TG and DTA investigation of ZrO_2–SO_4^{2-} catalysts exposed to hexane, methylcyclopentane and cyclohexane

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ZrO_2–SO_4^{2-} catalysts with different sulfur contents were analysed with thermal methods coupled with mass spectrometry after exposure to mixtures of hexane, methylcyclopentane, and cyclohexane in argon. The reaction of the hydrocarbons led to carbonaceous deposits, but an important part of hydrocarbon remained chemisorbed as well. Heating these samples in He atmosphere provoked the decomposition of these deposits with evolution of CO_2 and CO, and also of SO_2 and SO. At the same time, COS was evidenced in the reaction products. The release of these molecules occurred below the activation temperature of the catalysts. The behavior of the catalysts depended both on reactant molecule and sulfur content. The analyses clearly evidenced the oxidation ability of ZrO_2–SO_4^{2-} catalysts.

Keywords: sulfated zirconia, hexane, methylcyclopentane, cyclohexane, TG–DTA, deactivation

1. Introduction

An intense research activity has been focused in the last ten years on sulfated zirconia catalysts in relation with two important catalytic processes: isomerization of butane to isobutane, extensively used in the production of oxygenates and alkylates as additives to the new carburants, and isomerization of paraffins with more than five carbon atoms for reformulated gasolines.

One of the problems of concern in the research on sulfated zirconia catalysts is the nature of the active sites and the mechanism involved in the activation of molecules as stable as low alkanes. Lewis acid sites, assumed at the beginning to be superacidic, were considered to be mainly responsible for this reaction [1–4]. The promotion of sulfated zirconia with iron and manganese was assumed by Cheung et al. [5] to consist of a supplementary increase of the acidity of sulfated zirconia.

Thermal methods were largely utilised in these studies. Lin and Hsu [6] evidenced in temperature-programmed desorption (TPD) profiles of benzene on non-promoted and on iron- and manganese-promoted sulfated zirconias, a peak at around 560 °C which was assigned to benzene strongly held on the superacid sites. Nascimento et al. [7] using infrared spectroscopy stressed the importance of the Brønsted to Lewis acid ratio of these catalysts, without considering these catalysts as superacid solids. A different viewpoint was adopted by other groups also using thermal methods. Farcasiu and collaborators [8–10] based on TPD of benzene and pyridine proposed that (i) the key point in the behavior of these catalysts is their oxidising ability, promoters such as iron and manganese modifying the one-electron acceptor ability of the sulfated zirconia, and (ii) deactivation of sulfated zirconia could be principally ascribed to coke deposition and to the loss of the oxidation ability as a result of the reduction of sulfur species. Keogh et al. [11] and Srinivasan et al. [12,13] investigated the interaction of benzene and pyridine with these catalysts by differential thermal analysis and also found that their oxidising function plays an important role. Other TPD studies reported by Davies and collaborators [14,15] proposed a “three-site” model for these catalysts. The first site results from air activation of the catalysts and consists of an oxy species; the second site is present in metal-promoted sulfated zirconia and is associated with those species in their reduced state, whereas the third one is a Brønsted or a Lewis acid site. In such a way, different active species can be generated according to the pretreatment conditions and catalyst composition. Other arguments supporting this model were provided by Dicko et al. [16] and Sayari et al. [17]. Dumesic and co-workers [18–20] concluded from kinetic and microcalorimetric measurements that (i) the acidic properties of sulfated zirconias are not stronger than those of acidic zeolites, and (ii) deactivation of the catalysts occurs in several steps, which constitutes an additional indication in favor of the multi-site model.

In the present study, sulfated zirconia catalysts with different sulfur contents exposed to hexane, methylcyclopentane, and cyclohexane have been investigated by thermogravimetric (TG), differential thermogravimetric (DTG), and heat flow (HF) analyses in order to provide additional information on the redox properties of these catalysts.

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Table 1
Surfur content of the investigated ZrO_2–SO_4 catalysts.

