Catalysis Today 53 (1999) 565–573

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Cracking catalyst additives for sulfur removal from FCC gasoline

P-O.F. Andersson [1],*, M. Pirjamali, S.G. Järås, M. Boutonnet-Kizling

KTH — Royal Institute of Technology, Chemical Technology, Teknikringen 42, SE-100 44 Stockholm, Sweden

---

Abstract

FCC catalyst additives for sulfur-compound cracking with the ability to reduce sulfur in gasoline have been produced by depositing various metals and metal oxides on different supports using the microemulsion technique. Three groups of additives have been studied. First, Zn on different supports: alumina, titania, and hydrotalcite. Second, different metals on alumina: Zn, Mn and Zr, and third, two different metals on hydrotalcite: Zn and Co. The additives were blended to 10 wt% with a reference FCC-catalyst. All the additives give lower yields of gasoline than the reference catalyst itself. The loss in gasoline is due to an increased amount of gas production and/or increase in coke production. Concerning the sulfur reduction, the order of activity of the four best additives is the following: Zn/hydrotalcite > ZrO/alumina > Zn/titania > Mn/alumina. Zn/hydrotalcite has a value of ≈80% reduction of sulfur in sulfur-spiked gasoline at the microactivity test (MAT)-level. ©1999 Elsevier Science B.V. All rights reserved.

---

1. Introduction

Gasoline sulfur is not only a direct contributor to SO_x emissions, it is also a poison affecting the low-temperature activity of automotive catalytic converters and, therefore, it has an effect on volatile organic compounds (VOCs), NO_x and total toxic emissions [1]. As a result, the environmental legislation has placed limits on gasoline sulfur content and future limits of 150 ppm, and lower, sulfur content are proposed [2]. Sulfur in gasoline originates from FCC gasoline, coker naphtha and straight-run naphtha. Although the coker and straight-run naphthas are high in sulfur, they only contribute with 10% of the total gasoline sulfur, because their contribution to the gasoline pool is small. FCC gasoline, accounting for ca 1/3 of the U.S. gasoline pool, accounts for about 90% of the total gasoline sulfur [3,4]. When addressing sulfur in gasoline the main target, therefore, is sulfur in FCC gasoline.

Several different routes to gasoline sulfur reduction can be considered, i.e. hydrotreatment of the FCC feed, and hydrodesulfurization of the FCC gasoline or fractions thereof. However, the hydrotreatment methods entail the great disadvantage of increased operating and capital costs for the FCC process and, furthermore, hydrodesulfurization of FCC gasoline leads to a significant loss of octane number which must be restored in subsequent processing [5]. Hydrodesulfurization of only the heavy portion of the gasoline is, in most cases, inadequate in reducing overall sulfur to desired levels [6,7]. The capital expenditure can be avoided by improving desulfurization in the FCC unit. This can be accomplished by improving the cracking of sulfur compounds in the gasoline range or by selective adsorption of these compounds. The latter method would result in greater transport of sulfur to the regenerator and an increase in flue gas SO_x that then must

---

* Corresponding author. Tel.: +46-8-790-82-57; fax: +46-8-10-85-79

E-mail address: jack@ket.kth.se (P-O.F. Andersson)

[1] Present address: R & D Department, Nynas Naphthenics, SE-149 82 Nynäshamn, Sweden

PII: S0920-5861(99)00144-3

Table 1
Cracking catalyst additives prepared by the microemulsion method

Catalyst name	Active metal	Support	Metal concentration	Ternary system[a]	Metal precursor	Agent of precipitation	Surface area (m^2/g)
Zn/HT	Zn	hydrotalcite	5 wt%	H_2O/cyclohexane/PEGDE	Nitrate	NH_3	235
Co/HT	Co	hydrotalcite	1 wt%	H_2O/*n*-octane/PEGDE	Acetate	Oxalic acid	232
Zn/alumina	Zn	γ-alumina	10 wt%	H_2O/cyclohexane/B02	Nitrate	Oxalic acid	217
Mn/alumina	Mn	γ-alumina	10 wt%	H_2O/cyclohexane/B02	Nitrate	Oxalic acid	219
ZrO/alumina	ZrO	γ-alumina	10 wt%	H_2O/cyclohexane/B02	Isopropoxide	H_2SO_4	213
Zn/titania	Zn	titania (anatase)	10 wt%	H_2O/cyclohexane/B02	Nitrate	Oxalic acid	46
Zn/FCC	Zn	FCC-catalyst	10 wt%	H_2O/cyclohexane/B02	Nitrate	Oxalic acid	209

[a] PEGDE, pentaethyleneglycol-dodecylether; and B02, polyoxyethylene-nonylphenylether.

be addressed [8]. In the present project, the former method to decrease the sulfur content in gasoline by direct cracking of sulfur compounds has been considered. This method is based on the following consideration: if the sulfur compounds can be cracked into H_2S directly in the riser, almost all of the above problems would be solved, that is to say no capital expenditure and no further processing is needed and the SO_x production is not increased [9,10]. However, if the sulfur compound cracking is not selective enough, it may lead to less selective hydrocarbon cracking with resulting increases in coke and dry gas production and possible loss of octane. The aim of the project of which this work is a part is to develop an FCC catalyst additive that will reduce the sulfur in gasoline by at least 40% in an FCC unit [11]. The additive should also be able to withstand FCC conditions and should not increase production of coke or dry gases. For this purpose, additives based on metal oxides on different supports have been prepared using the microemulsion technique [12].

