

SELECTIVE HYDRODESULPHURIZATION OF FULL RANGE FCC GASOLINE ON PtPd/USY-ZEOLITE

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Abstract

FCC gasoline is generally responsible for more than 90% of the sulphur compounds in the engine gasoline, its desulphurization is thus required to produce ultra low sulphur gasoline (sulphur content <10 ppm). In this paper the possibilities of reducing the sulphur content of FCC gasolines are summarized. In the experimental section the results of hydrodesulphurization carried out over PtPd/USY zeolite with full range FCC gasoline feeds of different sulphur content are presented. The original 66 ppm sulphur content of the gasoline was increased to 196 ppm by adding benzothiophene. For comparison the feed was hydrotreated on conventional CoMo/Al₂O₃ catalyst, too. The results indicated that PtPd/USY-zeolite is suitable for the selective desulphurization of FCC gasoline cracked from pre-treated FCC feed. Aiming 10-20 ppm sulphur content in the products the loss of research octane number was ca. 2.5-3.0 units lower on PtPd/zeolite than on conventional CoMo/alumina.

Key words: FCC gasoline, selective desulphurization, PtPd/USY-zeolite, olefin saturation

Introduction

For further reduction of the emission of new passenger cars, high performance catalytic converters have to be applied with short light-off time [1]. Sulphur content of the engine fuels has to be decreased to a very low level to keep the conversion efficiency and extend the run length of these exhaust gas after-treatment systems and sustain very low levels of tail-pipe emissions even after 150-200 thousand kilometers of service. Table 1 summarizes the actual and target sulphur levels of motor gasoline in several countries/regions [2].

A more stringent sulphur specification of 50 ppm will come into force in the European

Union from 2005 but motor gasoline of <10 ppm sulphur content has to be made available regionally for the car owners in a geographically balanced manner.

The gasoline fraction of the fluid catalytic cracking unit (FCCU) usually provides a substantial amount (approximately 35-50%) of the refinery gasoline pool. FCC gasoline (and coker naphtha) has the highest concentration of sulphur compounds among gasoline blending components. Sulphur content of the FCC gasoline largely depends on the quality of the FCCU feed. It is a rule of thumb that the sulphur content of FCC gasoline is generally about one tenth of that of the FCCU feed. If the feed of FCCU is not

hydrotreated, FCC gasoline contains 500-5000 ppm sulphur, depending on the quality of the crude oil, type and composition of FCC catalyst, process conditions of the FCC unit, etc. Therefore, FCC gasoline is the largest contributor of sulphur compounds in the gasoline pool of the refinery. If FCCU

feed is pre-treated, the sulphur content of FCC gasoline can be relatively low (ca. 20-500 ppm) but mostly still not low enough to produce ultra low sulphur gasoline. Therefore, desulphurization of the catalytic cracked naphtha is necessary in most cases to meet the stringent specifications.

Table 1. Current and target sulphur limits of engine gasoline in selected developed countries

Country/region	Sulphur limit, ppm		Target date
	in 2002	target level	
European Union	150	10	2009
Germany	50	10	2003
USA	500	30	2005
Canada	150	30	2005
Japan	100	10	2008
Australia	500	150	2005

Basically, three strategies are available for reducing the sulphur concentration of FCC gasoline:

1. pre-treating the feed of FCCU (hydrodesulphurization/mild hydrocracking),
2. in-situ desulphurization in the FCCU (with additives for FCC catalyst, new catalyst matrix, etc.),
3. desulphurization of FCC gasoline (post-treating).

The first method has several advantages, e.g., higher yield and better quality of FCC products, lower SO_x emission of FCC regenerator, lower coke formation on the catalyst, etc., but the investment costs of such a unit are too high for a low ROI (return on investment). With the second method, the sulphur content can generally be reduced by 15-35%.

The first and second strategies are mostly not effective enough to produce ULSG (ultra low sulphur gasoline). Consequently, desulphurization of the FCC gasoline is necessary. FCC gasoline has a relatively high octane number (RON= 90-94; MON= 80-84) as a result of its high olefin and aromatic content (15-30%). If the cracked naphtha is hydrotreated on conventional CoMo/alumina catalyst, major part of the olefins are hydrogenated, therefore its octane number becomes substantially lower (even by 10 units). In addition, considerable amount of valuable hydrogen is consumed to saturate the double bonds of the alkenes, so the operating costs are high.