Catalyst	SO_4 (wt%)
#I	25.8
#II	19.3
#III	18.2
#IV	12.3
#V	8.6
#VI	8.0
#VII	7.1

2. Experimental

Samples #I–III were prepared via the colloidal sol–gel technique using $ZrOCl_2$ as precursor and sulfuric acid as peptising agent. Samples #IV–VII were prepared by impregnation with sulfuric acid of ZrO_2 samples obtained via precipitation of $ZeOCl_2$ with NH_3. The characteristics of the investigated catalysts are given in table 1. After activation at 550 °C in air, the catalysts were exposed at 140 °C for 40 min to a 15% (vol/vol) hydrocarbon/Ar mixture, at a space velocity 20 h^{-1}. The reactions were carried out in a fixed-bed quartz microreactor, using hexane, methylcyclopentane, and cyclohexane (Aldrich) as reactants. After 40 min, the samples were cooled in flowing Ar (50 $ml\,min^{-1}$). Non-activated samples as well as catalysts exposed to the hydrocarbons were submitted to TG, DTG and HF analyses. The measurements were carried out using a SETARAM 92 16.18 equipment one-line coupled with a quadrupole QMG 311 spectrometer (MS) from Balzers, scanning the masses between 28 and 96. Prior to the analyses, the samples were purged in flowing He at 50 °C until the MS signal due to hydrocarbons was no longer detected. The MS was connected to the TG–DTG–HF unit with a teflon tubing kept at 150 °C in order to avoid eventual condensation. The runs were conducted in a stream of helium (99.99% purity, from Belgair). The reactant-loaded samples (typically 75 mg) were heated from ambient temperature to 780 °C at a heating rate of 10 $^{\circ}C\,min^{-1}$, with a plateau of 30 min at the final temperature, and then cooled at 50 °C. Soon after, the thermal cycle was repeated, and the data of the second cycle were automatically subtracted from the first cycle data using the apparatus routine programme. Both cycles were carried out in flowing helium (200 $ml\,min^{-1}$). Platinum pans were used as sample holders, and Al_2O_3 was the reference material. A third cycle was also carried out soon after the samples were again cooled at 50 °C in flowing a 10% air/He mixture (Belgair) instead of He, with on-line MS analysis of the evolved gases.

3. Results

3.1. Fresh catalysts

Fresh catalysts dried for 10 h at 110 °C exhibit typical TG–DTG–HF curves for such materials. A weight loss occurred for temperatures higher than 630 °C and, in this step, only SO_2 was released. The weight loss was dependent on the sulfur content of the catalysts.

3.2. Reaction with hexane

Figure 1(a) shows the typical TG–DTH–HF curves recorded for the catalyst #II previously exposed to hexane. The corresponding MS curves are shown in figure 1(b).

The DTG curves exhibited a first weight loss with a minimum at about 210 °C corresponding to the release of hexane as established by MS. As this peak appears at nearly the same temperature for all the catalysts, it is inferred that the adsorption strength is independent of the sulfur content and, in addition, the chemisorption of hexane is not very strong. As the amount of hexane desorbed depends on the sulfur content, sulfate groups probably act as chemisorption sites (figure 2(a)). Note that the MS curves of hexane versus temperature (figure 1(b)) differ from those of Wan et al. [15] for benzene and alkylaromatic hydrocarbons. Hexane is majoritary desorbed below 300 °C, whereas for the alkylaromatic hydrocarbons, only a slight desorption peak was observed near 700 °C. This behavior is obviously related to hydrocarbon–catalyst interactions.

A second DTG peak appeared at temperatures between 300 and 350 °C according to the sulfur content. Samples #V–VII with lower sulfur contents exhibited a weight loss at around 300 °C, while for those with more sulfur (#I–III), this loss occurred in the range 317–345 °C (figure 2(a)). The temperature–sulfur-content dependency was not accidental, because at this step, part of sulfur was released. Up to now, all the TPD studies using aromatic molecules [12,13,15] or isopropylamine [15] so far mentioned the presence of SO, SO_2, and SO_3 in the gaseous effluent. In addition to these species, CO and COS (m/z 28 and 60) were also found (figure 1(b)). It should be noted that, in this temperature range, the catalysts previously exposed to hexane behaved more like those exposed to benzene [12,13,15] than catalysts having chemisorbed alkylaromatics [15] in the sense that SO_2 release occurred at rather low temperatures. Simultaneous to SO_2 liberation, COS and CO_2 were also released.

The main part of the desorption occurred at temperatures above 450 °C with, again, a dependency of DTG peak position on sulfur content. For the samples with high sulfur content, the desorption peak was located at relatively lower temperature (near 500 °C for #I, and at around 523 °C for #III) than for those with less sulfur (near 550 °C). In an almost concomitant release, SO_2, SO, COS, CO, O_2, and CO_2 were found in the gaseous effluent. The shape of the MS COS curves (figure 1(b)) seems to correlate with SO_2 and CO release, whereas the MS CO_2 curve exhibits several peaks, possibly due to different species requiring different temperatures for total oxidation. Also, a clear proportionality exists between the area of MS CO_2 peaks and the