2. Experimental

2.1. Catalyst preparation

A number of additives have been prepared using the microemulsion technique. This method utilizes the properties of microemulsions in the following manner. On mixing a surfactant, a solvent and water to a ternary system in certain concentrations, a microemulsion is obtained which contains small aggregates called reversed micelles. In the aqueous core of the micelles, it is possible to solubilize a metal particle precursor. Thus, by adding an appropriate precipitating agent to the solution, small metal particles can be obtained. The size of these particles will depend on the size of the micelles, which, in turn, is influenced by the ratio of the surfactant to water (with metal precursor) concentrations [12–14]. By this method, it is possible to obtain small metal and metal oxide particles of narrow size distributions. In the present study, the composition of the ternary system was 18–20% surfactant, 70–72% solvent and the balance water with dissolved metal precursor.

In order to prepare supported metal oxide particles, rather than supported metal particles, the microemulsion technique was used in a slightly different manner than the one described above. Two sets of microemulsions were prepared: one containing the metal nitrate solution and the other containing the oxalic acid solution. When these two microemulsion sets are mixed, a suspension of metal oxalate particles is formed. Subsequently, the metal oxalate particles are separated and deposited on the desired support and the obtained additive precursor is dried. For the purpose of removing the remaining solvents and forming the desired metal oxide, the additives were calcined for 12 h in air at 350°C. Table 1 compiles a list with information on the content, preparation, and surface area of the additives used in this study.

2.2. Characterization

The crystal phases of some additives were identified by X-ray diffraction (XRD) using a Siemens diffractometer 5000 scanning 2θ from 10–80° using monochromatic CuK_α radiation. The crystal phases were identified using JCPDS-files in order to determine the proper calcination temperature and make sure that the preparation method yielded metal oxides.

The strength and number of acid sites are important properties of FCC catalysts. Therefore, all catalysts were characterized for acid-site strength and amount using ammonia–temperature-programmed desorption (NH_3–TPD) on a Micromeritics TPD/TPR 2900 equipped with a TCD. The TPD-samples were pretreated by heating them at 25°C/min up to 600°C while flushing with N_2. After 2 h at 600°C, the purge gas was changed to dried He and the samples were cooled to 150°C. Pulses of dried, pure NH_3 were then sent through the sample until it was saturated and then flushing with dried He for 30 min commenced. The NH_3 desorbed from the sample during heating at 10°C/min up to 600°C.

Electron spectroscopy for chemical analysis (ESCA) was performed on a V.G. Scientific ESCA Mark III to estimate the oxidation state and the dispersion of metal oxides on the hydrotalcite-based additives. The instrument was equipped with an Al (K_α) X-ray source (1486.6 eV) and a hemispherical analyzer. The pressure in the spectrometer was $<10^{-8}$ Torr, while collecting data. The scanning rate was 0.2 eV/s, and the pass energy 20 eV. Spectra were stored in the digital form.

A study of the distribution of Zn on Zn/alumina as well as the distribution of sulfur on used FCC-catalyst and additive was made by secondary-ion mass spectroscopy (SIMS) using a CAMECA IMS-6F SIMS. Small pieces of the additive were mounted on a silver print ink dot on a copper support. The sample surface was coated with a 200-nm thick gold layer to minimize charging effects. Positive primary cesium ions were used to study the sulfur distributions, while negative primary oxygen ions were used to study the positive secondary ions, such as Zn. As the material is non-conducting, electron flooding was necessary to analyze negative secondary ions. Also, high mass resolution mode was demanded as the O_2-molecule is very close to sulfur of mass 32.

2.3. *Activity testing*

Cracking activities (for hydrocarbons and sulfur compounds) were tested in a microactivity test (MAT) reactor, where the additives were mixed with a commercial FCC catalyst to an amount of 10 wt%. The feed was a commercial gas oil spiked with some common sulfur compounds, viz. thiophene, 2-methylthiophene, benzothiophene and dibenzothiophene, to an amount of 1000 ppm of sulfur each. The MAT tests were performed according to the ASTM D 3907-92 standard method with some minor modifications; the time-on-stream was 30 s, the temperature was set to 510°C and the liquid product collecting system consisted of two receivers immersed in −18°C ethanol. MAT results for all the additives were compared with the MAT results achieved with the commercial FCC-catalyst used as a reference.

