ray Diffraction (XRD)

Diffraction patterns were obtained using a D5000 Siemens diffractometer with a Bragg-Brentano geometry and a copper tube and also a graphite mono-chromator. The 2Θ scans were performed from 5° to 80°, with a 0.05° step and a 5s acquisition time per step. Diffractograms were analyzed employing the TOPAS 4.2 software (Cheary and Coelho, 1992). Both fresh and used samples (catalyst + SiC) were analyzed. After the reaction, the samples were exposed to X-ray diffraction without any special treatment.

### Temperature-Programmed Reduction (TPR)

The TPR experiments were carried out using a multipurpose analytical system. Firstly, the fresh catalysts (100 mg) were dried at 200 ºC for 30 min under nitrogen flow. After that, the analyses were performed employing the following experimental conditions: 2% H$_2$/He, 30 mL min$^{-1}$ and 10 ºC min$^{-1}$. The FT-Ru catalyst and the physical mixture of FT-Ru + HZSM-5 were evaluated. The same FT-Ru/HZSM-5 weight ratio was employed in the catalytic test.

### Temperature Programmed Desorption of CO (TPD of CO)

The TPD of CO experiments were carried out using a microreactor system coupled to a QMS200 Balzers mass quadrupole spectrometer. Fresh samples of FT-Ru, HZSM-5 and the physical mixture of FT-Ru+HZSM-5 were analyzed. The masses of the samples were 200, 300, and 500 mg for FT-Ru, HZSM-5 and FT-Ru+HZSM-5 (1:1.5), respectively. The samples were reduced at 450 ºC for 6 h under 5%H$_2$/He. Afterwards, they were exposed to 10% CO/He at room temperature for 1 h (12mLmin$^{-1}$). The TPD measurements of CO were carried out heating the samples under He flow (80 mLmin$^{-1}$) at 20 ºCmin$^{-1}$ up to 500 ºC, and then remaining at that temperature during 30 min. The CO ($m/z = 28$) fragment was continuously monitored.

### X- Ray Photoelectron Spectroscopy (XPS)

The experiments were performed in an Omicron UHV chamber (base pressure below 10$^{-7}$ Pa during measurement). The chamber was equipped with a concentric hemisphere analyzer EAC2000 SPHERA and a monochromatic AlKα (1486.6 eV) X-ray beam. Each spectrum was calibrated by using the C$_{1s}$ signal with a peak position of 284.6 eV. A pass energy (Epass) of 50 eV (5 scans) was employed to obtain the wide scan spectra, while 20 eV was used for the short range (20 scans). The samples, probed before and after reaction, were diluted using SiC.

Some experiments were also carried out using FT-Ru (reduced) and FT-Ru+ZSM-5 (reduced) and

FT-Ru+ZSM-5 (oxidized). The reduction of the samples followed the same procedure described for the TPD experiments. After that, the reduced samples were passivated employing a 5%$O_2$/He mixture and using a bath of isopropyl alcohol and liquid $N_2$ for 1h. Then, the samples remained for another hour under 5%$O_2$/He at room temperature.

## Catalyst Evaluation

The reaction studies were carried out using a fixed bed reactor and the following catalysts: FT-K, FT-Ru and physical mixtures of these catalysts with a commercial HZSM-5 (SAR=41 and 393 m$^2$/g). The weight ratio between the FT catalysts and the zeolite was 1:1.5. The mass of the FTS catalysts was 200 mg and of the physical mixtures 500 mg (200 mg of FT-Ru and 300 mg of HZSM-5). The reactor volume was kept constant by using SiC as a diluent. The catalysts were reduced at 100 °C for 1 h, then at 200 °C for 1 h, and finally, at 500 °C during 36 h under 5% $H_2$/He at 30 mLmin$^{-1}$ (5 °C min$^{-1}$). The reaction conditions were 230 ºC, 34 atm, $H_2$/CO=2, GHSV=900 h$^{-1}$. Reactants and products were analyzed by online gas chromatography (CG) every 30 min. The CG employed was an Agilent 7890, with two detectors (TCD and FID) and four columns (Porapak-Q, DC-200, molecular sieve and Pona).

