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A study on sulfur reduction in FCC gasoline using Zn–Mg–Al spinels

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Abstract

It has been previously demonstrated that zinc aluminates are useful additive materials for gasoline sulfur reduction. To enquire about the nature of the catalyst active site in Zn aluminates, in the present work, $[Zn_{(x)}{}^{2+}Mg_{(1-x)}{}^{2+}]Al_2O_4$, ternary spinels with $0 \leq x \leq 1$ were synthesized to obtain samples with different Lewis acidity. The Zn–Mg–Al spinels were tested as FCC sulfur reduction additives, using the elimination of sulfur from thiophene at 793 K as model test. The thiophene conversion with the Zn–Al spinel was higher than with ternary Zn–Mg–Al spinels or the commercial cracking catalyst. It was found that although to a small extent, the Zn-free Mg–Al spinel converted thiophene. The IR study on the adsorption of CO_2 over Zn–Mg–Al spinels with different amounts of Zn and over ZnO suggested that: (i) no strong Lewis sites are located on Zn and (ii) the Lewis acidity of the ternary spinels is due to aluminum sites and increases with the Zn content. So, it appears that the Lewis acid sites located on aluminum are responsible for the adsorption of thiophene and that one of the benefits of Zn incorporation is the increase of this acidity, which would lead to increased adsorption and reactivity.

Keywords: Gasoline FCC sulfur reduction additives; Zn; Acid Lewis sites

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1. Introduction

The refining industry is facing the problem of processing greater proportion of heavy petroleum and at the same time adjusting the specification of transport fuels to more and more strict environmental regulations. For example, by 2006 sulfur in gasoline must reach between 30 and 50 ppm of sulfur [1,2].

Of the total gasoline production volume approximately a third comes from the FCC process, which contributes with about 90% of the total sulfur content in the gasoline pool. It is therefore necessary to reduce the sulfur content in this stream. Several alternatives have been identified, among them; FCC feed hydrotreatment and gasoline hydrodesulfurization [3,4]. The first process implies high capital and operation costs, and the second one decreases the octane number due to the saturation of the olefins [5]. From an economical point of view, it would be interesting to remove the sulfur inside the FCC unit using a sulfur reduction additive. This alternative is attractive because it does not require an additional process and the capital costs would be low compared to the other alternatives.

Although the commercial cracking catalyst can convert some of the sulfur containing molecules, a great part of the thiophenic compounds remain untransformed. To explain how sulfur reduction additives work Wormsbecher and Kim [6,7] proposed the following scheme: (a) sulfur containing species such as thiophene, tetrahydrothiophene or alkylthiophenes are adsorbed by the additive; (b) the second step presents two possibilities—in the first, the adsorbed sulfur species remains in the additive surface until it is oxidized in

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the regeneration unit, and then is released as SO_x; the second one is the cracking of the organic sulfur compound inside the raiser to form H_2S and an organic molecule. However, in Wormsbecher proposal the localization of the cracking sites in Zn-aluminate was not disclosed. Taking into account the Lewis basic character of thiophenic compounds, sulfur reduction additives must have acidic nature. Wormsbecher and Kim [6,7] tested Ni, Cu, Zn and Ag aluminates. The results showed that Zn/Al_2O_3 mixed with 10% wt. of a commercial cracking catalyst reduced significantly the sulfur content in the gasoline showing the important role of Zn in this kind of reactions.

Andersson et al. [8] tested different materials as additives in the sulfur reduction of FCC gasoline. Of the synthesized materials the activity towards sulfur removal followed the order: Zn/hydrotalcite (Zn/HT) > Zr/alumina > Zn/titania > Mn/alumina.

Shan et al. [9] used Zn/Al_2O_3 as additive mixed with 10% weight with zeolite USY. They proposed that Zn/Al_2O_3 provides the Lewis acid sites that can selectively adsorb sulfides, while the zeolite provides the cracking sites. The results showed that sulfur content was reduced remarkably and that the material has excellent selectivity towards sulfur compounds cracking. Regarding the effect of the cracking catalysts acid sites in sulfur compounds removal Corma et al. [10] presented a study of the reaction mechanism.