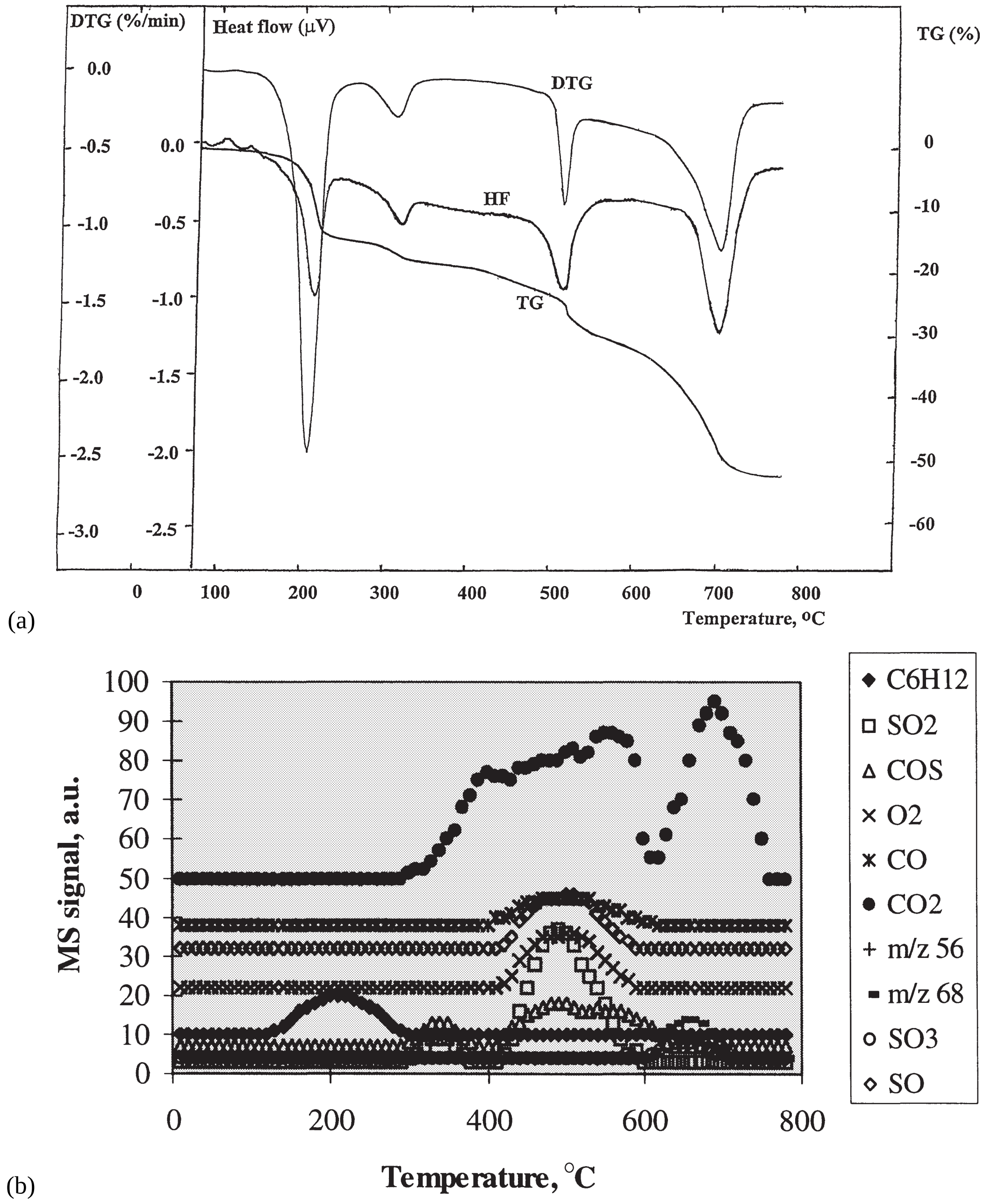


Figure 1. TG, DTG and HF curves (a) and MS signal curves (b) for the catalyst #II exposed to hexane.