## RESULTS AND DISCUSSION

Figure 1 shows the CO conversion over FT-Ru and FT-K catalysts and the physical mixtures of these catalysts with HZSM-5 in the FTS. The K-promoted catalyst (FT-K) exhibits higher activity than that promoted by Ru (FT-Ru), (Farias et al., 2011). Both physical mixtures show a very low CO conversion, suggesting that HZSM-5 promotes a decrease of the activity of the FT-catalysts. All these catalytic systems generate hydrocarbons in the range of C1-C12. When physical mixtures were employed, a decrease of the catalyst activity was noticed immediately, i.e., the traditional smooth decrease in conversion with time on stream was not observed (Figure 1). Therefore, it can be suggested that the deactivation process is either extremely fast or it occurs during the pretreatment (reduction) of the catalytic system.

In order to investigate this specific phenomenon the following techniques were employed: XRD, XPS, TPR and TPD of CO. Considering that the catalytic behavior of both FT-Ru and FT-K in the physical mixtures was quite similar, only the former and its physical mixture were characterized.
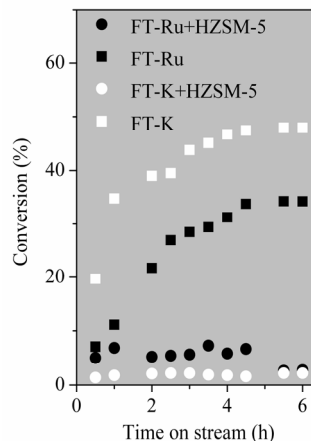


**Figure 1:** CO conversion obtained with promoted FT catalysts (Ru and K) and their physical mixtures.

Figure 2 shows the XRD patterns of the used FT-Ru catalyst. It also shows the patterns of the fresh and used (after the reaction) physical mixtures. The XRD pattern of the fresh physical mixture depicts the diffraction peaks of $Fe_2O_3$, HZSM-5 and SiC, and mostly SiC-6H, as expected. The fresh FT-Ru catalyst also shows peaks of $Fe_2O_3$, but its diffraction is not displayed in Figure 2. As can be observed, the used physical mixture exhibits diffraction peaks of SiC, HZSM-5 and a very small amount of $Fe_2C$, with a major peak at 42.7. The amount of $Fe_2O_3$ suffered a sharp reduction when compared with the fresh physical mixture and its peaks are no longer visible. However, no major changes were observed in the lattice parameters of HZSM-5 when these mixtures were compared once again. The used FT-Ru catalyst also showed the disappearance of $Fe_2O_3$. It was replaced by nanocrystalline $Fe_3O_4$, depicting a major and broad peak at 18.3. This catalyst does not show $Fe_2C$.
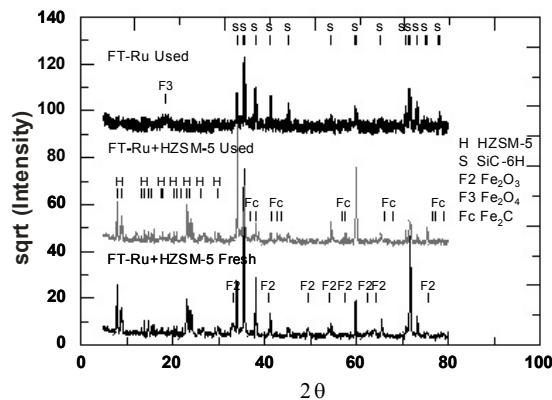


**Figure 2:** XRD patterns of the samples.

As well known, X-ray diffraction (XRD) can only detect inorganic structures that show long-range periodicity. It is not sensitive to amorphous or well-dispersed Fe species. Therefore, the phases described above can not be associated with the catalytic activity. However, the FT-Ru and FT-Ru+HZSM-5 catalytic systems employ the same FT catalyst and show different phases after the reaction. Thus, it can be suggested that, during the pretreatment or the reaction, or during both of them, HZSM-5 interacts with the FT catalyst, changing its composition and phases.