According to the above studies Zn-containing materials provide good activity for sulfur elimination in gasoline. The present work has the goal enquire on the role of Zn in Zn–Al spinels used as additives for sulfur elimination in FCC. To achieve this aim, ternary Zn–Mg–Al spinels with the incremental substitution of Zn by Mg were prepared. In this way, the Lewis acidity of the material was decreased in a controlled manner. The synthesized materials were evaluated as FCC sulfur reduction additives using the transformation of thiophene as model reaction. No attempt was made to study other important factors that affect the performance of sulfur removal additives in FCC processes like hydrogen transfer reactions, feed composition, type of FCC catalyst used and reactivity of the different sulfur compounds present in the feed [11,12].

2. Experimental

2.1. Synthesis of additives

The general formula for a spinel is $M^{II}Al_2O_4$, consequently for a ternary Zn–Mg–Al spinel, the formula will be $[Zn_{(x)}{}^{2+}Mg_{(1-x)}{}^{2+}]Al_2O_4$, where x, the molar fraction of zinc, was varied between 0 and 1. In the synthesis, the Zn^{2+}/Mg^{2+} metal ratio was changed keeping the total number of moles for M^{II} in the materials constant, maintaining the stoichiometry of the spinel. The materials will be named $S(X,Y)$ where X and Y are the zinc and magnesium molar content, respectively. The spinel precursor was synthesized by precipitation at constant temperature and pH. The method used here followed the synthesis reported by Kustova et al. [13], Li et al. [14] and Sreekumar et al. [15]. A solution of magnesium, zinc and aluminum nitrates with the required concentrations was added dropwise to an ammonium carbonate aqueous solution at 50 °C. After the precipitation was completed, the slurry was kept under vigorous agitation for 24 h. Later, the slurry was filtered in vacuum and washed with de-ionized water and ethanol (analytical degree, J.T. Baker). The precipitate was dried at 100 °C during 24 h and calcined at 850 °C during 4 h. The reagents used for precursor synthesis were $Mg(NO_3)_2\cdot 6H_2O$ (99% purity, J.T. Baker), $Zn(NO_3)_2\cdot 6H_2O$ (99% purity, Merk), $Al(NO_3)_3\cdot 9H_2O$ (99.7% purity, J.T. Baker), $(NH_4)_2CO_3$ (analytical, Mallinckrodt) and NH_4OH (30%, J.T. Baker). The different synthesized materials with their molar content of zinc, magnesium and aluminum are displayed in Table 1.

Table 1
Molar content of metals and pH of synthesis for the synthesized spinels

Additive	Molar content			pH of synthesis
	Zn	Mg	Al	
S(1,0)	1	0	2	7.5
S(2/3,1/3)	0.667	0.333	2	7.5
S(1/2,1/2)	0.5	0.5	2	7.5
S(1/3,2/3)	0.333	0.667	2	8.5
S(0,1)	0	1	2	9.5

2.2. Characterization

The synthesized materials were identified by X-ray diffraction (XRD), and characterized by specific area and CO_2 adsorption analyzed by infrared spectroscopy (FT-IR) to determine the acidity of the materials.

The X-ray diffraction was made on a Siemens D-500 diffractometer using monochromatic Cu Kα radiation ($\lambda = 1.5409$ Å). Crystal phases were identified using ASTM card files.

The IR spectra were obtained on a 510 FT-IR Nicolet spectrometer, in the 1000–4000 cm^{-1} infrared region with a resolution of 2 cm^{-1} and 500 scans. Self supporting sample wafers (0.04 g) were placed in a specially designed quartz cell with calcium fluoride (CaF_2) windows. The sample pretreatment consisted of slow warming up to 923 K on vacuum, and maintaining at this temperature for 3 h. After pretreatment the samples were allowed to reach room temperature and a spectrum was taken. Then a CO_2 pulse (40 mmHg) was introduced and a new spectrum was taken. Finally, high vacuum was applied during 2.5 h to eliminate the CO_2, and another spectrum was obtained.

The measurements of specific area were made by N_2 physisorption and the BET method with a Micromeritics ASAP 2000 equipment.