The researchers of the petroleum companies gave many answers to this technical challenge. One of the first innovations was fractionation of the gasoline into two or three cuts, because the light naphtha contains most of the olefin hydrocarbons, while the heavy naphtha contains most of the sulphur compounds [3]. Another favourable aspect of the fractionation is that most part of the sulphur content of light FCC naphtha is present in mercaptans which can be removed by caustic treatment without any loss of octane number. Proper design of the fractionating column is vital for optimal FCC gasoline desulphurization [4].

In order to exploit the different characteristics of the FCC gasoline fractions, numerous new desulphurization processes were developed. Some of these are designed to treat one particular fraction of the FCC gasoline, other processes are selective enough to treat the full range FCC gasoline without significant loss of octane number. The main characteristics of the new FCC gasoline desulphurization processes are given in Table 2 [5].

A number of catalysts were suggested in the literature for selective hydrodesulphurization of FCC gasoline with low level of octane number loss. For example, Dai et al. [6] and Sudhakar [7] disclose a process for selective hydrodesulphurization of FCC gasoline on a catalyst containing hydrotalcite-like compounds as support material. Sudhakar et al. suggest a novel

catalyst composition comprising non-noble metals supported on sulphided "manganese oxide octahedral molecular sieve" [8]. Kukes et al. reported a catalyst comprising molybdenum and cobalt components and a support containing magnesium and sodium components for selective hydrotreating of cracked naphtha [9]. Klimova et al. prepared Mo and NiMo HDS catalysts supported Al_2O_3 -MgO(x) mixed oxides and tested them in the hydrodesulphurization reaction of thiophene [10]. Zhao et al. evaluated fundamental functions of molybdenum sulfide catalysts on Mg-Al-O mixed oxide supports by hydrodesulphurization of model compounds and FCC gasoline [11]. In another work they investigated magnesium-

Experimental

Apparatus. The catalytic measurements were carried out in a high-pressure reactor system comprising a tubular reactor and all the main equipments of a commercial scale gasoline hydrotreating unit (pumps, separators, heat exchangers, controllers, etc). The reactor is free of back-mixing and its effective volume is 100 cm^3 . The gasoline product samples were taken under steady-state catalyst activity.

Catalysts. The hydrodesulphurization experiments were carried out on PtPd/USY-zeolite catalyst (Table 3). A commercially available CoMo/ Al_2O_3 catalyst was used as a reference.

Feeds. The feed was an industrial full boiling range FCC gasoline produced by cracking of pre-treated FCCU feed. The main characteristics are summarized in Table 4. The original sulphur content (66 ppm) of this base FCC gasoline was increased to 196 ppm by adding benzothiophene.

aluminum, copper-aluminum, zinc-aluminum hydrotalcite compounds synthesized by coprecipitation method for selective hydrodesulphurization [12].

Noble metals supported on USY-zeolite are reported to have high and stable activity for desulphurization of thiophene [13]. The objective of this work is to evaluate the performance of PtPd/USY-zeolite compared to a conventional CoMo/ Al_2O_3 catalyst for the desulphurization of full range FCC gasoline. It is known that the sulphur tolerance of these catalysts is limited. That is why we used a full range FCC gasoline of relatively low sulphur content for our experiments.

Process parameters.

The process parameters of the experiments are given in Table 5. The same process conditions were applied for both catalysts, except H_2 /hydrocarbon ratio.

Methods.

Composition of the vapor phase products leaving the reactor was determined with online gas chromatograph, according to ASTM D 5134-99. Composition of the feedstock and liquid products were also determined by gas chromatography, called CHROMOCTANE method. Octane numbers were calculated from the compositions by software (CARBURANE). Sulphur and nitrogen contents were measured with APS analyzer (type APS-35) according to ASTM D-6428-99 and ASTM-D 6366-99, respectively.