Figure 3 shows the TPR profiles of FT-Ru and FT-Ru+HZSM-5. The FT-Ru catalyst shows two main broad peaks at 232 and 832 ºC. According to Li *et al.* (2002), these peaks are related to the reduction of $Fe_2O_3$ to $Fe_3O_4$ and $Fe_3O_4$ to $Fe^o$, respectively. The TPR profile of the physical mixture is similar to that of the FT-Ru catalyst, suggesting that the zeolite seems not to change the reduction process of the FT catalyst. In other words, HZSM-5 does not seem to interact with the FT catalyst during the reduction process under these conditions.
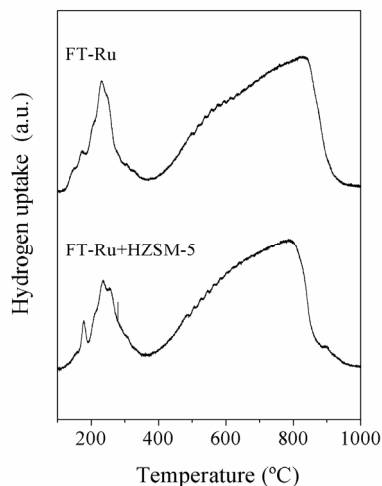


**Figure 3:** TPR profiles of FT-Ru and physical mixture FT-Ru+HZSM-5 catalysts (fresh samples).

The CO desorption profiles are depicted in Figure 4. Fresh samples of FT-Ru, HZSM-5 and FT-Ru+HZSM-5, previously reduced, were analyzed. As can be observed, the FT-Ru catalyst exhibits two desorption peaks: one at 137 ºC and another at 497 ºC, which are related to two distinct CO adsorption sites. The adsorption of CO on the FT-Ru catalyst is mainly related to the presence of $Fe^o$ on the catalyst surface. The HZSM-5 sample shows only a very small peak at low temperature, which is assigned to the CO interaction with Lewis acid sites (Binet *et al.*, 1999). The FT-Ru+HZSM-5 physical mixture does not show desorption peaks. Therefore, the concentration of $Fe^o$ on the physical mixture surface (FT-Ru+HZSM-5) should be very low as this system is not able to adsorb CO.
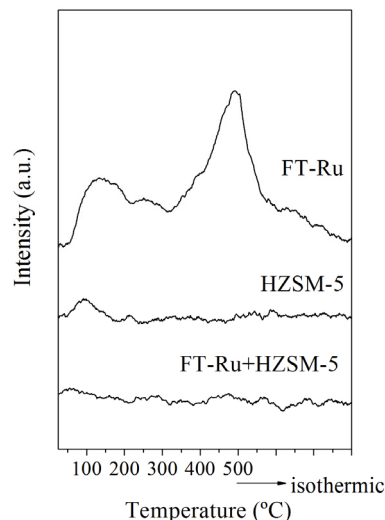


**Figure 4:** TPD spectra of CO (fresh samples).

The results obtained employing the TPD of CO suggest that the FT catalyst interacts with HZSM-5 during the reduction step, leading to a very low concentration of $Fe^o$ on the catalytic surface and, consequently, low activity for the FTS.

On the one hand, the TPR experiments expose the catalysts to a fast reduction process and the results obtained do not suggest any interaction between FT-Ru and HZSM-5. On the other hand, the pretreatment of the catalysts (reduction) employed in the TPD of CO is a slow process (see experimental section) and the results show that FT-Ru and HZSM-5 interact. Thus, it can be proposed that this phenomenon occurs at a low rate during the reduction of the catalyst.