Table 2
Properties of the commercial equilibrium catalyst used as reference

Property	Value
Re_2O_3 (w%)	1.55
Al_2O_3 (w%)	32.3
Total specific area (m^2/g)	148
Zeolite (m^2/g)	110
Matriz (m^2/g)	38
Zeolite/matriz ratio (Z/M)	2.89
Pore volume (cc/g)	0.193
V (ppm)	1480
Ni (ppm)	378
Na (ppm)	3300

2.3. Activity test

The FCC unit operates at 793–823 K in a reducing atmosphere, to simulate this; the catalytic tests were performed in a spouting bed microreactor, working in differential mode at 793 K, the reaction rates were evaluated accordingly. The reactor is equipped with online gas chromatography analysis (Hewlett Packard 5890 series II, FID detector) for reactants and products analysis.

The experimental reaction procedure was as follows. (a) Prior to the activity test, the additive was heated for cleaning purposes in N_2 flow (20 ml/min) to the reaction temperature (793 K) using a heating rate of 10 °C/min. (b) The additive was stabilized in N_2 flow at the same temperature for 2 h. (c) The gas flow was changed to the gas mixture (thiophene (3.5 mol%)/H_2) to initiate the reaction. The specific rate for thiophene conversion was evaluated at initial time and after stabilization (approximately, 19 h at reaction temperature). One additional test was made with a commercial equilibrium cracking catalysts as reference, the properties of this cracking catalysts are shown in Table 2.

Using mass spectroscopy and gas chromatography, the following compounds were identified at the outlet of the reactor: thiophene, H_2S, 1-butene, *cis* and *trans* 2-butene, 1 propene, propane, methane and in small quantities: 1 butine, 1,2-butadiene and 2 methyl-1 propene.

3. Results and discussion

3.1. Characterizations

X-ray diffractograms of Zn–Mg–Al spinels can be observed in Fig. 1. The XRD diffractogram for γ-alumina was also included (Fig. 1a) as reference. The synthesized materials are shown in Fig. 1b, sample *S*(0,1) displays main reflections at 36.85°, 44.83° and 65.23°, which correspond with the most intense reflections of the magnesium spinel ($MgAl_2O_4$) the planes (3 1 1), (4 0 0) and (4 4 0), respectively, identified by the ASTM 21-1152 card.

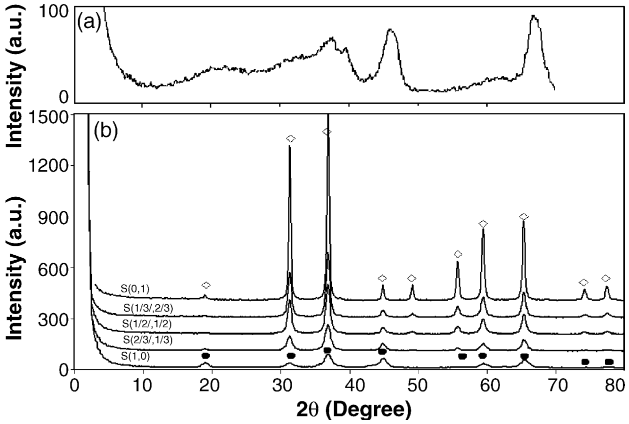

Fig. 1. Diffractograms for alumina and the synthesized spinels: (a) γ-alumina; (b) synthesized spinels and its characteristic reflections for: (●) Mg spinel, (◇) gahnite, Zn spinel.

For the Zn–Al spinel, *S*(1,0) sample, the main reflections in decreasing intensity order are located in 36.83°, 31.26° and 65.23°, respectively; these contributions correspond with the planes (3 1 1), (2 2 0) and (4 4 0) of the ASTM 05-0669 card which identify gahnite ($ZnAl_2O_4$). Additionally, the relative intensities of the sample peaks correspond well with those reported in the reference card, so the synthesized material can be ascribed as gahnite.