The olefin saturation was calculated as follows:

$$\text{olefin saturation} = 100 (\text{olefin}_{\text{feed}} - \text{olefin content}_{\text{product}}) / \text{olefin}_{\text{feed}}$$

where:

- $\text{olefin}_{\text{feed}}$: olefin content of the feed, wt%
- $\text{olefin}_{\text{product}}$: olefin content of the products, wt%

Table 3. Main characteristics of PtPd/USY zeolite catalyst

Properties	Data
Composition, %	
Palladium content	0.45
Platinum content	0.15
Y-zeolite and binder	remaining
Physical properties	
loading density, g/cm ³	0.5
crush strength, N/mm	6.2
BET surface area, m ² /g	650

Table 4. Main characteristics of the FCC gasoline feed

Properties	Feed "A"	Feed "B"
Density (15.6°C) g/cm ³		0.7699
Sulphur content, ppmw	66	196*
Nitrogen content, ppmw		18
Research octane number		90.8
Motor octane number		79.4
Composition, wt%		
n-paraffins		4.0
i-paraffins		31.8
olefins		24.9
naphthenes		8.1
aromatics		31.2
Distillation properties, °C		
Initial boiling point		46
10 V/V%		73
30 V/V%		95
50 V/V%		121
70 V/V%		149
90 V/V%		184
Final boiling point		205

*increased to 196 ppm by adding benzothiophene

Table 5. Process conditions of the tests

Temperature, °C	230-320
Pressure, barg	30
Liquid hourly space velocity (LHSV), h ⁻¹	1.0-3.0
H ₂ /hydrocarbon ratio, Nm ³ /m ³	PtPd/Y-zeolite : 200 ; CoMo/Al ₂ O ₃ : 300

Results and discussion

CoMo/Al₂O₃ catalyst. The results of the desulphurization experiments carried out over the commercial CoMo/Al₂O₃ catalyst indicated that the yield of liquid products was higher than 99,5%, so hydrocracking reactions did not significantly proceed under the investigated process conditions.

Figure 1 shows the sulphur content of the liquid products as a function of temperature. The continuous curves relate to the results obtained with the base FCC gasoline feed and the dashed curves represent the data when benzothiophene was added to the base FCC gasoline and thereby its sulphur content was increased to 196 ppm. By increasing the temperature and decreasing the space velocity, the sulphur content of the products became lower. In order to obtain products having <10 ppm sulphur content, the temperature of the reactor should be at least 260°C with LHSV of 1.0 and at least 280°C with all other investigated LHSVs when the base FCC gasoline of 66 ppm sulphur content was used. When feed "B" is introduced, the following process conditions can be applied to decrease the sulphur content of 196 ppm below 10 ppm: T=300°C, LHSV=1.0 or T=320°C, LHSV= 1.0-2.0.

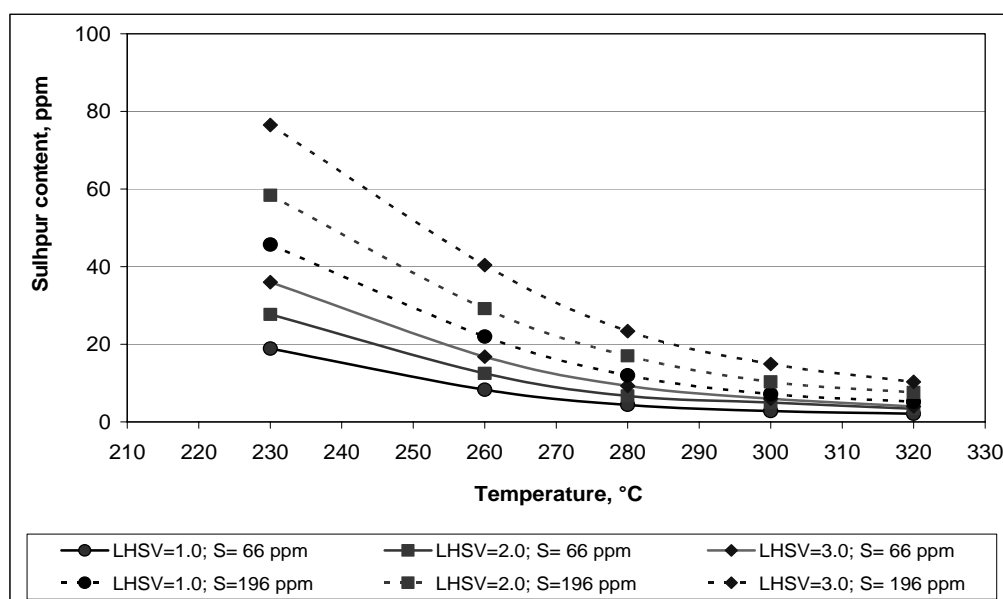


Figure 1. Sulphur content of the products at different LHSVs as a function of temperature (catalyst: CoMo/Al₂O₃)