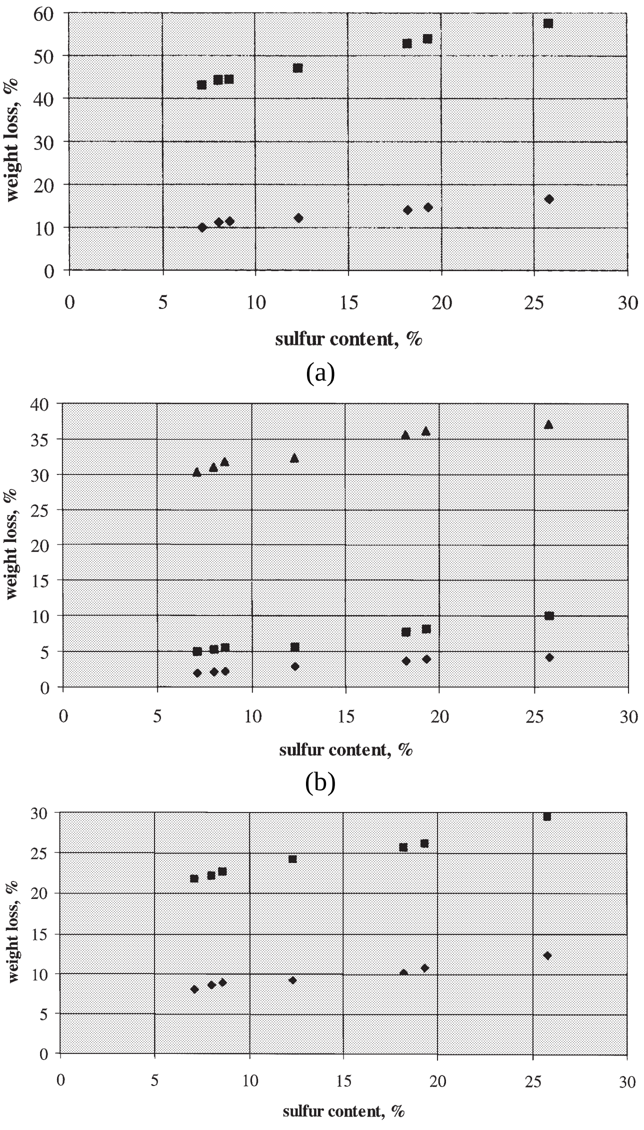
sulfur content, thus in direct relation with the total amount of hexane retained on these catalysts (figure 3(a)).

A last peak appeared at temperatures higher than 690 °C, namely at 715 °C for low sulfur containing samples (#V–VII), and below 700 °C for those with higher sulfur contents. Mainly CO_2 was released in this step together with small amounts of cracking products (with m/z 56 and 68) and SO_3 (m/z 70). MS analyses showed that the elimination of these species occurs above 600 °C. The intensity of the MS SO_3 peak was again in direct relation with the sulfur content of the catalysts.

In the third cycle carried out in a flowing 10% air/He gas mixture, only CO_2 was withdrawn and this release occurred at around 650 °C. No other masses were observed in the MS spectrum. At the end of the run, the catalyst was completely white.

3.3. Reaction with methylcyclopentane

Figure 4 (a) and (b) shows the thermal analysis curves and the corresponding MS curves of the catalyst #I exposed to methylcyclopentane, respectively. The TG curves of the other samples had a similar shape with weight losses depending on the sulfur content, also pointing to the intervention of sulfate groups as chemisorption sites. While the TG curves showed a continuous loss at temperatures above 200 °C, the DTG curves once more were useful to distinguish the different steps. The first