Figure 5 depicts the photoelectron spectra (XPS) of the $Fe_{2p}$ binding energy region for both catalysts FT-Ru and FT-Ru+HZSM-5 after the reaction. The samples analyzed were diluted in SiC (see methodology). Despite the fact that the signal/noise ratio was very low, it could be observed that the spectrum of the FT-Ru catalyst showed a low Fe signal, whereas the FT-Ru+HZSM-5 physical mixture exhibits a $Fe_{2p}$ line which could only be observed in the background. The data show that, in the case of the physical mixture, Fe is almost undetectable. These results agree with the ones described above which are related to the catalytic performance of these systems. Indeed, a very low concentration of Fe on the surface leads to a very low catalytic activity.
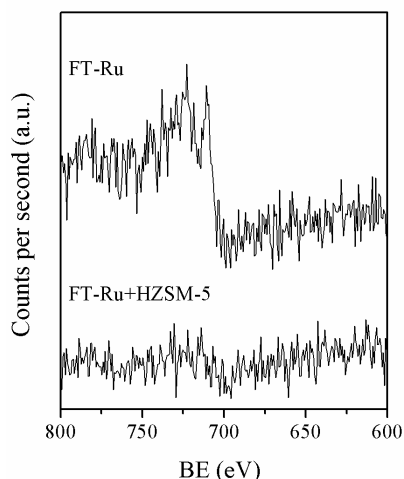
**Figure 5**: XPS spectra of catalysts after reaction (used samples)

The XPS analyses were also carried out employing fresh samples of FT-Ru and FT-Ru+HZSM-5, which had been previously reduced (see methodology). The photoelectron spectrum of the FT-Ru+HZSM-5 physical mixture before reduction was also collected. It was observed that the Ru atomic superficial concentration was almost the same for both the reduced and oxidized physical mixtures. This metal seems not to be affected by the reduction process or by the interaction with the zeolite. Therefore, Ru was used as a reference. Table 1 shows the ratios of Fe/Ru and Si/Al. When comparing, the Fe/Ru ratio of FT-Ru and FT-Ru+HZSM-5 (both reduced), it can be observed that the physical mixture shows a lower Fe concentration, which can be related to the interaction between the FT catalyst and HZSM-5. These data agree with the results of TPD of CO and also with the results of the catalytic tests. Indeed, the TPD of CO shows less Fe than XPS. This result is related to the fact that the TPD results are associated with the outermost layer of the solid, whereas some layers near the external surface of the catalyst are analyzed by XPS. Table 1 also shows the values of the Si/Al ratios. It can be inferred that, for both the oxidized and reduced mixtures, the values are almost similar. Therefore, when employing XPS analysis, it is not possible to associate the decrease of the Fe concentration with changes on the HZSM-5 surface.

Some previous works have showed that the catalytic behavior of physical mixtures can be completely different from the behavior of each of the components of the system (Ramos *et al*., 2005), (Zonetti *et al*, 2011). Taking the results described

above into account, it can be inferred that the sinterization of Fe is promoted by HZSM-5, generating a catalytic system which shows very poor activity. However, at the moment, it is not possible to describe this phenomenon in details.

**Table 1: Fe/Ru and Si/Al atomic ratios by XPS analyses**

| Samples | Fe/Ru | Si/Al |
|---|---|---|
| FT-Ru (reduced) | 20.6 | - |
| FT-Ru + HZSM-5 (reduced) | 5.5 | 17.6 |
| FT-Ru + HZSM-5 (before reduction) | 10.4 | 17.1 |

It is worth stressing that these results have never been described in the literature. They are related to a solid-solid interaction phenomenon in which different parameters can change its intensity. Considering former publications which have already studied physical mixtures of FT catalysts with zeolites, it can be inferred that some of these works employed lower reduction temperatures (Yoneyama *et al*., 2005), larger particle sizes (Botes and Bohringer, 2004) and lower zeolite/FT catalyst ratios (Botes and Bohringer, 2004) when compared with the conditions employed in this study. As these parameters change the intensity of the solid-solid interactions, it can be suggested that this phenomenon might have also occurred in these former studies, but at lower intensities when compared with the data shown above. Moreover, the other modes of deactivation, which have already been proposed in the literature, may have also occurred together with this phenomenon.

## CONCLUSION

This work shows that, when HZSM-5 is added to an Fe-based FT catalyst, it interacts with this catalyst, decreasing the Fe concentration on the catalytic surface, leading to a low activity of the catalytic system in the Fischer-Tropsch Synthesis (FTS).

## ACKNOWLEDGMENTS

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