The change of olefin saturation as a function of temperature and LHSV in case of CoMo/Al₂O₃ catalyst is illustrated in Figure 2. The catalyst showed very high alkene hydrogenation activity even under mild process conditions. Even the lowest value of olefin saturation was ca. 50% when feed "A" was used (T=230°C; LHSV=3.0).

The results indicated that higher sulphur content of the feed has very little effect on the olefin hydrogenation activity of CoMo/Al₂O₃ catalyst, since the difference between olefin content of the products obtained under the same operating conditions from feed "A" and those produced from feed "B" was less than 3 absolute % in every case. Considering the relationship between the olefin hydrogenation and hydrodesulphurization activity of the catalyst, products having <10 ppm sulphur content can only be produced with at least 85% olefin saturation in case of feed "A" and at least 96% olefin saturation in case of feed "B". Our results correlate with other tests and confirm that conventional CoMo/alumina catalysts are not suitable for selective desulphurization of FCC gasolines.

The octane numbers of the olefins are significantly lower than those of the corresponding alkanes in most cases. For example the research octane number (RON) of n-hexene is by 51.6 units higher than that of n-hexane. If the double bond of an isoolefin is saturated, the loss of RON is generally lower than in the case of n-olefin saturation; e.g., when 2-methyl-butene is hydrogenated, the RON loss is "only" 37.4 units instead of 51.6. The RON loss, due to the saturation of the

double bond, generally increases with the carbon number of the olefins. The differences between the RON of the feed and of the products are shown in Figure 3. Due to high olefin hydrogenation activity of the catalyst the loss of RON was high even at low temperatures. The lowest RON loss was ca. 2.2 units in case of feed "A" but at a product sulphur level of 10 ppm it was at least 5.3 units which is considerable. Summarizing, the sulphur content of the FCC gasolines can only be reduced below 10 ppm with inadmissible loss of octane number.

PtPd/USY-zeolite catalyst. Despite the fact that the Y-zeolite has very high cracking activity at higher temperatures (>400°C), it had no significant hydrocracking activity in the investigated temperature range and therefore the yield of liquid products was high (>99,5%), similarly to the CoMo/Al₂O₃ catalyst.

The desulphurization activity of PtPd/USY-zeolite catalyst was very similar to that of the commercial CoMo/Al₂O₃ (cf. Figures 1 and 4). The sulphur content of the products obtained by hydrotreating the base FCC gasoline was lower than 10 ppm even at 280°C and LHSV of 2.0 (Figure 4). In case of feed "B", the temperature had to be at least 300°C to produce ultra low sulphur FCC gasoline. Thus, considering desulphurization activity, PtPd/Y-zeolite has no significant advantage compared to CoMo/alumina.

PtPd/Y-zeolite is much more advantageous, however, when olefin hydrogenation is regarded. Its olefin saturation activity is substantially lower (Figure 5) than that of the CoMo/Al₂O₃ catalyst (Figure 2). The olefin

saturation was lower than 50% at $\leq 280^\circ\text{C}$ at all LHSV. On PtPd/Y the olefin hydrogenation decreased to higher degree by sulphur content of the feed than on CoMo/Al₂O₃. Olefin content of the products of feed "B" was still by 3-4 abs. % higher than in case of feed "A" on PtPd/Y compared to that on CoMo/Al₂O₃ (cf. Figures 4 and 2).

Considering 10 ppm sulphur content of the products, the olefin saturation was only ca. 35% in case of feed "A" and ca. 45% in case of feed "B". Using CoMo/Al₂O₃ catalyst these values were 85% and 96%, respectively. Based on the previous results we suggest that PtPd/USY zeolite catalyst can be preferably applied for selective hydrodesulphurization of FCC gasolines having relatively low sulphur content (<300 ppm). An explanation for the selectivity of PtPd/USY-zeolite may be that desulphurization reactions hinder the hydrogenation of alkenes since sulphur

compounds are preferentially adsorbed on the metal sites, inhibiting the adsorption of alkenes.

