

## Oxidative desulfurization of thiophene on TiO<sub>2</sub>/ZSM-12 zeolite

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In this work the hydrothermal synthesis of ZSM-12 zeolite was performed, varying the MTEACl/SiO<sub>2</sub> ratio, where the synthesis temperature was 140 °C and the crystallization time was 144 hours. The catalysts were characterized by XRD, FTIR and TG. TiO<sub>2</sub>/ZSM-12 catalysts were used with titanium ions concentrations of 5, 10 and 15%. The oxidative desulfurization (ODS) reactions were performed using a model mixture containing *n*-heptane as solvent and thiophene as sulfur compound, H<sub>2</sub>O<sub>2</sub> as an oxidizing agent, and acetonitrile as an extractor solvent at reaction temperatures of 30, 50 and 70 °C. The obtained results shows that TiO<sub>2</sub>/ZSM-12 with 15% of Ti catalyst has a better performance in the ODS reaction converting thiophene at about 60%.

**Keywords:** Desulfurization, ZSM-12 zeolite, Oxidation

### 1. Introduction

Motor vehicles emission produces sulfur compounds, such as sulfur oxides (SO<sub>x</sub>) generated in the burning of fuels containing contaminants, such as mercaptans, thiophene and its alkylated derivatives, benzothiophene, dibenzothiophene, and naftobenzothiophene. Nowadays, there is a great need to reformulate the types of fuels and production technologies, focusing on minimizing these emissions, improving, especially in big cities, the quality of life, the environment and human health<sup>1,2</sup>.

The removal of sulfur from petroleum fractions is a transaction that has already been carried out using some processes, such as the hydrodesulfurization (HDS), which uses catalysts that operate in the sulfur removal. However, this process requires high temperatures and pressures, besides consuming a high amount of hydrogen. The oxidative desulfurization, associated with the use of catalysts through electronic affinity and selectivity, performs the removal of sulfur molecules, and this has been the subject of scientific research, aiming at reducing the amount of sulfur present in petroleum fractions<sup>2,3</sup>.

The catalytic oxidative desulfurization (ODS) is an option for the reduction of sulfur content on sulfur compounds<sup>4</sup>. The reaction occurs with the use of an oxidizing agent, such as hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>. After the oxidation reaction, the extraction of the sulfone is carried out using, for example, acetonitrile as an extractor solvent<sup>4,5</sup>. Despite the catalytic oxidative desulfurization's route be well-known and consolidated, it is necessary to search for an improvement in

operating conditions and the optimization of catalysts, and, therefore, an improvement on the reaction efficiency. The use of catalytic materials containing titanium is an interesting alternative to ODS processes<sup>4</sup>. Thus, the use of ODS has a great potential to become a complementary process to traditional HDS<sup>5</sup>.

In this work, catalyst supports were developed with ZSM-12 zeolitic structure and deposition of active phases based on titanium ions in order to develop efficient catalysts for the oxidative desulfurization process of oil fractions. ZSM-12 is a microporous zeolite and its first synthesis was performed by Rosinski and Rubin in 1974<sup>6</sup>. The ZSM-12 is a one-dimensional 12-membered rings (12MR) system, in a channels system with a pore opening size of 5.7 x 6.1 Å. The acid form of ZSM-12 has been used very successfully in the cracking, hydrocracking catalysis, and various other processes of petroleum refining. ZSM-12 shows excellent resistance to deactivation by carbon deposits, in hydrocarbon conversion reactions. There is some difficulty to incorporate aluminum into the structure, which is suggested to be the limiting of the Si/Al ratio for the ZSM-12 synthesis<sup>7</sup>. TiO<sub>2</sub> is one of the more important transition metal oxides, widely used as catalyst support, a semiconductor photo-catalyst, in solar cells. TiO<sub>2</sub> in the forms anatase and rutile has been used in heterogeneous photocatalysis, wherein the anatase usually has a higher catalytic activity<sup>1</sup>. The use of solid catalysts in ODS processes has been developed in recent years, and some types of solid catalysts have been studied, such as Ti molecular sieves.