It is should be mentioned that the reflections that identify magnesium spinel and gahnite are very similar; nevertheless, the reflection with the second higher intensity peak is different in each case. This fact allows differentiating between the two compounds. For the ternary spinels, Zn–Mg–Al, named as *S*(2/3,1/3), *S*(1/2,1/2) and *S*(1/3,2/3), it is observed that intensity of the peak located at 31.26° increases with the Zn content. This same effect is observed with the (3 3 1) plane located at 49.06°. In the *S*(1/2,1/2) spinel, all the planes corresponding to gahnite are present. This indicates that in the synthesized materials zinc is present in a spinel structure, although it is not possible to assure if the three metals (Zn, Mg and Al) are present in the same crystalline network.

The specific area of the synthesized Zn–Mg–Al spinels decreased with Zn content from 140 for the *S*(0,1) to 50 m^2/g for the *S*(1,0), see Table 3.

Table 3
Specific area of additives (m^2/g) and specific reaction rate (thiophene mol g^{-1} s^{-1}) results, for initial time and 19 h of reaction

Additive	Specific area (m^2/g)	Specific reaction rate ($\times10^6$)	
		Initial *t*	*t* = 19 h
S(1,0)	22.7	3.57	1.64
S(2/3,1/3)	63.8	2.65	2.07
S(1/2,1/2)	91.9	2.63	2.20
S(1/3,2/3)	125.9	1.74	1.75
S(0,1)	173.1	1.43	1.29
Cat. FCC		2.74	1.79

3.2. Evaluation of additives

Thiophenes are sulfur compounds difficult to eliminate in the FCC process. For this reason, the transformation of thiophene (see below) was used as test reaction.

$$\text{thiophene} \xrightarrow[\text{Additive}]{H_2,\, 520\,^{\circ}\text{C}} \text{HC} + H_2S$$

1-Butene, *cis* and *trans* 2-butene, 1-propene, propane and methane and in small quantities of 1-butine, 1,2-butadiene and 2-methyl-1-propene were identified in the outlet reactor stream. A reaction test with empty reactor showed no thiophene conversion, indicating the absence of thermal cracking.

Initially, the additives present a period of deactivation but after operating 19 h all arrive at a stable conversion. To analyze the possibility that deactivation was the result of ZnS formation as occurs in the sulfur traps, X-ray diffraction analysis made. The diffractograms of samples after deactivation did not show any type of metallic sulfide, and the phases identified corresponded to $ZnAl_2O_4$ and $MgAl_2O_4$ spinels, indicating that deactivation was due to some other reason like a very strong adsorption of the sulfur compound on the Lewis acid site of the additive or coke formation on the additive surface. Nevertheless, it must be considered that for FCC applications the important activity is the initial activity because of the low residence time in the raiser, a few seconds.

In Fig. 2, it is observed that the initial specific reaction rate increases with the zinc content in the spinel. These results indicate that the presence of zinc increases the removal of sulfur, being the zinc spinel additive, *S*(1,0), the one with the highest activity. Since this additive was the one with the smallest surface area, then there is no direct correlation between the specific area and the ability for sulfur removal.

Wormsbecher and Kim [6] proposed that Lewis acid sites on the additive adsorb sulfur compounds and subsequently cracking reactions take place. Similarly, Shan et al. [9] proposed that in the system USY zeolite-additive the zeolite provides the cracking site to enhance activity. Both authors mix their additive with a cracking catalyst and therefore it is difficult to explain from their experiments if these cracking sites responsible for C–S bond cleavage are located on the additive, over the cracking catalyst or over both. Our results indicate that the additive by itself has a significant cracking activity. In fact, the activity of *S*(1,0) was 35% superior to the one presented by the commercial cracking catalyst (see Table 3).

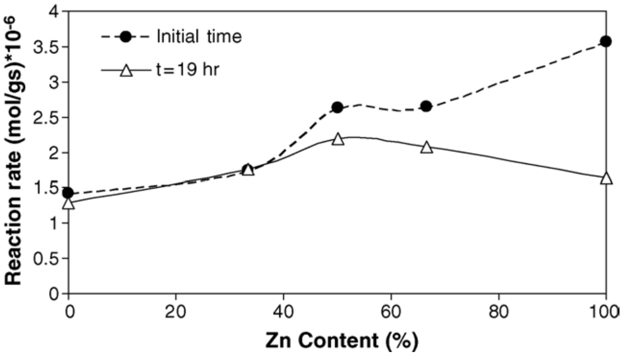

Fig. 2. Activities for thiophene conversion versus zinc content in the synthesized additives, at initial and 19 h of reaction time.

