

Gasoline Desulphurization by Reactive Adsorption on ZnO /Bentonite

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Desulfurization of atmospheric distillation (DA) gasoline was performed by reactive adsorption on ZnO/bentonite. The adsorbent was characterized by determining the distribution of particle sizes of zinc oxide powdered, adsorption isotherm and textural characteristics of granulated adsorbent. Adsorption experiments of atmospheric distillation gasoline were performed in continuous system at 280-320°C, 5-25 bar and volume hourly space velocities of 1-1.5 h⁻¹. The adsorption on ZnO/bentonite has been favored by increased pressure and operating temperature.

Keywords: reactive adsorption, desulphurization, gasoline, ZnO, sulphur

Crude oil contain both hydrocarbons as well as compounds with sulfur, nitrogen and oxygen. The sulfur contained in crude oil tends to grow as stocks drop and the content in compounds with complex structures such as cyclic aromatic compounds like thiophenes, benzothiophenes, dibenzothiophenes, benzonaphthylthiophenes and dinaphthothiophenes, compounds whose desulfurization is cumbersome.

The decrease of sulfur content involves reducing of productivity and leads to higher consumption of energy. It is known that the usual hydrodesulphurization processes shows some disadvantages, such as the high consumption of hydrogen and the expensive catalysts used. Thus, this process involves the use of supported catalysts [1-4]. The support has the role of improving the main properties of the catalysts: (i) the degree of dispersion of the active phase; (ii) stability to the formation of inactive phases; (iii) stability to the modification by reduction of the oxidic precursors by modification of the interaction between the active phase and the support and (iv) the stability to deactivation by coking. The efficiency of the supported catalysts is closely related to the amount and degree of dispersion of the active phase that can be influenced by the nature and mode of preparation of the support as well as the calcination temperature of the catalytic material [5]. The main disadvantage of the hydrodesulfurization process is generated by the fact that it occurs through a carbocationic mechanism [6,7]. Thus, the presence of acidic centers in the catalyst composition, centers that generate carbocation, favors the formation of coke. This coke is responsible for deactivating the catalysts [8].

In conclusion it is necessary to develop alternative technologies and systems adequate which reduce energy costs in the desulfurization process. One of these alternative desulfurization processes can be the reactive adsorption process [9,10]. The main advantage of this process is the absence of acidic centers in the adsorbent and implicitly the reduction of the risk of coke formation. Adsorbents can also be granulated in the presence of cheap filler materials and allowing the sulfur compounds to reach the reaction centers. Reactivating adsorbents through a controlled oxidation process is another important advantage. Several types of adsorbents, such as zeolites, activated carbon, nickel, copper adsorbents based on noble metals (gold, silver, platinum, palladium), oxides of metals, have been investigated regarding their efficiency in the desulfurization of hydrocarbon liquids.

Although there are many studies which addresses classic refining processes for petroleum products such as hydrodesulfurization, hydrotreatment [11, 12], the number of publications that address the desulfurization by chemical adsorption is relatively low. In this paper we studied obtaining of a adsorbent based ZnO for desulfurization by reactive adsorption to reduce the content of sulfur in gasoline.

Experimental part

Chemicals

The raw materials used in experiments were zinc oxide powders (Sigma-Aldrich), powdered bentonite (Sigma-Aldrich), nitrogen purity from Linde Company and atmospheric distillation (DA) gasoline with a content of 2005 ppm sulfur. The main characteristics of the atmospheric distillation gasoline used in the experiment are shown in [13].

Adsorbent preparation

Zinc oxide particles were prepared by grinding in a Fritsch Pulverisette 6 planetary mill equipped with a stainless steel grinding pot and 10 mm stainless steel balls with a diameter of 20 mm at a mass ratio of ZnO 1/3, grinding time 60 min at 500 rpm. Zinc oxide / bentonite adsorbent granules were obtained by mixing the powdered ZnO with bentonite powder at a mass ratio of 1/3 in a mixer in the presence of water to homogenize to give the necessary consistency for extrusion. The paste was extruded into the extruder manually using a 2 mm diameter nozzle. The wet extrudates were dried at room temperature in air for 24 h and in drying stove at 105 °C for 4 h, the adsorbent being kept in the desiccator until use.