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## 2. Experimental

The ZSM-12 zeolite was obtained using the hydrothermal method in accordance with the procedure adapted from Pedrosa et al.,<sup>8</sup>. In order to reduce the amount of materials for synthesis, and thus the cost for production of zeolites, syntheses were performed varying the MTEACl/SiO<sub>2</sub> ratios. The composition of the catalysts to be obtained was:

20 MTEACl : 10 Na<sub>2</sub>O : 100 SiO<sub>2</sub> : 2000 H<sub>2</sub>O 0.5 Al<sub>2</sub>O<sub>3</sub>  
(MTEACl/SiO<sub>2</sub> = 1:5)

10 MTEACl : 10 Na<sub>2</sub>O : 100 SiO<sub>2</sub> : 2000 H<sub>2</sub>O 0.5 Al<sub>2</sub>O<sub>3</sub>  
(MTEACl/SiO<sub>2</sub> = 1:10)

5 MTEACl : 10 Na<sub>2</sub>O : 100 SiO<sub>2</sub> : 2000 H<sub>2</sub>O 0.5 Al<sub>2</sub>O<sub>3</sub>  
(MTEACl/SiO<sub>2</sub> = 1:20)

The gel formed after the hydrothermal synthesis was washed with distilled water and filtered under vacuum, until the resulting liquid from the filtration reached pH = 7. Once this pH was reached, the filtrate was dried in an oven for 12 hours at 100 °C. The description and the characteristics of each prepared sample are shown in Table 1.

After drying the material, the thermal treatment of the samples (calcination) was performed in order to remove the organic template present in the porous structure of the prepared samples. The calcination starts at a temperature of 30 °C and at a heating rate of 5 °C min<sup>-1</sup> and synthetic air flow until the temperature of 550 °C is reached. The sample is then maintained at constant temperature of 550 °C for 12 hours under air flow.

The deposition of the titanium based active phase on ZSM-12 was performed by impregnation with a slight excess of solvent, starting from an aqueous solution of TiCl<sub>3</sub>, where this was dripped onto the support (ZSM-12). The calculations for the desired concentrations of Ti were made according to the mass of the zeolite used. The materials obtained using different levels of titanium were dried at 100 °C for 24 hours, followed by calcination at 450 °C at a heating rate of 5 °C min<sup>-1</sup>, under synthetic air flow for 2 hours.

The non-calcined and calcined samples of the zeolite ZSM-12 and the calcined samples of  $\text{TiO}_2/\text{ZSM-12}$  supported zeolitic catalyst with concentrations of 5%, 10% and 15% of Ti were analyzed by X-ray diffraction. This technique was used to provide the information on changes in the crystal lattice of the ZSM-12 support and catalysts with the thermal deposition of the titanium precursor. The XRD were obtained in a Miniflex II equipment by Rigaku, applying a CuK $\alpha$  radiation source with voltage of 30 kV and 15 mA current. Data were collected in the range of 2 $\theta$  from 5 to 55° for the not supported samples, with angular scan speed of 2°min<sup>-1</sup>,

with step of 0.02 °min<sup>-1</sup>, and in a range from 5-70° for the supported samples contain TiO<sub>2</sub>.

The absorption spectra in the infrared region were obtained for samples of ZSM-12 and  $\text{TiO}_2/\text{ZSM-12}$ . The samples were mixed with KBr at 1:4 ratio. The spectra were obtained on Perkin Elmer equipment, Spectrum BX model, in the region of 4000 to 400 cm<sup>-1</sup>. The thermogravimetric curves were obtained under the following conditions: initial temperature of 30 °C; final temperature of 900 °C; heating rate of 10°C min<sup>-1</sup> in a N<sub>2</sub> atmosphere.

The catalytic oxidative desulfurization tests were performed in a bench scale system. For the catalytic tests, the following reagents were used: a model mixture composed of *n*-heptane with 5000 ppm of thiophene, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidizing agent, and acetonitrile as an extractor solvent. A mixing ratio of 2/1/1 model mixture/acetonitrile/H<sub>2</sub>O<sub>2</sub> was applied. The catalyst mass used in each oxidative desulfurization test was 100 mg. The analysis of the oxidative desulfurization reactions products was performed using a Gas Chromatograph GC-450 by Varian, containing a flame ionization detector (FID). The capillary column is 30 meters long, and has 0.25 mm internal diameter and 0.39 mm film thickness. Each run was performed with a time of 7.33 minutes.

## 3. Results and discussions

Figure 1a shows a diffractogram of newly crystallized ZSM-12 zeolites, with different MTEACl/SiO<sub>2</sub> ratios, where the peaks show the formation of the ZSM-12 crystalline phase, similar to those published in the literature<sup>8,9</sup>, indicating also that no other phase was found. Among the characterized supports, the one which showed a higher crystallinity was Y6 non-calcined sample, indicating that the optimum MTEACl/SiO<sub>2</sub> ratio was 1:10, followed by sample X6 non-calcined (MTEACl/SiO<sub>2</sub> = 1:5), and W6 non-calcined sample (MTEACl/SiO<sub>2</sub> = 1:20). These findings also indicate that the hydrothermal method for zeolite synthesis was effective. The variation of the template/silica ratio did not affect the pH of the sample after 144 hours of crystallization, since the three samples remained with alkaline pH 12. The decrease in the MTEACl/SiO<sub>2</sub> ratio shows that there is a decrease in the crystallinity of the sample, which may have resulted in the formation of a larger amorphous phase. Samples X6, Y6 and W6 were subjected to a thermal treatment via calcination, having the aim of removing the organic template molecules present on the porous of the crystalline zeolite structure. Figure 1b shows the diffractogram of the calcined supports, where it is possible to observe that the crystalline structure was not affected after the thermal treatment. Based on these data, it was possible to evaluate that the zeolite Y6 (MTEACl/SiO<sub>2</sub> = 1:10) would be chosen to be used as a support for titanium oxides.