If the active sites (Lewis acid sites) were related to zinc, the *S*(0,1) a Mg spinel would not present any thiophene conversion since it does not contain zinc; however, it has some activity. The Lewis acid sites in this material are however related to aluminum, which indicates that over these sites the conversion of the thiophene molecules can take place. Moreover, it has been identified that alumina has a small activity in sulfur compounds conversion [17]. This suggests the possibility that aluminum participates in the active site. To explore this possibility the initial reaction rates were referred to the molar content of both Zn and Al and the trends of these reaction rates were analyzed, these calculations appear in Table 4. The intrinsic rates referred to zinc decrease with the Zn content. In contrast, the rates of thiophene conversion referred to aluminum increase despite that the amount of aluminum present in the additives was constant. This result indicates that if the reaction takes place on the aluminum sites, they become more active as the amount of Zn in the spinel increases.

To enquire more about the location and nature of the reaction active sites infrared spectroscopy of adsorbed CO_2 was made.

3.3. FT-IR spectroscopy: adsorption of CO_2

At ambient temperature the adsorption of CO_2 onto oxidic solid leads to two different types of interactions: (i) carbonates and (ii) CO_2 linear species, which arise from the interaction of CO_2 with uncoordinated superficial cations (Lewis acid sites), showing two IR bands in the 2400–2300 cm^{-1} [16]. We used this band to identify the different Lewis acid sites in the additives. Also as reference, CO_2 adsorptions over ZnO and Al_2O_3 were made. The spectrum of CO_2 adsorbed on ZnO (Fig. 3a) shows that no CO_2 is adsorbed on this sample, indicating the absence of Lewis acid sites strong enough to adsorb CO_2 in ZnO.

Table 4
Intrinsic reaction rate referred to Zn or Al (mol of thiophene/(mol of metal s)) in the stable conditions

Additive	Intrinsic rate ($\times 10^4$)	
	Zn	Al
S(1,0)	6.54	3.27
S(2/3,1/3)	6.74	2.25
S(1/2,1/2)	8.56	2.14
S(1/3,2/3)	8.15	1.36
S(0,1)		1.01

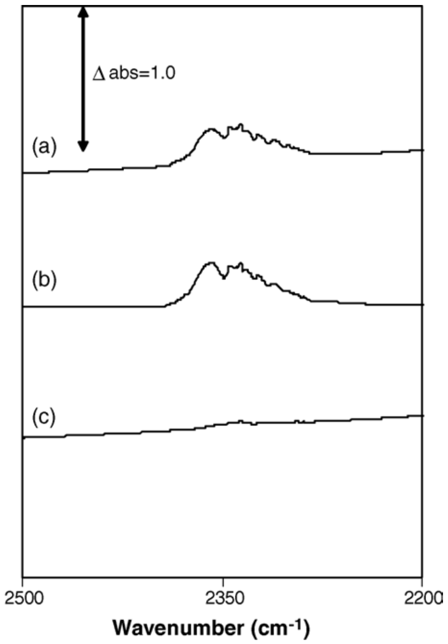

Fig. 3. FT-IR spectra for: (a) CO_2 pulse on ZnO, (b) CO_2 Pulse in the empty cell, (c) difference between the spectra a and b.