Analyses of the different products (gas, liquid and solid) were made with the following analysis methods. The gaseous products were analyzed in an HP6890 gas chromatograph (HP-GC) equipped with a flame ionization detector (FID) for detection of hydrocarbons and a sulfur chemiluminescense detector (SCD) for detection of sulfur-containing compounds. The liquid products were analyzed using a simulated distillation technique in an HP-GC equipped with an FID for hydrocarbon detection and an SCD for the sulfur-containing compounds. The solid material, present as coke on the used catalyst, was analyzed for total carbon and sulfur contents in an LECO-analyzer.

3. Results and discussion

3.1. *Characterization results*

In order to determine the proper calcination temperature for the oxalate-based additives, and to make sure that the method yielded a metal oxide, some XRD analyses of precipitated pure Zn-oxalate, calcined at different temperatures, were performed. In Fig. 1, it is shown that at lower calcination temperatures (150°C) Zn-hydroxide is formed which, subsequently, at higher temperatures is fully converted to the desired Zn-oxide (350°C).

Two of the additives, Zn/HT and Co/HT, were studied with ESCA in order to estimate the oxidation state and the dispersion of the metal oxide (Fig. 2). In the

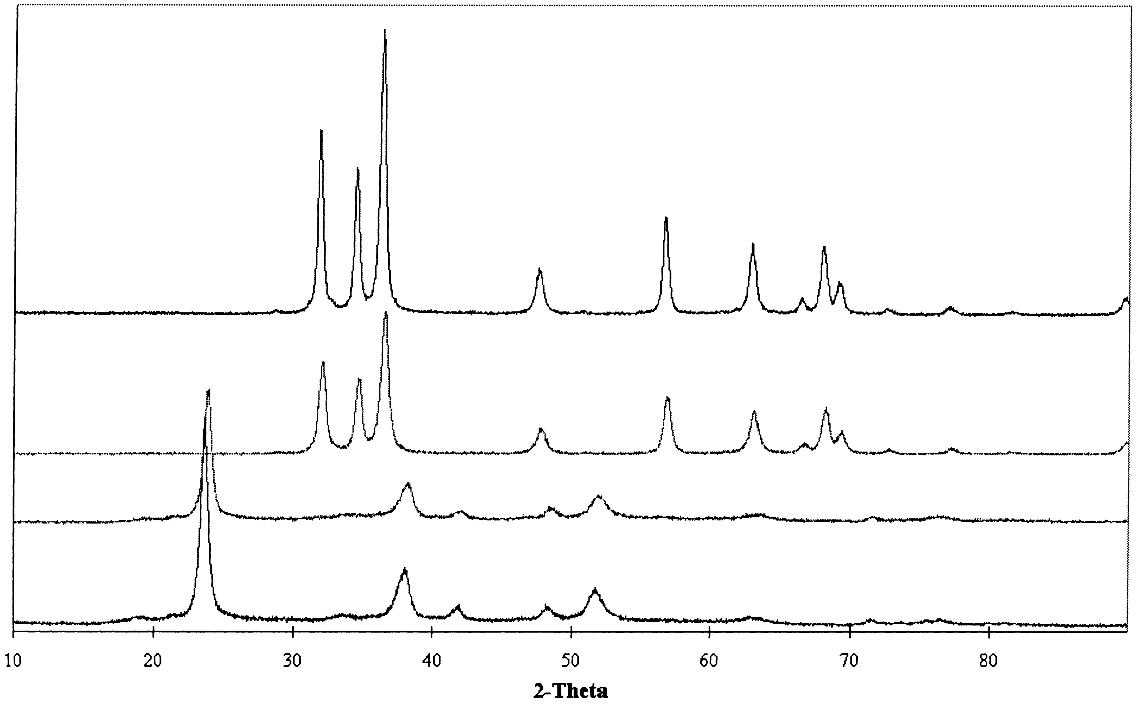

Fig. 1. XRD results of precipitated pure Zn-oxalate calcined at different temperatures. The curves for 150 and 250°C (the two lower lines) are characteristic for Zn-hydroxide and the curves for 300 and 350°C (the two upper lines) are characteristic for Zn-oxide.

Table 2
NH_3–TPD results for Mn/alumina, ZrO/alumina and Zn/titania

Additive	NH_3 adsorbed (mg/g cat)	Peak 1 (°C)	Peak 2 (°C)
Mn/alumina	12.32	230	400
ZrO/alumina	4.00	250	–
Zn/alumina	13.68	250	–
Zn/titania	12.84	300	–

case of Co, the shake-up of Co2*p* is too small to be characteristic of CoO, but also too big to be characteristic of pure Co_3O_4. Hence, the additive consists of a mixture of CoO and Co_3O_4. No attempt to deconvolute the peaks in order to estimate the proportion between the oxides was made. The Zn/HT spectra exhibit peaks typical for ZnO, which concludes that Zn was present as pure ZnO.