Adsorbent characterization

Adsorbent characterization was performed by determining the particle size of the powdered ZnO and the textural characteristics. The distribution of particle sizes of zinc oxide powder was measured with a particle size measurement by dynamic light scattering (DLS). The instrument used for measuring is a Nano ZS (Red badge). Textural characteristics of the adsorbent (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on Autosorb 1 Quantacrome. Texture data have been obtained by automatic processing of adsorption-desorption isotherms of nitrogen. The specific surface area was calculated using the equation in the linear part of the

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BET desorption isotherm. In order to assess the distribution of pores and the pore size was used desorption branch of isotherms with hysteresis, by applying the BJH method.

The experimental program was performed on fixed bed reactor in isothermal conditions presented in recent scientific papers [13, 14]. Reaction conditions were:

- pressure: 5-25 bar;
- temperature: 280-320°C;
- volume hourly space velocities (VHSV): 1-1.5 h⁻¹;
- nitrogen/ raw material ratio: 400Nm³/m³.

The sulfur content of atmospheric distillation gasoline subjected to the desulphurization process was determined according to the EN ISO 2084: 2004 standard method.

Results and discussions

The distribution of particle sizes of zinc oxide powder grinded is presented in figure 1. It was observed that particles with an average size of 905 nm with narrow particle size distribution were obtained.

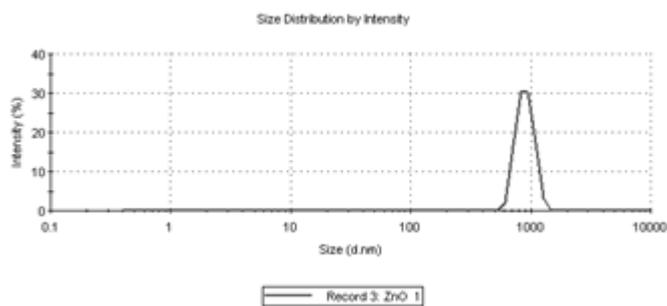


Fig. 1. The size distribution of ZnO particles obtained by milling

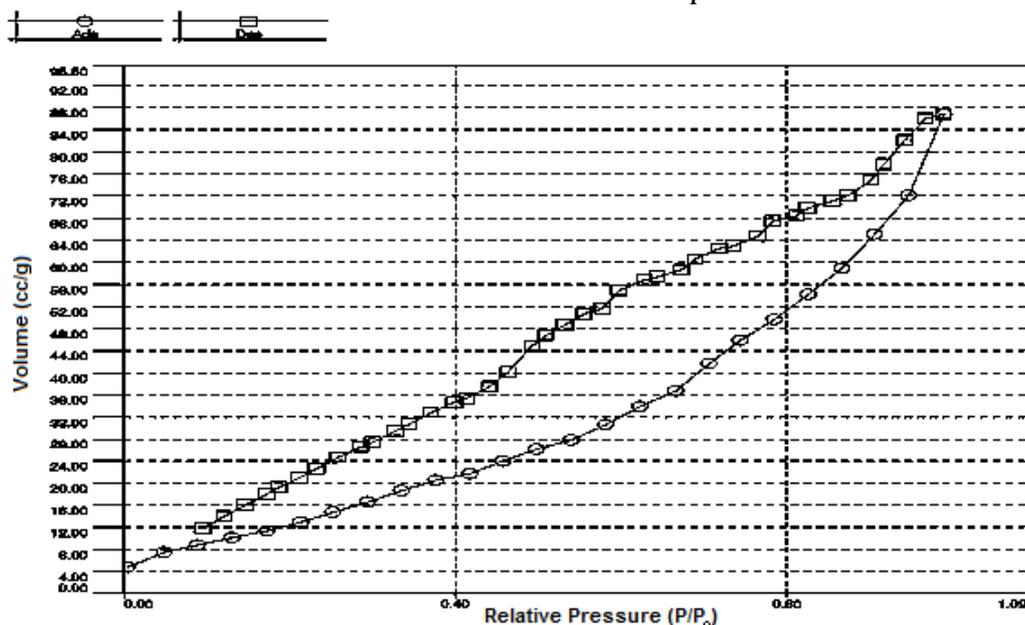


Fig. 2. The isotherm of adsorption-desorption of ZnO / bentonite

Table 1
CHARACTERISTICS OF ZnO-BENTONITE ADSORBENT

Characteristics	Values
Specific surface area, m ² /g	81.300
Pore Volume, cm ³ /g	0.123
Average Pore Diameter, nm	3.847

Isotherms of adsorption-desorption are shown in figure 2. The adsorption isotherm reveals a hysteresis effect on almost the entire range of partial pressure variation, a phenomenon specific to mesoporous structures that favor multilayer adsorption.

Textural characteristics of granulated adsorbent, are presented in table 1. The average pore diameter has values specific to the mesoporous structures and the specific surface has relatively high values, close to those specific to the hydrodesulphurization catalysts.