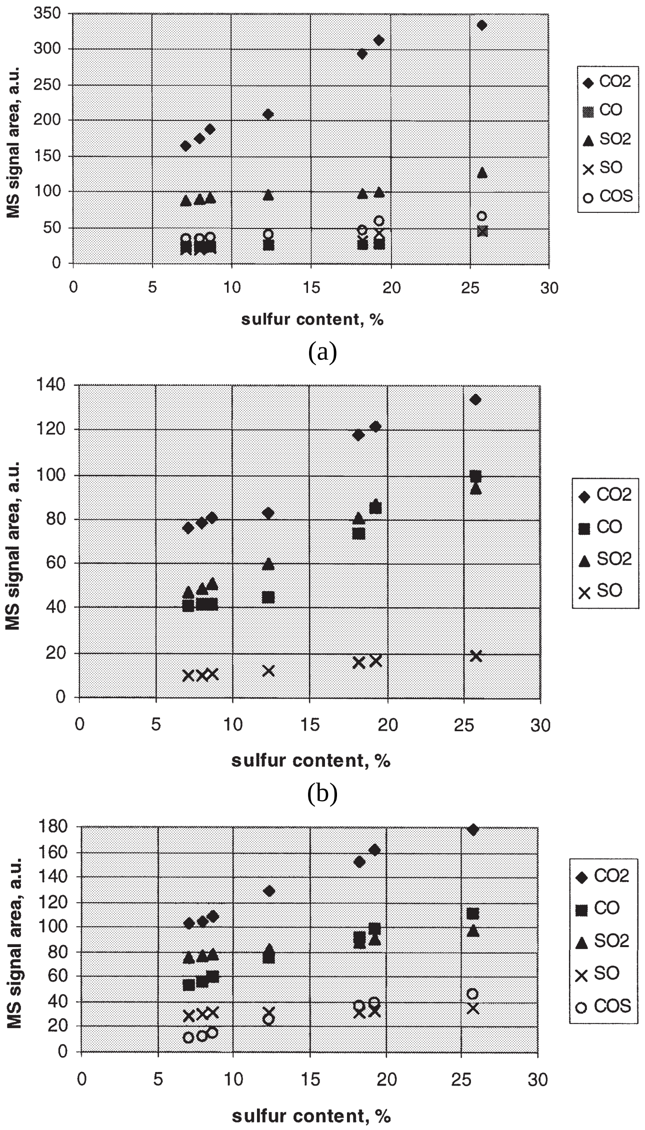


(a)

(b)

(c)

Figure 2. Weight loss versus sulfur content for the catalysts exposed to hexane (a), methylcyclopentane (b), and cyclohexane (c). (a): (■) Total weight loss, (♦) hexane released; (b): (▲) total weight loss, (♦) cyclohexane released, (■) methylcyclopentane and cyclohexane released; (c): (■) total weight loss, (♦) cyclohexane released.



(a)

(b)

(c)

Figure 3. MS signal area versus sulfur content for the catalysts exposed to hexane (a), methylcyclopentane (b) and cyclohexane (c).

two peaks, near 210 and 275 °C, corresponding to the removal of chemisorbed C_6H_{12} (m/z 84), could be associated with the two isomers (methylcyclopentane and cyclohexane). As for hexane, there was no relation between desorption temperature and sulfur content, but the amount of the chemisorbed hydrocarbon increased with the sulfur content (figure 2(b)). Compared with hexane, the higher desorption temperatures indicate that methylcyclopentane is more strongly chemisorbed on these catalysts.

The DTG minimum, located at 425 °C for the low-sulfur samples, and at around 398 °C for the one with more sulfur (figure 4), coincides with the release of CO, CO_2 and, partly also, of SO_2. The maximum elimination of CO and CO_2, and of SO, SO_2, and O_2 occurred at a lower temperature than in the case of hexane, but these releases were again simultaneous. A temperature dependency of these maxima on the sulfur content was also observed. Sample #I with more sulfur exhibited a DTG peak at 591 °C, while for samples #IV and #V, as examples, this peak was centered at nearly the same temperature (648 °C). For this series of samples, the signal associated to COS release (m/z 60) was weak. Also, the MS profiles recorded during the thermal measurements were much similar to those reported for benzene [12,13,15]. The formation of CO (m/z 28) and, particularly, of the cracking products (with m/z 56 and 68) was more important than in the case of hexane. The variation of the MS signal area with the sulfur content is shown in figure 3(b). Except for SO, a proportionality between the amount of the released component and the sulfur content was found.

In the third cycle, as in the experiments with hexane, only CO_2 was released, and this elimination occurred at