Fig. 3 and Table 2 show the results of NH_3–TPD measurements on Zn/titania, Mn/alumina, Zn/alumina and ZrO/alumina. The comparison reveals that Mn/alumina, Zn/alumina and Zn/titania has more and stronger acid sites than ZrO/alumina. It is also shown that Mn/alumina contains two types of acid sites, one that desorbs NH_3 at 230°C and the other at 400°C, in contrast to the other three additives, which exhibit peaks only at the lower temperature.

The SIMS study was made on the reference FCC-catalyst and on the Zn/alumina additive. Samples were taken for analysis, both prior to reaction and afterwards. The images in Fig. 4 are those of an FCC-catalyst with additive that has undergone MAT-testing. Mass number 64 correlates to both, TiO and Zn. However, the contribution of Zn to this SIMS image is far lower than that of TiO. Mass number 68 corresponds almost exclusively to Zn. Hence, Fig. 4 shows that a small amount of Zn has been transferred from the Zn/alumina to the FCC-catalyst during the cracking process and that Zn is uniformly distributed in the additive. Also seen in SIMS was the fact that sulfur, deposited on the FCC-catalyst during cracking, was uniformly distributed on the particle.

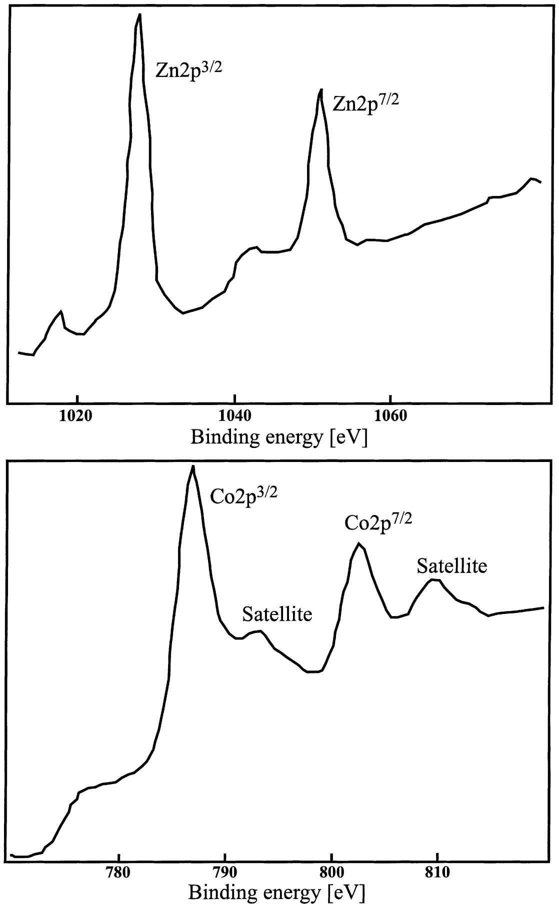

Fig. 2. ESCA results for Zn/hydrotalcite and Co/hydrotalcite.

3.2. Activity test results

The sulfur-reducing ability of each additive was calculated as the difference between the sulfur reduction of the reference FCC catalyst and that obtained in the MAT-unit of the additive blended with the reference catalyst. The comparison was made at comparable conversion levels. A bar chart of the sulfur-reducing abilities of all additives is shown in Fig. 5. To make the study more comprehensive and the results easier to interpret, the activity of the additives in sulfur reduction were compared by dividing them into three groups. First, Zn on different supports: Zn/alumina, Zn/titania, and Zn/hydrotalcite. Second, different metals on alumina: Zn/alumina, Mn/alumina, and ZrO/alumina, and the third, two different metals on hydrotalcite: Zn/hydrotalcite and Co/hydrotalcite. The results of the first group show that neither surface area (Table 1) nor acidity (Table 2) can be correlated to sulfur-reducing ability. Moreover, the additive with the lowest metal loading (5 wt% Zn/HT) is the most active. These facts suggest that the support has significant impact on the nature of the active sites formed and their ability to reduce sulfur. Exactly which properties of the metal/support system are important is yet to be determined, but it is possible that the capacity to adsorb sulfur is one of them. The results show that acidity, although it may have an effect, is definitely not the most important property, as reflected in a paper by Hopkins et al [15]. This is also clearly seen in the second group of additives, Zn, Mn and Zr on alumina. In fact, the additive with the lowest amount of acid sites, ZrO/alumina, is most active among these additives in reducing sulfur. Mn/alumina exhibits an effect on the MAT-reaction behavior very different from the other additives. It has the same negative impact on gasoline yield as the other additives but does not show the same increase in coke production. Instead, it selectively promotes the production of gases under MAT-conditions. This correlation between production of gases and sulfur reduction is yet to be explained. Regarding the third group of additives, both Co and Zn on hydrotalcite exhibit the same behavior in MAT-reactions. They both balance the loss in gasoline yield with an increase in coke production. The lower sulfur-reducing activity of Co/hydrotalcite compared to Zn/hydrotalcite can possibly be explained by the fact that CoO has a propensity to be reduced to a zero-valence metal under MAT-conditions and can then serve as a dehydrogenation catalyst.