Figure 3 shows that ZnO/ bentonite adsorbent possesses more maximum pore size of pore and a maximum distribution centered around 38Å.

Figure 4 shows the variation in sulfur content of a DA gasoline with the pressure after desulphurization by reactive adsorption on the ZnO-bentonite adsorbent at a volume hourly space velocities of DA gasoline of 1h-1 for three temperature values of work (280, 300 and 320 °C). It is noticed that the decrease of the sulfur content with the pressure takes place with a slow slope similar for temperature values of 300 and 320° C. At 280° the sulfur content decreases with a pressure increase of between 5 and 15 bar after a slower slope than in the 15-20 bar pressure range.

The variation of the sulfur compounds conversion in DA gasoline with the pressure after desulphurization by reactive adsorption on the ZnO-bentonite adsorbent at a volume hourly space velocities of DA gasoline of 1h-1 for the three temperature values is shown in figure 5. It can be seen that the conversion of sulfur compounds increases with increasing pressure, the increase being more evident at higher temperatures. This positive influence of the pressure on the conversion of the sulfur compounds is

explained by increasing the liquid gasoline fraction with increasing pressure. Consequently, it can be admitted that the reactive adsorption proceeds preferentially in the liquid phase.

The variation in the sulfur content of the DA gasoline with temperature, at two values of the volume hourly space velocities, is shown in figure 6. The decrease of the sulfur concentration with the temperature takes place with a similar slope between 280 and 300°C for the two volume hourly space velocities and steeper between 300 and 320°C at the 1.5 h⁻¹ volume hourly space velocities.

The variation of the conversion of sulfur compounds in DA gasoline with temperature at a pressure of 5 bar is shown in figure 7. It observed an increase of the sulfur

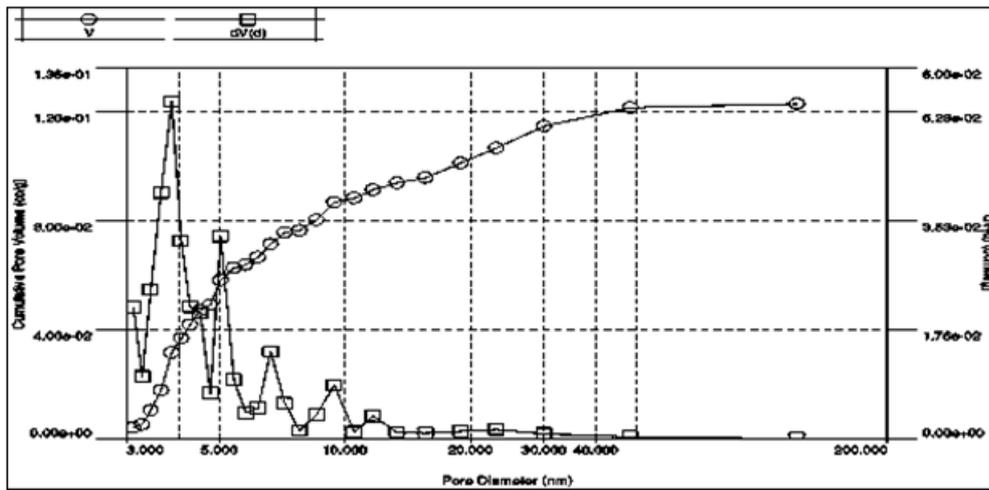


Fig.3. The pore size distribution of the adsorbent ZnO / bentonite by BJH method desorbition