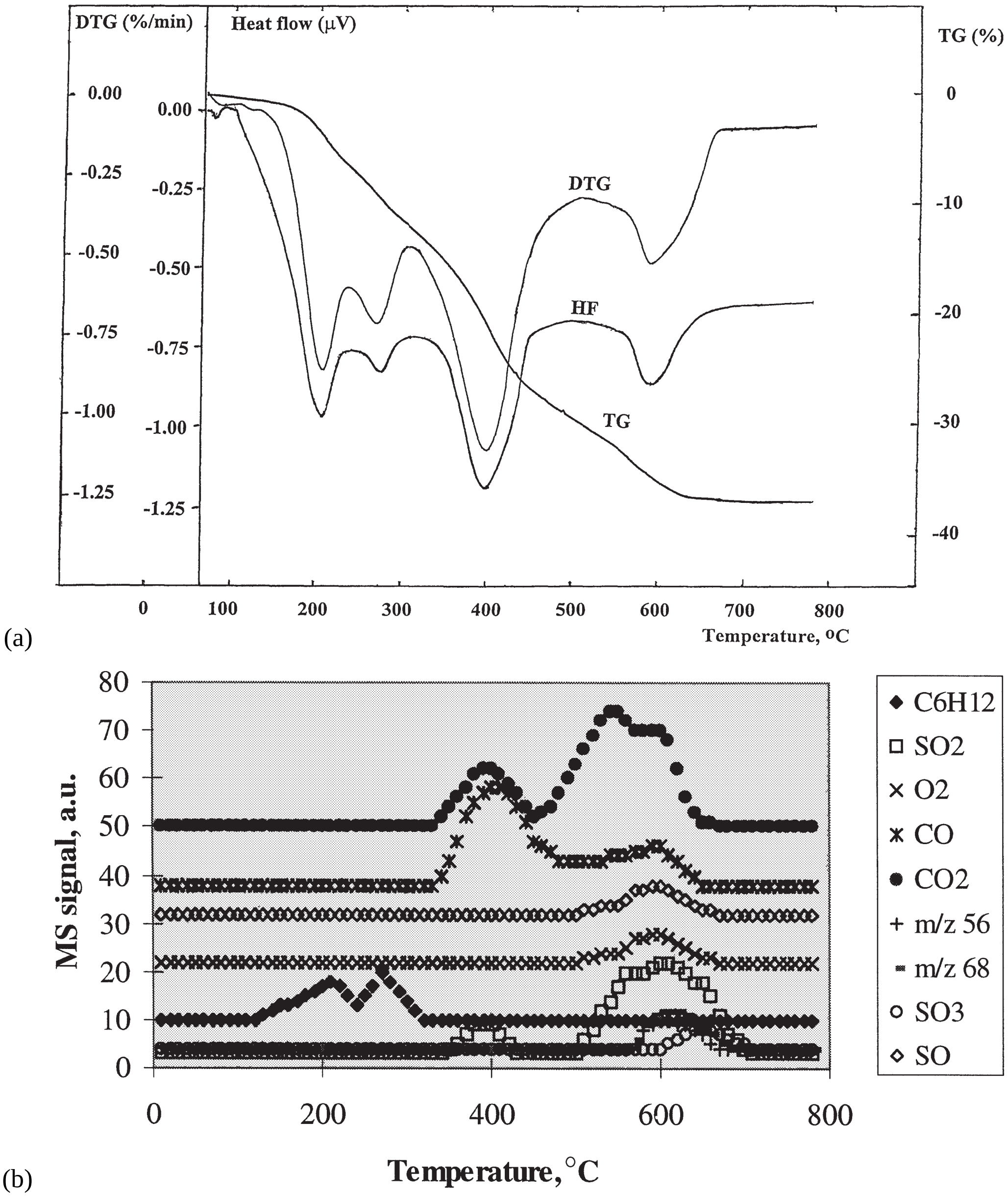


Figure 4. TG, DTG and HF curves (a) and MS signal curves (b) for the catalyst #I exposed to methylcyclopentane.

a similar temperature (650 °C) to the one observed for hexane, probably indicating a same kind of coke. Again, the catalysts recovered at the end of the runs were completely white.

3.4. Reaction with cyclohexane

The thermal analysis and the MS curves recorded for catalyst #II previously exposed to cyclohexane are shown in figure 5 (a) and (b), respectively. The DTG curves exhibited a first weight loss at 215 °C (desorption of cyclohexane) and an inflexion at around 257 °C. The MS spectra corresponding to m/z 84 showed two components, as for methylcyclopentane. The location of these components as well as the MS areas are much similar to those obtained for samples exposed to methylcyclopentane and could be due to the desorption of cyclohexane (first peak) and of methylcyclopentane (second peak). Again, no relation is observed between the weight loss temperature (minimum of the DTG peak) and the sulfur content of the catalysts, but, as for the other hydrocarbons, the amount of the cyclohexane released increases with increasing sulfur content (figure 2(c)).

The DTG–HF curves showed a second minimum at 310–315 °C. At this temperature, the corresponding MS curves showed a small release of SO_2 and COS (figure 3(c)). The DTG minimum at around 424 °C for #II, and at 454 °C for #V, corresponded to the simultaneous elimination of SO_2, COS, CO_2, and CO, while the one near 522 °C for #II, and near 552 °C for #V, was associated to another elimination of CO_2, CO, SO_2 and COS. In this step, O_2 and SO were also released. The last DTG minimum at 585 °C for #II, and at 595 °C for #V, coincided with maxima of O_2