From the obtained results, it was observed that four of the additives exhibit significantly higher levels of sulfur-compound cracking activity and the order of activity for these additives are: Zn/hydrotalcite > ZrO/alumina > Zn/titania > Mn/alumina. Besides the sulfur reduction activity, the production of gasoline, coke and gases has been taken into consideration. In order to make the MAT-results easier to interpret, the results for the other two additives, that is Mn/alumina and Co/hydrotalcite, have been omitted in Figs. 6 to 8. Fig. 6 shows the yield of gasoline produced by the additives and the reference FCC-catalyst compared to the reference MAT-tests

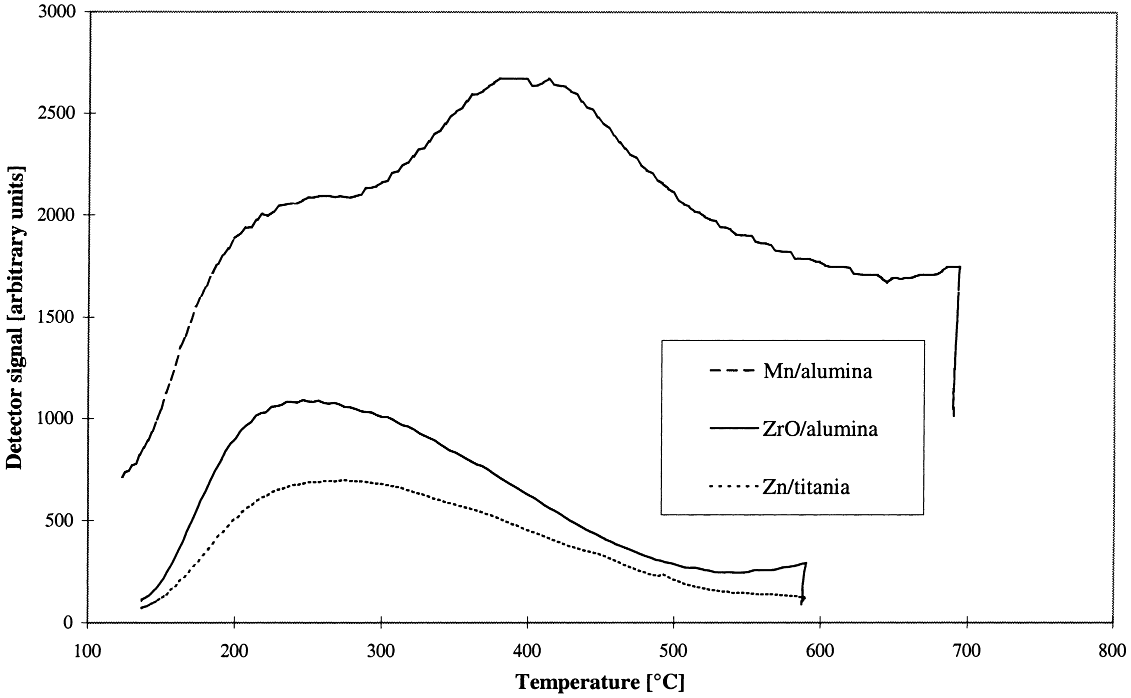

Fig. 3. NH_3–TPD results for Zn/titania, ZrO/alumina and Mn/alumina.

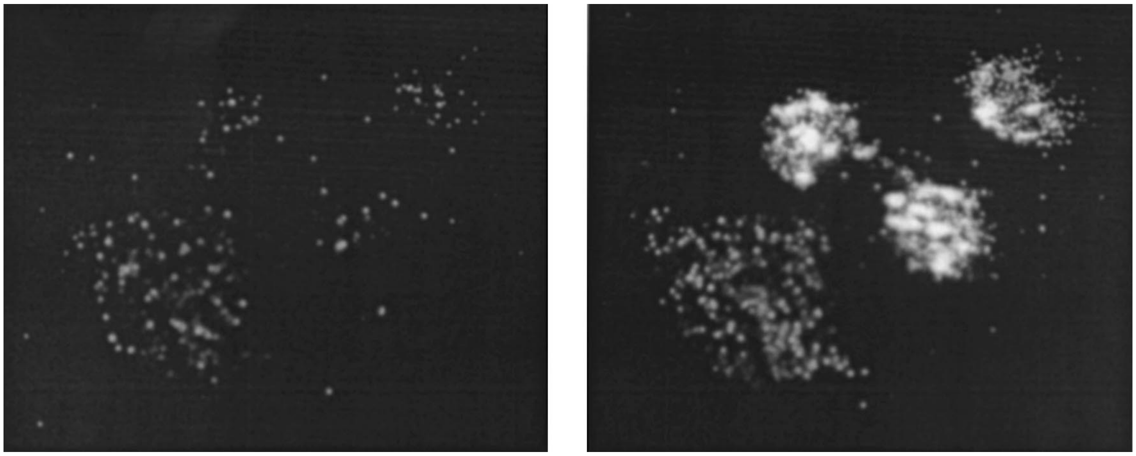

Fig. 4. SIMS images of FCC-catalyst (three upper right) and Zn/alumina (bottom left) for the mass numbers 68 (left image) and 64 (right image). The images are of an FCC-catalyst with additive that has undergone MAT-testing.

with the FCC-catalyst only. All the additives give lower yields of gasoline than the reference and their addition also gives a higher, apparent cracking activity, for the same catalyst/oil ratio, in the MAT-tests. One of the additives, viz. Mn/alumina, gives remarkably high yields of gaseous products (Fig. 7) which accounts for the loss in gasoline yield. This effect on the gas oil cracking is not exhibited by any of the other tested additives. The low gasoline yield obtained with the other additives is explained in Fig. 8.