Figure 2 (a, b, c) show the diffractograms of the  $\text{TiO}_2/\text{ZSM-12}$  samples with 5, 10 and 15% of titanium. The samples showed peaks attributed to the crystalline phase of ZSM-12, similar to those published in the literature<sup>4,8</sup> and due TiO<sub>2</sub> phase. In all samples there was a gradual reduction of the crystallinity of the supports regarding titanium contents, which characterized the emergence of titanium dioxide on the surface of the zeolites. The peaks for TiO<sub>2</sub> evidenced

**Table 1.** Characteristics of the synthesized samples X6, Y6 and W6 from ZSM-12 samples.

Sample	Si/Al	MTEACl/SiO <sub>2</sub>	Crystallization time (h)
X6	100	1:5	144
Y6	100	1:10	144
W6	100	1:20	144

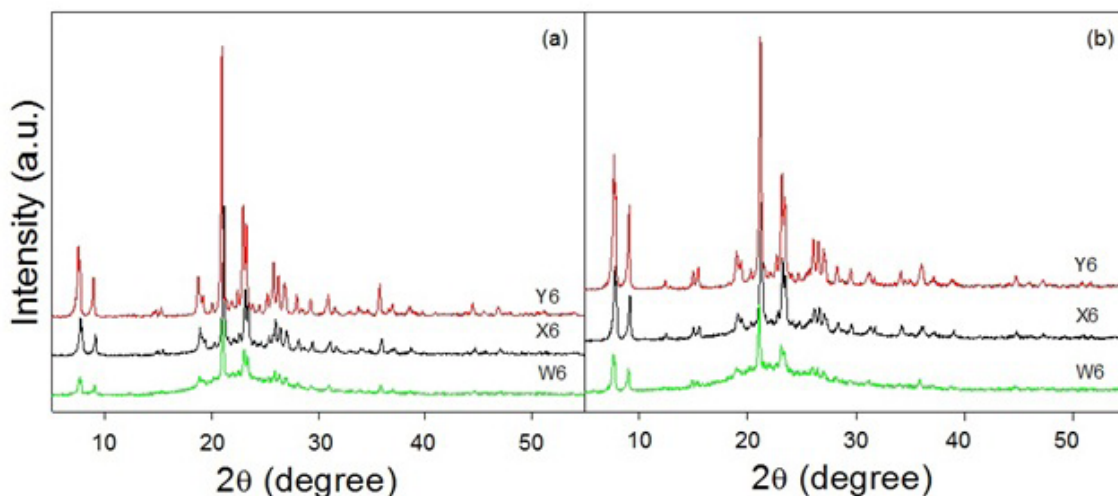


Fig. 1. X-ray diffractogram of X6, Y6 and W6 ZSM-12 samples: (a) non-calcined and (b) calcined samples.

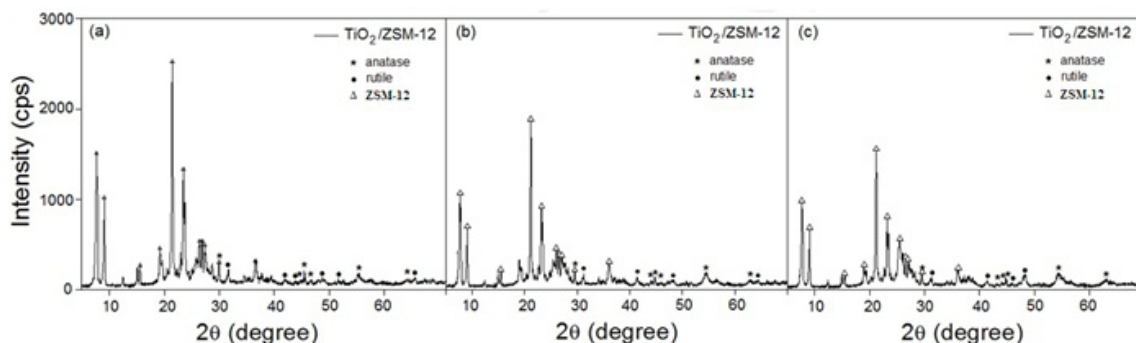


Fig. 2. X-ray diffractogram of the calcined  $\text{TiO}_2/\text{ZSM-12}$  samples: (a) 5% of Ti, (b) 10% of Ti and (c) 15% of Ti.

the formation of more than one phase related to titanium (anatase and rutile)<sup>10</sup>.