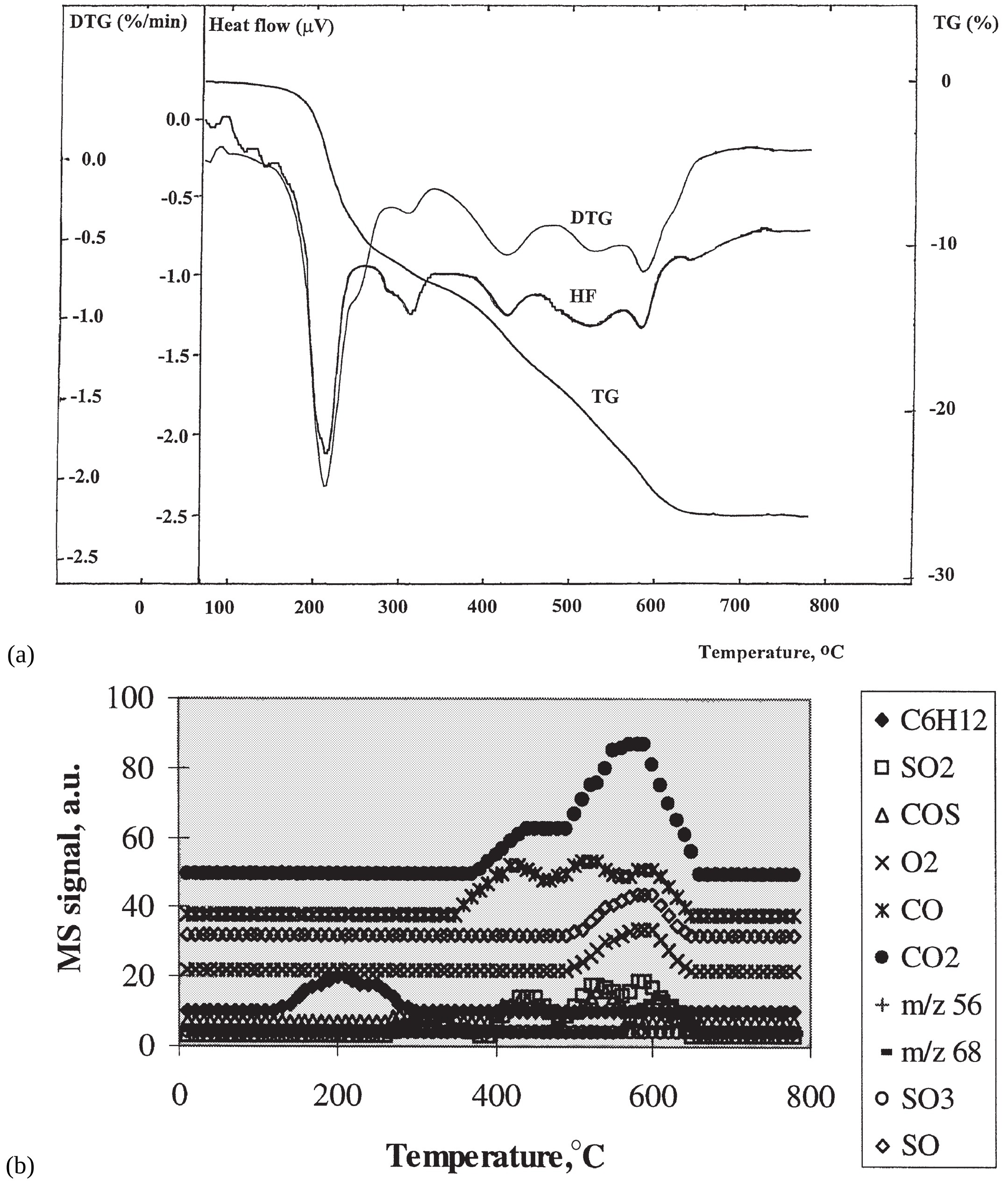


Figure 5. TG, DTG and HF curves (a) and MS signal curves (b) for the catalyst #II exposed to cyclohexane.

and SO evolution and with an important formation of CO and CO_2. Cracking products (m/z 56 and 68) were also eliminated.

Compared with the results obtained on the same catalysts exposed to hexane or methylcyclopentane and with data previously reported in the literature for sulfated zirconia exposed to benzene, alkylbenzenes, and isopropylamine [12,13,15], the samples treated with cyclohexane released more easily SO_2, O_2, CO_2, and CO and, above 660 °C, no weight loss was noticed. Moreover, during the third cycle, no change of the catalysts weight was observed, indicating that the carbonaceous deposit was completely eliminated using the oxygen released merely from the sulfate groups. It is worth to note that very small amounts of SO_3 were released from these catalysts.

4. Discussion

Previous studies [15] established the essential contribution of the redox sites in the reactions involving sulfated zirconia. It was suggested that the desorption channels for the various probe molecules are different on sulfated and promoted sulfated zirconia, and that the release of active oxygen at relatively low desorption temperatures (565 °C) should be associated with the decomposition of iron species. Studies made in the presence of benzene or pyridine confirmed that, indeed, the sulfate species on the catalyst surface were responsible for the oxidation capacity of these solids [13] and proposed that this process is a consequence of the fact that the support and promoters alter the energy of the lowest unoccupied orbital of the sulfate. At the same time, some structural oxygens also take part in this process.