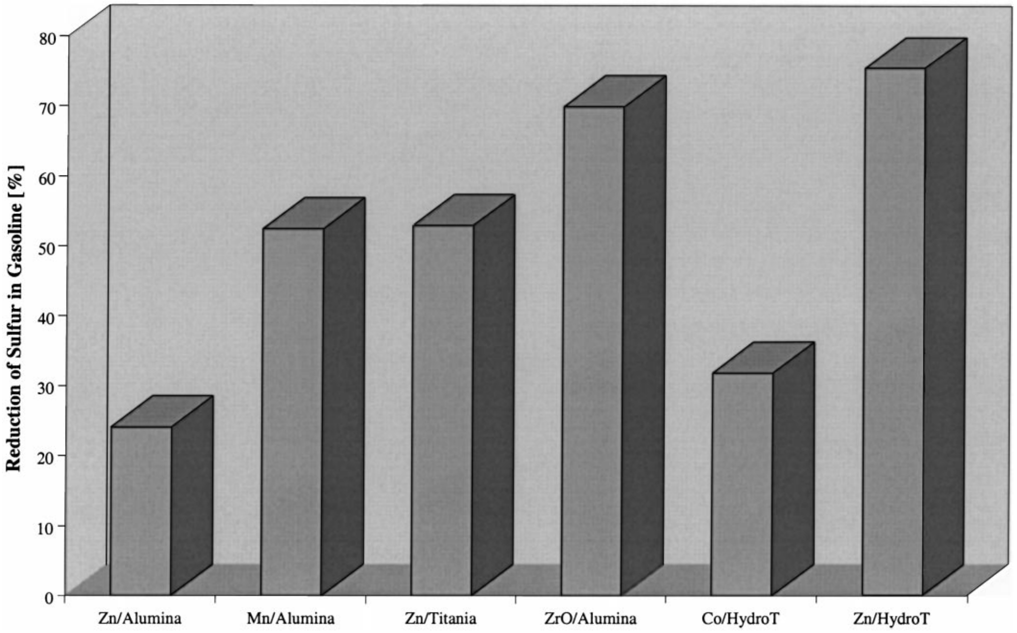

Fig. 5. Percentage decrease in sulfur in gasoline compared to the reference catalyst.

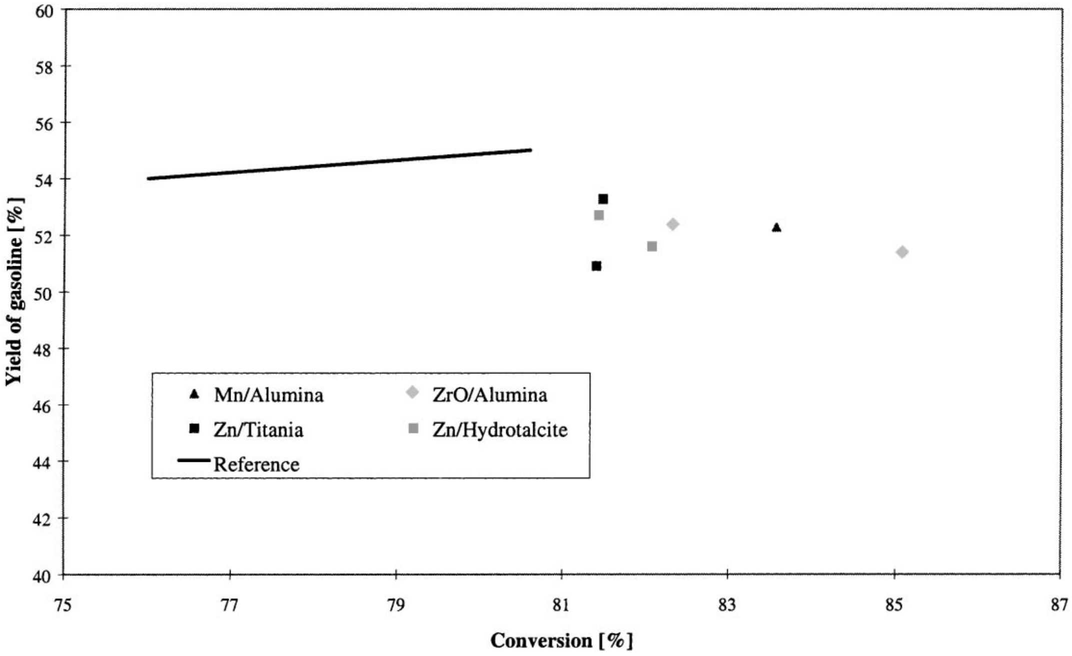

Fig. 6. Yield of gasoline for the four best additives and the reference.