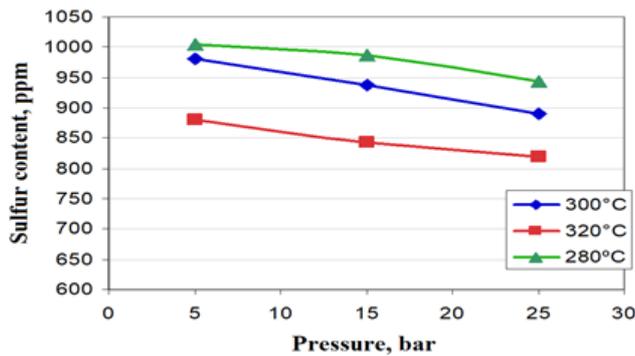


Fig.4. Sulfur content of DA gasoline variation with pressure

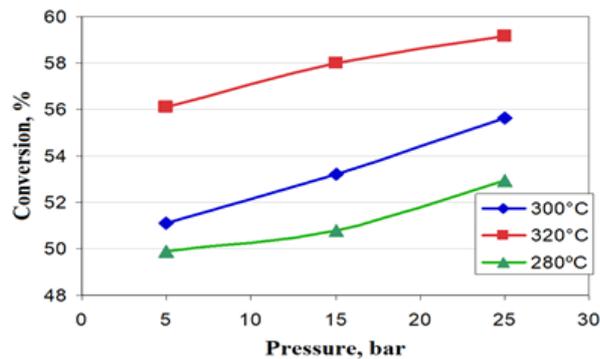


Fig.5. Conversion of sulfur compounds in DA gasoline with pressure

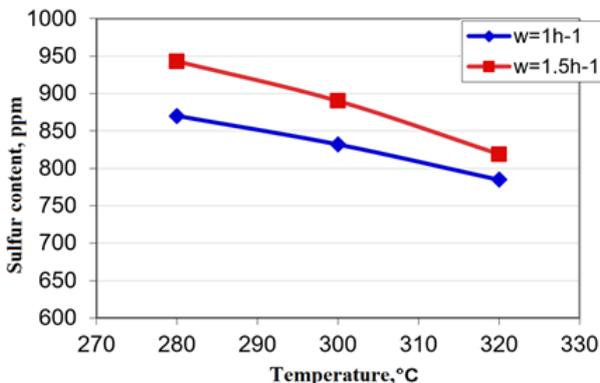


Fig. 6. Variation of sulfur content of DA gasoline with temperature, at a pressure of 5 bar

compounds conversion with temperature by a gradient similar to the curves of lowering the sulfur content with temperature. The increase in conversion is approximately 5% across the temperature range studied for both volume hourly space velocities.

The influence of temperature on the efficiency of the reactive adsorption process of sulfur was studied as well

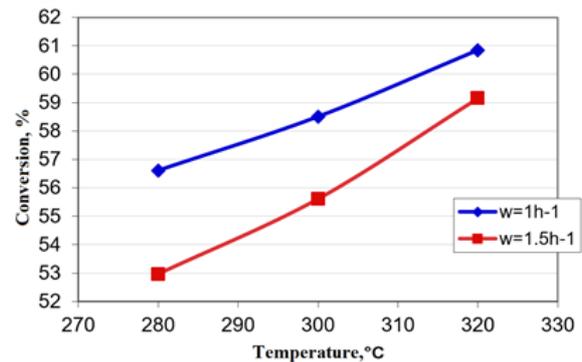


Fig. 7. Conversion of sulfur compounds in DA gasoline with temperature, at a pressure of 5 bar

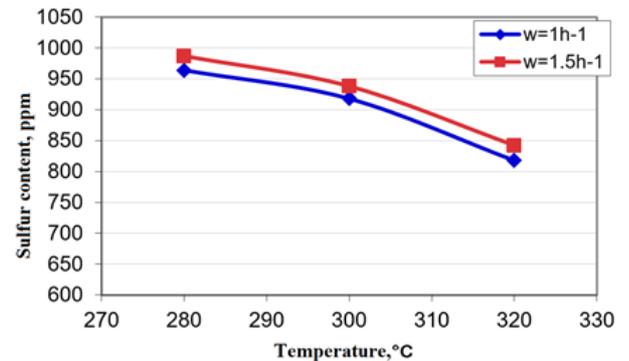


Fig. 8. Variation of sulfur content of DA gasoline with temperature, at a pressure of 15 bar

at a pressure of 15 bar. The sulfur content of gasoline dropped after a similar slope of the variation curve for the two volume hourly space velocities values; at higher temperatures the slope of the variation had higher values (fig. 8).

The variation of the conversion of sulfur compounds in DA gasoline with temperature at a pressure of 15 bar is shown in figure 9. Conversion of sulfur compounds in gasoline increased after a similar slope of the variation curve for the two volume hourly space velocities studied. The variation slope of the conversion with temperature had higher values at higher temperatures, compared to the values obtained at 5 bar. Thus, the conversion rate was approximately seven units for temperature range studied, for both volume hourly space velocities.

The conversion of sulfur compounds decreases with volume hourly space velocities by a similar slope in the range of temperature studied. Thus, the conversion of sulfur compounds had higher values at lower volume hourly space velocities, on the range of pressures and temperatures studied.