In the present study, the release of active oxygen leading to the formation of oxygenated species (CO, CO_2, COS, SO, SO_2, and O_2) depends on the reactant molecule and on the sulfur content of the catalysts, which is also consistent with the results of Srinivasan et al. [14] and Wan et al. [15]. These two effects will be discussed separately.

4.1. *Influence of the reactant molecule*

Exposure of sulfated zirconia to hydrocarbons at 140 °C for 40 min generates an important deactivation of the catalysts. Two phenomena contribute to this behavior: (i) formation of strongly chemisorbed polyenilic and aromatic species [21,22], and of polycondensed species (coke), and (ii) partial removal of sulfur [23]. Kinetic measurements of Farcasiu et al. [24] have shown quite convincingly that an increase of temperature enhances the deactivation rate. In the case of methylcyclopentane (one of the most stable hydrocarbons), deactivation was faster than reaction even at 55 °C. Another source of deactivation, in agreement with Farcasiu et al. [9], could be the reduction of sulfate to sulfite, and even of sulfite to sulfide. In our case, the chemical analyses did not allow to detect, after 40 min, a loss of sulfur from the catalysts. But the thermal analyses of these samples exposed to the different hydrocarbons provided some information on the interactions of these molecules with the active sites.

A first one is that part of these hydrocarbons remained chemisorbed on the catalysts since a simple purge of the samples at 50 °C in flowing He was not sufficient to achieve desorption. Except for methylcyclopentane, which was a little more strongly chemisorbed, both hexane and cyclohexane desorbed at around 210 °C. The fact that for each molecule the temperature of the release was independent of the sulfate content, and that a proportionality existed between the sulfate content and the amount of hydrocarbon desorbing, suggests that these molecules are chemisorbed mainly on the strong sites.

The variation of the other components released (CO, CO_2, SO_2, O_2, SO, and COS) shows differences according to the nature of the hydrocarbon, indicating that the population and the nature of the species which are found on the catalyst surface are different. This is of course a consequence of the different reactivity of these molecules and reaction pathway. Such an explanation mainly accounts for the shape of the MS CO_2 and CO curves. The catalysts exposed to hexane exhibited the highest reactivity [21], and also large amount of CO_2 was produced, whereas for those exposed to methylcyclopentane or cyclohexane, the amount of CO became very important (figure 3). Another consequence of the presence of more polymerized species after exposure of the catalysts to hexane is that these species are removed only at about 700 °C and, in these conditions, there still remained a carbonaceous deposit which was eliminated in air at 650 °C, while those resulting from exposure to cyclohexane were withdrawn at least 50 °C lower, and the catalyst remained clean.

4.2. *Influence of the sulfur content in the catalyst*

The TG–DTA curves and the MS analyses showed a direct relation between the sulfur content and the amount of chemisorbed hydrocarbon. Also, the increase of the sulfur content made easier the release of the active oxygen and, consequently, the oxidation of the hydrocarbons. Elimination of SO, COS, and SO_2 occurred at lower temperatures than for the samples with lower sulfur content. This constitutes an additional evidence for the role of the sulfate species in the reaction of hydrocarbons. Samples with sulfur content higher than 10 wt% are expected to have an important part of sulfate in an adsorbed state, as it was observed by Riego et al. [25] in the case of silica. The main difference between catalysts with high and low sulfur contents concerns the amount of hydrocarbon retained and the temperature at which oxidation of the chemisorbed species is starting. It means that a higher sulfur content could lead to an easy elimination of active oxygen and, in that case, the redox potential of the catalyst is higher.

It seems, thus, probable that at low temperatures, the redox potential is manifested as a hydrogen subtraction, which is sufficient to generate radicals and alkene species which polymerize on the catalyst surface, whereas at high temperatures, it would generate active oxygen, able to oxidise completely the chemisorbed species. The sites responsible for these processes are those proposed by Davies and co-workers [14,15].

5. Conclusion

Exposure of sulfated zirconias for 40 min at 140 °C to a flow containing hexane, methylcyclopentane, and cyclohexane is sufficient to generate strongly chemisorbed species which contribute to the catalysts deactivation. TG–DTG analyses coupled with MS analyses have shown that the amount of chemisorbed species is related to the sulfur content. During the analyses, these species are oxidized to CO, CO_2, COS and some cracking products.

These results are consistent with the redox potential of these catalysts. Under reaction temperature, this potential is reflected, as previously stressed in the literature, by the abstraction of hydrogen atoms, and the increase of the temperature makes the oxygen more reactive. In parallel with the release of these oxygen species, SO_2 evolution also occurs, and part of these species react generating O_2.

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