Table 2 shows the crystallinity and crystallite sizes for calcined X6, Y6 and W6 samples, and  $\text{TiO}_2/\text{ZSM-12}$  at 5, 10 and 15% of titanium. For the ZSM-12 samples, it was observed that the higher crystallinity is represented by the sample Y6, which has the most intense and characteristic peaks of zeolite ZSM-12<sup>9</sup>, influenced by the MTEACl/SiO<sub>2</sub> ratio and the thermal treatment occurred on calcination at 550 °C. Among the  $\text{TiO}_2/\text{ZSM-12}$  samples, the most crystalline was the  $\text{TiO}_2/\text{ZSM-12}$  with 5% titanium, which may be due to greater retention of crystallinity of the support ZSM-12, with the  $\text{TiO}_2$  competitive phase. As for the  $\text{TiO}_2/\text{ZSM-12}$  samples with 10 and 15% of Ti, they had their crystallite size decreased, in relation to phase ZSM-12 due to the impregnation and higher presence of anatase and rutile competitive phases. The crystallinity for  $\text{TiO}_2/\text{ZSM-12}$  catalysts was calculated by taking the Y6 sample as reference (100% crystalline).

The variation in amount of MTEA<sup>+</sup> ions was determined by thermogravimetric analysis. Mass loss of not calcined zeolite ZSM-12 is characterized by three steps<sup>11</sup>: (I) Desorption of intracrystalline water, (II) decomposition of MTEA<sup>+</sup> ions located inside the zeolite ZSM-12 pores; (III) decomposition of

**Table 2.** Crystallinity and crystallite size of calcined ZSM-12 zeolites and for the  $\text{TiO}_2/\text{ZSM-12}$  catalysts impregnated with 5, 10 and 15% of Ti over the sample Y6.

Sample	Crystallinity (%)	Crystallite size (nm)
X6	68.0	46.5
Y6	100.0	71.3
W6	46.5	28.2
5%	91.3	40.6
10%	69.1	38.3
15%	64.1	23.6

MTEA<sup>+</sup> cations strongly bound to the surface. Figure 3 (a, b, c) show the mass loss of not calcined samples X6, Y6 and W6. It can be seen that in the first stage of mass loss for these three samples there was a reduction of about 11% of mass, corresponding to the desorption of the intracrystalline water contained in the sample. Similar to results showed by<sup>11</sup>, the second stage of mass loss may correspond to the decomposing MTEA<sup>+</sup> ions present in the zeolite pores. However, the third step can be characterized as the coke removing and residual amines decomposition formed from

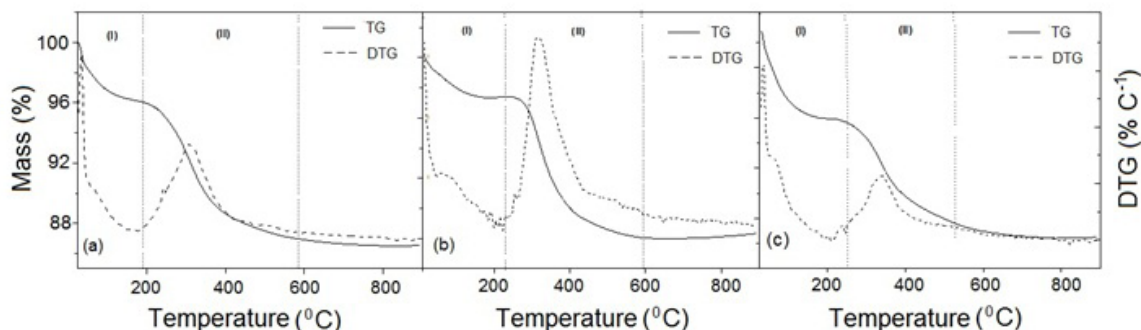


Fig. 3. TG/DTG curves for the non-calcined ZSM-12 zeolites, where: (a) X6, (b) Y6 and (c) W6 samples.

the decomposition of organic template products<sup>8</sup> contained in the samples. The temperatures at which the organic is eliminated were: 585 $^{\circ}\text{C}$  (X6), 595 $^{\circ}\text{C}$  (Y6) and 540 $^{\circ}\text{C}$  (W6).