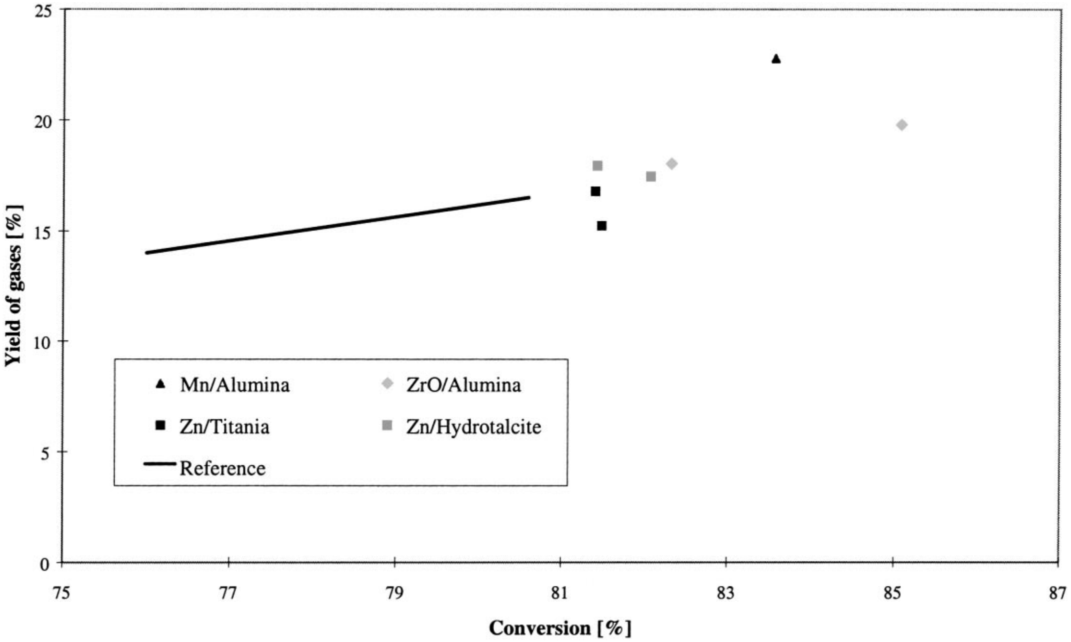

Fig. 7. Yield of gases for the four best additives and the reference.

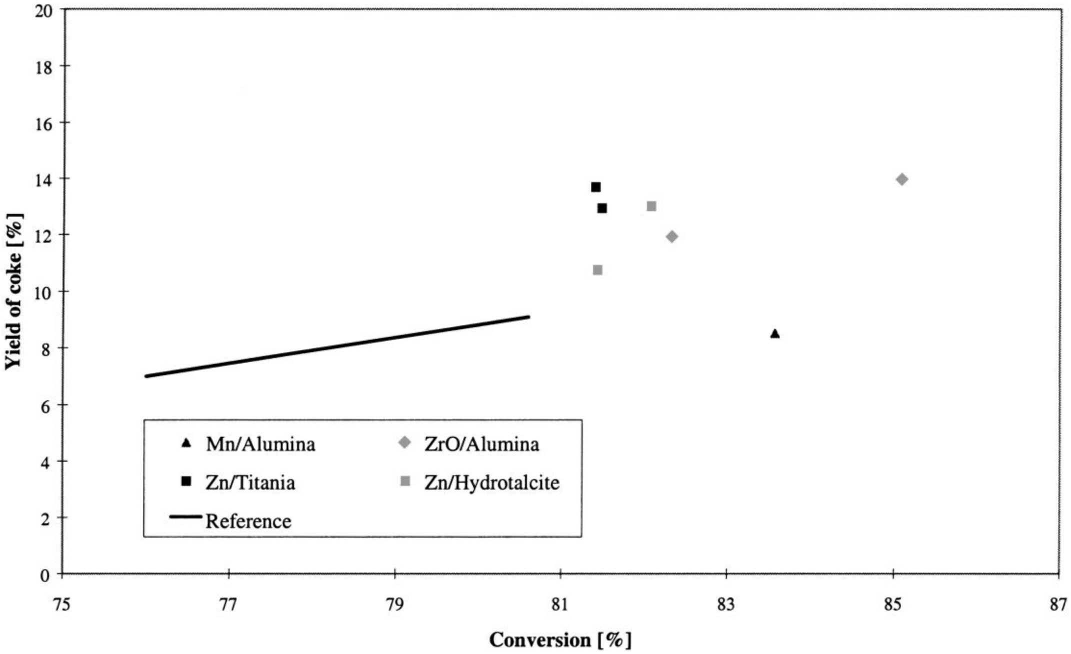

Fig. 8. Yield of coke for the four best additives and the reference.