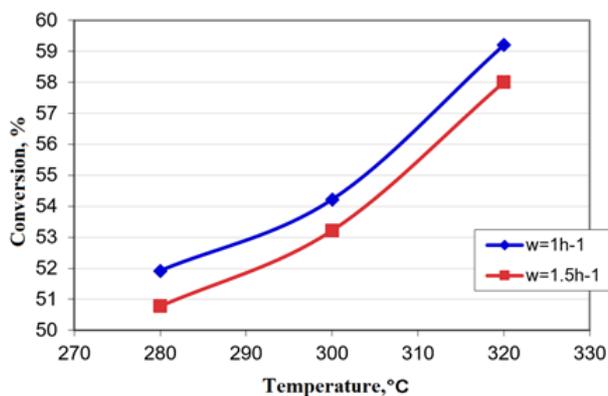


Fig. 9. Conversion of sulfur compounds in DA gasoline with temperature, at a pressure of 15 bar

Conclusions

Zinc oxide granulated with bentonite is an effective adsorbent for desulphurization of atmospheric distillation gasoline. The adsorbent was characterized by determining the distribution of particle sizes of zinc oxide powdered, adsorption isotherm and textural characteristics of granulated adsorbent. The distribution of particle sizes of zinc oxide particles grinded is narrow, with an average size of 905 nm. The adsorption isotherm reveals a hysteresis effect on almost the entire range of partial pressure variation, a phenomenon specific to mesoporous structures that favor multilayer adsorption. Textural characteristics of granulated adsorbent highlights a porous structure with average pore diameter specific to the mesoporous structures and the specific surface close to those specific to the hydrodesulphurization catalysts.

Adsorption experiments of atmospheric distillation gasoline were performed in continuous system at 280...320°C, 5-25 bar and volume hourly space velocities of 1-1.5 h⁻¹. The reactive adsorption of sulfur compounds of atmospheric distillation gasoline proceeds preferentially

in the liquid phase. Thus, the conversion of sulfur compounds increases with increasing pressure, the increase being more evident at higher temperatures. Conversion of sulfur compounds in gasoline increased with increasing temperature both at low pressures (5 bar) and at higher pressures (15 bar). The conversion of sulfur compounds decreases with volume hourly space velocities by a similar slope in the range of temperature studied.

References

1. ALI, A. S., AHMED, S., AHMED, W. K., AL-SALEH, A. M., *Fuel Process. Technol.*, **98**, 2012, p. 39;
2. VAZQUEZ-SALAS, P.J., HUIRACHE-ACUNA, R., ZEPEDA, T.A., ALONSO-NUNEZ, G., MAYA-YESCAS, R., MOTA, N., PAWELEC, B., *Catal. Today*, **305**, no.2, 2018, p. 65;
3. HAJI, S., ZHANG, Y., KANG, D., AINDOW, M., ERKEY, C., *Catal. Today*, **99**, 2005, p. 365;
4. PETZOLD, F.G., JASINSKI, J., CLARK, E., L., KIM, J., H., ABSHERA, J., TOUFAR, H., SUNKARA, M., K., *Catal. Today*, **198**, 2012, p.219;
5. KRALEVA, E., SPOJAKINA, A., SALADINO, M.L., CAPONETTI, E., JIRATOVA, K., *J. Alloys Compd.*, **513**, 2012, p. 310;
6. BATAILLE, F., LEMBERTON, J., L., MICHAUD, P., PE´ROT, G., VRINAT, M., LEMAIRE, M., SCHULZ, E., BREYSSE, M., KASZTELAN, S., *J. Catal.*, **191**, 2000, p.409;
7. LECRENAY, E., SAKANISHI, K., MOCHIDA, I., *Catal. Today*, **39**, 1997, p.13;
8. PRAJAPATI, R., KOHLI, K., MAITY, S.K., GARG, M.O., *Fuel*, **203**, 2017, p. 514;
9. SALEM, A., B., S., H., *Ind. Eng. Chem. Res.*, **33**, 1994, p.336;
10. SALEM, A., B., S., H., *Chem. Eng. Technol.*, **20**, 1997, p.342;
11. SAHU, R., JINSONG, B., SUNIM, J., PYOJEON, Y., WEELEE, C., *J. Ind. Eng. Chem.*, **27**, 2015, p. 12;
12. BABICH, I.V., MOULJN, J.A., *Fuel*, **82**, 2003, p. 607;
13. ION, C. S., BOMBOS, M., VASILIEVICI, G., BOMBOS, D., *Rev. Chim. (Bucharest)*, **68** no. 3, 2017, p.483;
14. ION, C. S., BOMBOS, M., VASILIEVICI, G., PANAITESCU, C., DRAGOMIR, R., *Rev. Chim. (Bucharest)*, **68**, no. 4, 2017, p.732.

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