Figure 4 (a, b, c) show the mass loss of not calcined samples impregnated with different titanium contents. It is possible to observe that there is an initial mass loss in all samples that can be related to the presence of intracrystalline water. In the second phase it is possible to observe that there is a second mass loss, whose characteristics are indifferent to the ZSM-12 zeolite, which can be justified by the decomposition of chloride ions coming from the  $\text{TiCl}_3$  solution required for impregnating the sample with titanium.

Figure 5a show the FTIR spectra of the ZSM-12 calcined samples (X6, Y6 and W6) and Figure 5b to the  $\text{TiO}_2/\text{ZSM-12}$  samples. The spectra show characteristic bands on the presence of vibration in 1229-1089  $\text{cm}^{-1}$ , which are explained as tetrahedrons'  $\text{TO}_4$  ( $\text{T} = \text{Al}, \text{Si}$ ) asymmetric stretching vibrations<sup>12</sup>. The presence of a 12-membered rings system were represented by the vibration at 470  $\text{cm}^{-1}$ , and the band at 803-591  $\text{cm}^{-1}$  on the external tetrahedrons symmetric stretch. Two bands were displayed in the spectra: the 3419  $\text{cm}^{-1}$  one, related to the stretching of OH bonds, and the 1644  $\text{cm}^{-1}$  band, related to the deformation of the OH bonds<sup>13</sup>. FTIR spectra of the  $\text{TiO}_2/\text{ZSM-12}$  samples showed an enlargement in two specific bands, 1097 and 803  $\text{cm}^{-1}$  in relation of the ZSM-12 calcined, which may be related to the presence of vibrations by Si-O-Si stretching and between these two bands, Ti-O-Si vibrations, as confirming the presence of titanium oxides in the samples<sup>14</sup>.

The oxidative desulfurization reactions were performed in order to obtain the conversion of thiophene to sulfone as function of the reaction time present in a *n*-heptane solution at a concentration of 5000 ppm, and also in order to analyze the catalytic potential of the supported catalysts with different titanium content (5, 10 and 15%).

Figure 6 (a, b and c) shows the catalytic activity of the  $\text{TiO}_2/\text{ZSM-12}$  catalysts (5, 10 and 15% of titanium) at different temperatures during 60 minutes of reaction. According to data previously discussed in the literature<sup>4,5</sup>, the reaction is processed by removal of the thiophene molecule through the oxidation reaction associated with the use of  $\text{H}_2\text{O}_2$  as the oxidant agent and acetonitrile as the extractor solvent. It could be observed that there was conversion in all cases, and that the minimum time for stabilization was 40 minutes for all reactions which used the catalysts. The data presented

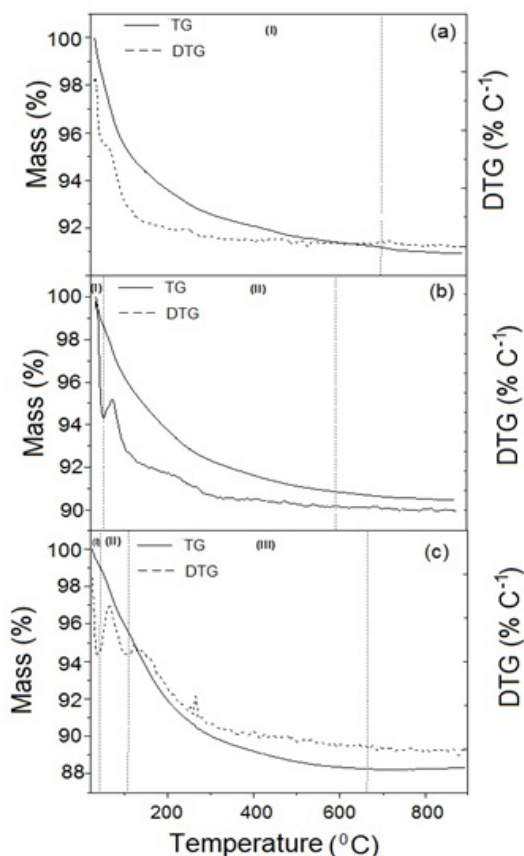


Fig. 4. TG/DTG curves for the non-calcined  $\text{TiO}_2/\text{ZSM-12}$  samples, where: (a) 5% of Ti, (b) 10% of Ti and (c) 15% of Ti.