High yields of coke are produced by the three most efficient sulfur reduction additives.

High activity for sulfur compound cracking for the additives tested correlate with either increased coke or gas production. The simultaneous increase in coke production and sulfur compound cracking can possibly be explained by the phenomenon of hydrogen transfer. If the additives increase the activity for coke production, a significant amount of hydrogen becomes available for reaction. The desulfurization of, for example benzothiophene which is a common sulfur compound in gas oil, is believed to take place through saturation of the aromatic ring and subsequent cracking to yield H_2S and hydrocarbons [10]. Since increased coke production is not acceptable from a process economics point of view, it is essential that an additive promotes sulfur compound cracking in a more selective way than through increased hydrogen transfer and, hence, increased coke production. To be able to utilize the sulfur-reducing activity of these additives, it is necessary to gain knowledge about the sulfur-reducing ability and the increased coke make are two results of the same mechanism/active site or if they are independent. If they are, it might be possible to design a catalyst that benefits from the sulfur-reducing ability without the penalty of increased coke production.

4. Conclusions

It is possible to prepare cracking catalyst additives by the microemulsion technique with high sulfur-reducing ability that achieves sulfur reduction, possibly through promotion of hydrogen transfer reactions. The coke productions of these additives are significant and it is possible that the sulfur-reducing capability is due to hydrogen transfer reactions that are initiated by the increased coke production. In the case of Mn/alumina, increased coke yields are avoided, but instead large amounts of gases are produced. It is not clear through which reaction path this additive enhances the sulfur reduction and further studies are needed to elucidate this behavior. Increased production of coke or gases is not acceptable for cracking catalyst additives, but if the reaction scheme for these additives are found it may be possible to design a new additive that has the high sulfur-reducing ability without the negative effect on production of coke or gases. An attempt to correlate the sulfur compound cracking activity and the additives acid site number and strength was also made. No apparent correlation between these properties was seen. In fact, the very capable sulfur-reducing additive ZrO/alumina has only one third of the acid sites found in the less active additives Zn/titania, Zn/alumina and Mn/alumina.

Acknowledgements

The presented results were obtained at KTH within the Brite-Euram project ‘Surena’, Contract No. BRPR-CT95-0102, in which the other partners are Cepsa and ITQ (Spain), Engelhard (Holland) and Statoil (Norway). Funding from the European Union is gratefully acknowledged.

References

[1] G. Tobin, P. Gladman, Hydrocarbon Eng. 1 (1996) 26.
[2] R.E. Evans, G.P. Quinn, in: J.S. Magee, M.M. Mitchell Jr. (Eds.), Studies in Surface Science and Catalysis, Fluid Catalytic Cracking: Science and Technology, Elsevier Science, Amsterdam, 1993, 563 p.
[3] G.H. Unzelman, Fuel Reformul. 2 (1992) 28.
[4] NPRA Gasoline Survey Section A, Revised Sulfur Data, National Petroleum Refiners Association, Washington, DC, 1991.
[5] M.R. Apelian, D.L. Fletcher, M.S. Sarli, S.S. Shih, Mobil Oil Corp., US Patent 5308471 (1994).
[6] J. Gosyns, G. Heinrich, J.W. Andrews, R. Gialella, Paper AM-92-21, NPRA Ann. Mtg., New Orleans, LA, 1992.
[7] B.A Orkin, Mobil Oil Corp., US Pat 3957625 (1976).
[8] A. Corma, A.E. Palomares, F. Rey, Appl. Catal. B 4 (1994) 29.
[9] R.F. Wormsbecher, G. Kim, W.R. Grace & Co, EP 0 609 971 (1994).
[10] W. -C. Cheng, G. Kim, A.W. Peters, X. Zhao, K. Rajagopalan, Catal. Rev.-Sci. Eng. 40 (1998) 61.
[11] M. Perez Pasqual, T. Myrstad, M. Hoffmeister, A. Corma, M. Boutonnet-Kizling, Erdöl Erdgas Kohle, in press.
[12] V. Pillai, P. Kumar, M.J. Hou, P. Ayyub, D.O. Shah, Adv. Coll. Interface Sci. 55 (1995) 241.
[13] M. Boutonnet, J. Kizling, P. Stenius, G. Maire, Coll. Surf. 5 (1982) 209.
[14] M. Boutonnet-Kizling, F. Regali, in: B. Delmon, P.A. Jacobs, R. Maggi, J.A. Martens, P. Grange, G. Poncelet (Eds.), Studies in Surface Science and Catalysis, Preparation of Catalysts VII, Elsevier Science, Amsterdam, 1998,. 495 p.
[15] P.D. Hopkins, J.T. Miller, B.L. Meyers, G.J. Ray, R.T. Roginski, M.A. Kuehne, H. H Kung, Appl. Catal. A. 136 (1996) 29.