For CO_2 adsorbed on alumina (Fig. 4) two bands appear at 2345 and 2360 cm^{-1}. According with Morterra and Magnacca [16] these bands correspond to CO_2 adsorbed on sites associated to octahedral ($Al^{VI}{}_{CUS}$) and tetrahedral ($Al^{IV}{}_{CUS}$) aluminum, respectively. The spectra for the Zn–Mg–Al spinels appear in Fig. 5. Bands in the same positions as for alumina were observed in all the spinels showing that the Lewis acid sites present on the ternary additives correspond essentially to aluminum. An interesting feature in Fig. 5 is that the intensity of the bands increases with the amount of zinc in spite that the surface area decreases with the zinc content. This would mean that there are some weak Lewis acid sites which in the absence of Zn do not adsorb CO_2 but when Zn is present in the spinel structure the strength of these sites increases allowing them to adsorb CO_2 and be detected. The explanation for this phenomenon can be based on the Pauling electronegativity for zinc (1.65) [18] which is a little higher than for aluminum (1.61) [18]. Hence, Zn withdraws electronic charge from the nearest Al. Magnesium, with an electronegativity of (1.31) [18], plays the inverse role causing a decrease in the acidity of the aluminum sites and leading therefore to a decrease in the thiophene transformation activity. These results suggest that the active Lewis site involved in the adsorption of a Lewis base like thiophene is associated to aluminum and that the acidity of this site can be enhanced by Zn and decreased by Mg. This agrees well with the highest activity displayed by the Zn–Al spinel.

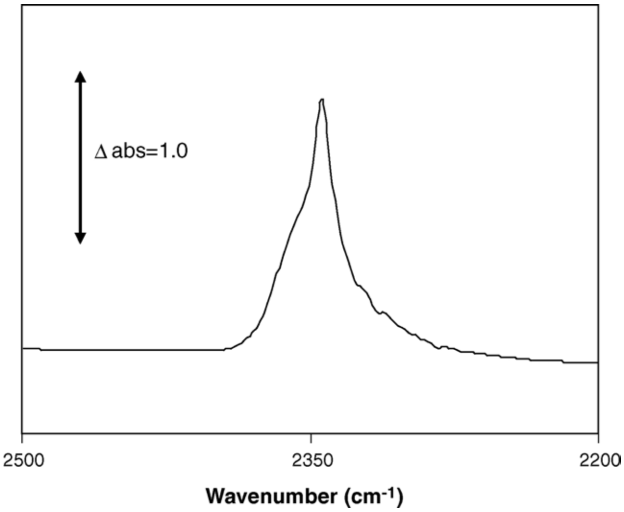

Fig. 4. FT-IR spectrum after CO_2 adsorption for Al_2O_3, in the CO_2 linear species region.

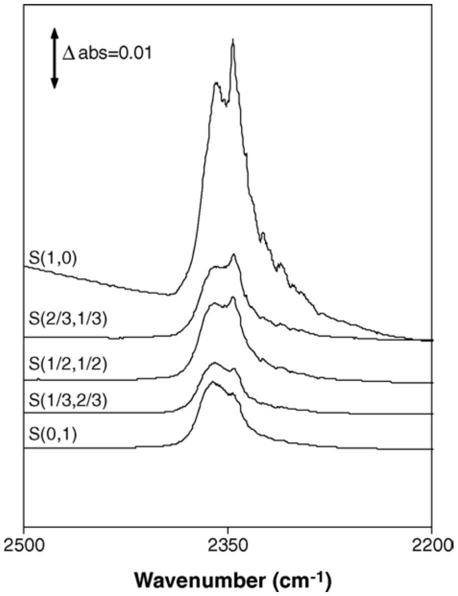

Fig. 5. FT-IR spectra for the synthesized spinel after CO_2 adsorption, in the 2200–2500 cm^{-1} region.

4. Conclusions

In the present study, Zn–Al and ternary Zn–Mg–Al spinels were synthesized and characterized to analyze about the nature of the catalyst active site in Zn aluminates used as additives for sulfur removal in FCC. The reaction results at short reaction times and at temperature conditions similar to those in FCC indicate that the binary zinc spinel is more active in thiophene conversion than any of the Zn–Mg–Al synthesized additives or the commercial cracking catalyst. For Zn–Mg–Al spinels, the activity for thiophene conversion increases with Zn content.

On the other hand, the IR study of CO_2 adsorption over ZnO suggests that no Lewis acid sites strong enough are located on Zn; while the same IR study over Zn–Mg–Al spinels with different amounts of Zn, reveals that Lewis acidity is due to aluminum sites but that it increases with Zn content. So, it appears that the Lewis acid sites located on aluminum are responsible for the adsorption of thiophene but that it is the presence of Zn that renders these sites active enough to perform sulfur removal.

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