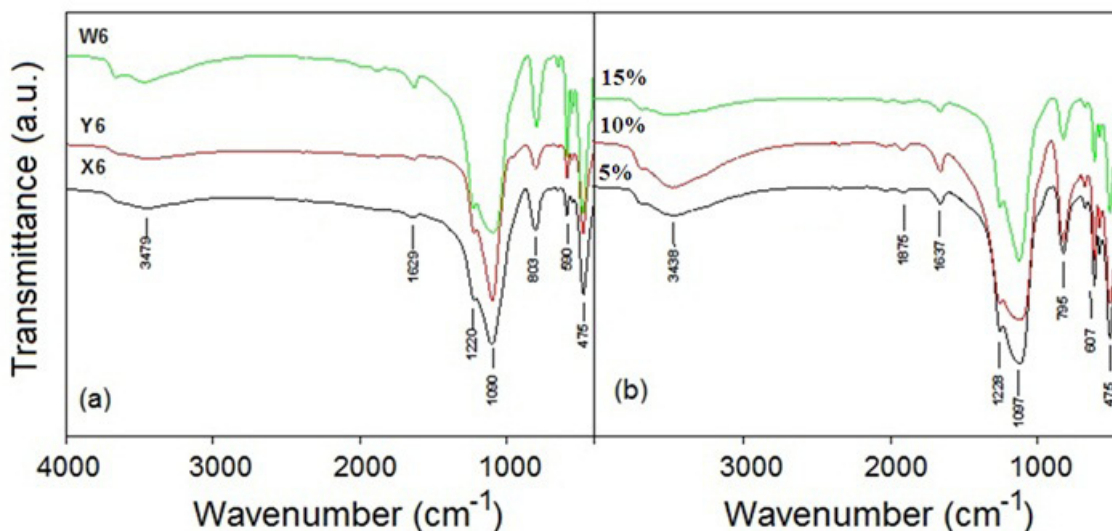
in Figure 6 (a, b and c) show that all the catalysts studied presented activity for reaction with conversions in the range 15 to 60% after 30 minutes of reaction.

As for the sample  $\text{TiO}_2/\text{ZSM-12}$  (15% of titanium) there was a conversion of 33% into sulfone, a low performance, which was expected due to no use of heating during the reaction (Figure 6a). Despite the low conversion, ODS reactions into dibenzothiophen performed by Huang et al.,<sup>15</sup> using mesoporous  $\text{TiO}_2$  obtained a similar conversion in

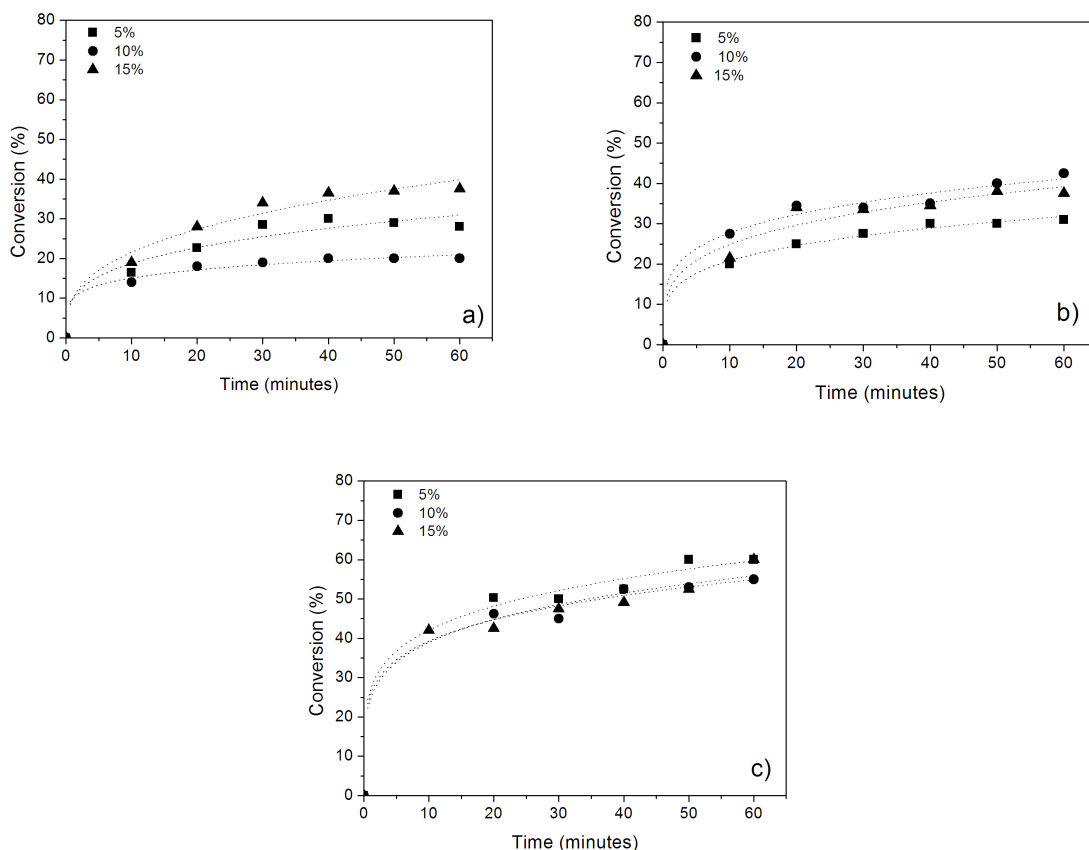


a reaction time of 10 minutes under a temperature of 60 °C, showing that, for the synthesized supported catalysts, using the ZSM-12 as the microporous support for  $\text{TiO}_2$  increases the contact area between reagents and  $\text{TiO}_2$ . Still according to the study by this author, it was observed that the higher

the concentration of dibenzothiophen in the model mixture, the lower the conversion into sulfone. The results presented in Figure 6a may also show that the activity of catalysts for the reaction did not present a linear correlation with the supported titanium content in the sample, although the



**Fig. 5** FTIR spectra for calcined ZSM-12 samples (X6, Y6 W6) (a) and FTIR spectra for calcined  $\text{TiO}_2$ /ZSM-12 samples of 5% of Ti, 10% of Ti and 15% of Ti (b).



**Fig. 6.** Conversion as time function to ODS reactions at different titanium loadings: (a) 30°C, b) 50°C and c) 70°C.

sample with 15% titanium has shown a better catalytic profile throughout the studied reaction time.

Figure 6b shows the catalytic activity of the  $\text{TiO}_2/\text{ZSM-12}$  (10% of titanium) catalyst by removing the thiophene molecule through the oxidation reaction associated with the use of  $\text{H}_2\text{O}_2$  and acetonitrile, under constant stirring and pressure and at temperature of 50 °C. It can be noticed that there was a better conversion when compared to reactions under ambient temperature. The reaction with the  $\text{TiO}_2/\text{ZSM-12}$  (10% of titanium) sample had a very similar behavior related to the reaction with the  $\text{TiO}_2/\text{ZSM-12}$  (15% of titanium) sample, showing that, in this case, a lower content of supported  $\text{TiO}_2$  is enough so that the conversion of 40% thiophene into sulfone occurs.

Figure 6c shows the catalytic activity of the  $\text{TiO}_2/\text{ZSM-12}$  (15% of titanium) catalyst by removing the thiophene molecule through the oxidation reaction associated with the use of  $\text{H}_2\text{O}_2$  and acetonitrile, under constant stirring and pressure and at temperature of 70 °C. These results showed that the highest conversion of thiophene into sulfone was obtained with the catalyst  $\text{TiO}_2/\text{ZSM-12}$  (15% of titanium) at a temperature of 70 °C and 60 minutes of reaction. This can be justified by the need to have a higher concentration of titanium, and due to the influence of a higher temperature for a higher conversion occur.

The increase in temperature of reaction resulted in an increase of conversion for all the catalysts studied. The conversion after 60 minutes of reaction was in the range 15-35% for the test conducted at 30 °C, in the range of 25-45% for the catalytic test at 50 °C while for the test conducted at 70 °C the range of conversion was in the range of 45-60%. The data shown in Figure 6c show more clearly the importance of the temperature in the ODS catalytic reaction on the catalysts studied. For the other hand, the activity of the  $\text{TiO}_2/\text{ZSM-12}$  catalysts with different content of titanium not presents a linear correlation with the supported titanium content in the sample, although for the tests in the temperatures of 30 °C and 70 °C the sample with 15% titanium has shown a better catalytic profile. The catalytic activity profiles at 30 °C of the  $\text{TiO}_2/\text{ZSM-12}$  catalysts followed the trend: 15% Ti > 5% Ti > 10% Ti. With the increase of temperature for the 50 °C, the catalytic activity profiles

follow the trend 10% Ti > 15% Ti > 5% Ti. Data do not yet exhibit a linear correlation between the content of titanium and the conversion, showing that this should be influenced by the combined effects of parameters such as temperature, time, and the active phase. For the tests at 70 °C, in general the catalytic activity was slightly influenced by the titanium content. In this case, the catalytic activity profiles followed the trend: 5% Ti > 10 Ti > 15%Ti.

## Conclusions

The variation in the  $\text{MTEACl}/\text{SiO}_2$  ratio during the synthesis of the ZSM-12 zeolite is of fundamental importance for the formation of the crystalline phase, where the best ratio found in this study was 1:10 (sample Y6). The diffractograms showed that for samples of zeolite ZSM-12, the one which obtained a larger degree of crystallinity was the sample Y6, which was, then, selected for carrying out the impregnation with titanium. Regarding impregnated samples, there was the appearance of peaks for the two phases of titanium, anatase and rutile, being the anatase the phase which showed the highest ratio.

The FTIR spectra showed characteristic bands related to the synthesized ZSM-12 zeolite. The thermogravimetric analysis showed that for a complete removal of the organic structural template the temperature of 550 °C is effective. As for the impregnated samples, the temperature of 450 °C was also effective for removing intracrystalline water as well as removing chloride anions, resulting from the impregnation phase by  $\text{TiCl}_3$  solution;

ODS reactions showed a dependence of the conversion with increasing reaction temperature, as well as with the content of titanium supported on ZSM-12, where the highest conversion of 60% was found, showing the effectiveness of the catalytic potential of the  $\text{TiO}_2/\text{ZSM-12}$  catalysts with 15% of titanium at temperature of 70 °C and 60 minutes of reaction.

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## References

- Speight JG. *Handbook of Petroleum analysis*. Nova Jersey: John Wiley & Sons; 2002.
- Samatov PP, Dzhemilev UM, Sharipov AK. Oxidation of sulfides in petroleum diesel fraction with hydrogen peroxide catalyzed by molybdenum compounds. *Petroleum Chemistry*. 2006; 46(6):439-441. doi.org/10.1134/s0965544106060107.
- Mei H, Mei BW, Yen TF. A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization. *Fuel*. 2003;82(3):405-414. doi.org/10.1016/s0016-2361(02)00318-6.
- Caero LC, Jorge F, Navarro A, Gutiérrez-Alejandro A. Oxidative desulfurization of synthetic diesel using supported catalysis. Part II. Effect of oxidant and nitrogen-compounds on extraction-oxidation process. *Catalysis Today*. 2006;116(4):562-568. doi.org/10.1016/j.cattod.2006.06.031.
- Lanju, C, Shaohui G, Dishun Z. Oxidative desulfurization of simulated gasoline over metal oxide-loaded molecular sieve. *Chinese Journal Chemical Engineering*. 2007;15 (4):520-523. doi.org/10.1016/s1004-9541(07)60118-9
- Rosinski EJ, Rubin MK. U.S. Patent 3832 449; 1974.
- Yoo K, Kashfi R, Gopal S, Smirniotis PG, Gangoda M, Bose RN. TEABr directed synthesis of ZSM-12 and its NMR characterization. *Microporous and Mesoporous Materials*. 2003; 60(1): 57-68. doi.org/10.1016/s1387-1811(03)00317-2.
- Pedrosa AM, Souza, MJ, Silva AO, Melo DM, Araujo AS. Synthesis, characterization and catalytic properties of the cobalt and nickel supported on HZSM-12 zeolite. *Catalysis Communications*. 2006;7(10):791-796. doi.org/10.1016/j.catcom.2006.02.012.
- Gopal S, Yoo K, Smirniotis PG. Synthesis of Al-rich ZSM-12 using TEAOH as template. *Microporous and Mesoporous Materials*. 2001;49(1):49-156. doi.org/10.1016/s1387-1811(01)00412-7.

10. Saleiro GT, Cardoso SL, Toledo R, Holanda JN. Evaluation of the crystalline phases of supported titanium dioxide in red ceramic. *Cerâmica*. 2010;56(338):162-167. doi.org/10.1590/s0366-69132010000200011.
11. Araujo AS, Silva AO, Souza MJ, Coutinho, AC, Aquino JM, Moura JA, Pedrosa AM. Crystallization of ZSM-12 Zeolite with Different Si/Al Ratio. *Adsorption*. 2005;11(1):591-595. doi.org/10.1007/s10450-005-4909-8.
12. Souza MJ, Silva AO, Pedrosa, AM, Araujo AS. Catalytic properties of HZSM-12 zeolite in the *n*-heptane catalytic cracking. *Reaction Kinetics and Catalysis Letters*. 2005; 84(2): 287-293. .doi.org/10.1007/s11144-005-0221-6.
13. Gopal S, Smirniotis PG. Pt/H-ZSM-12 as a catalyst for the hydroisomerization of C5-C7 *n*-alkanes and simultaneous saturation of benzene. *Applied Catalysis A: General*. 2003;247(1): 113-123. doi.org/10.1016/s0926-860x(03)00096-6.
14. Alaoui OT, Nguyen QT, Rhilalou T. Preparation and characterization of a new TiO<sub>2</sub>/SiO<sub>2</sub> composite catalyst for photocatalytic degradation of indigo carmin. *Environmental Chemistry Letters*. 2009;7(2):175-181. .doi.org/10.1007/s10311-008-0154-1.
15. Huang D, Wang YJ, Cui YC, Luo GS. Direct synthesis of mesoporous TiO<sub>2</sub> and its catalytic performance in DBT oxidative desulfurization. *Microporous and Mesoporous Materials*. 2008; 116(1): 378-385. doi.org/10.1016/j.micromeso.2008.04.031.