Accordingly, the loss of research octane number was significantly lower on the Y-zeolite supported bimetallic catalyst (Figure 6). The shape of the curves is completely different as in Figure 3. The loss of octane number under mild process conditions is small and it increases moderately with temperature.

In order to illustrate more clearly the differences between the relationship of desulphurization and olefin hydrogenation for the two catalysts, the loss of RON as a function of sulphur content of the products is shown in Figure 7. It is well demonstrated that at a product sulphur level of 20 ppm the RON loss is ca. 3 units and at 10 ppm product sulphur level 2.5-3.0 units lower on PtPd/USY-zeolite than on conventional CoMo/alumina.

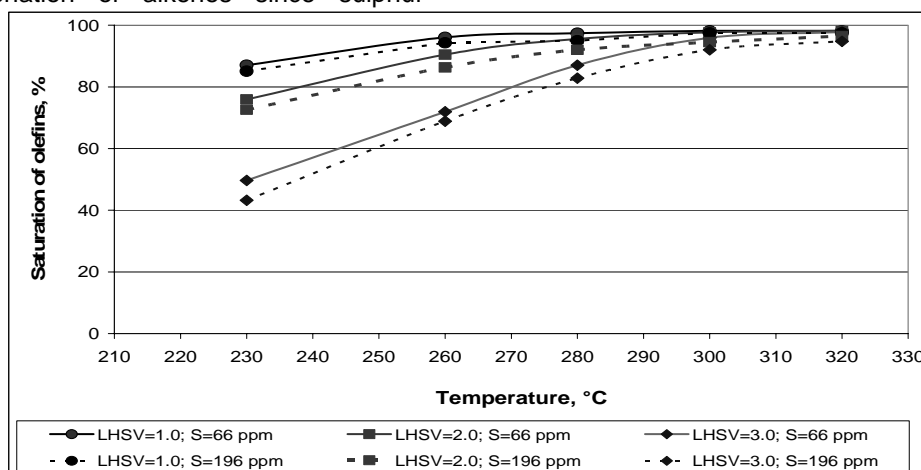


Figure 2. Olefin saturation at different LHSV as a function of temperature (catalyst: CoMo/Al₂O₃)

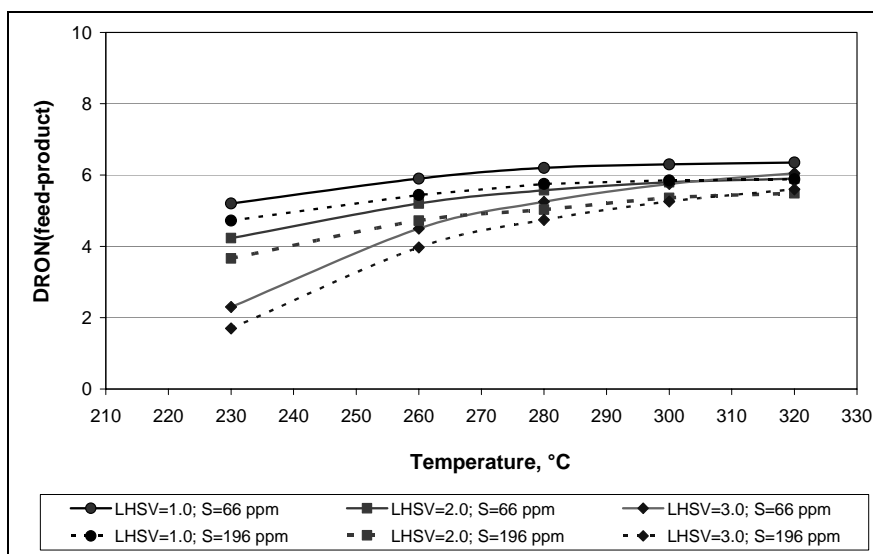


Figure 3. Loss of research octane number at different LHSVs as a function of temperature (catalyst: CoMo/Al₂O₃)

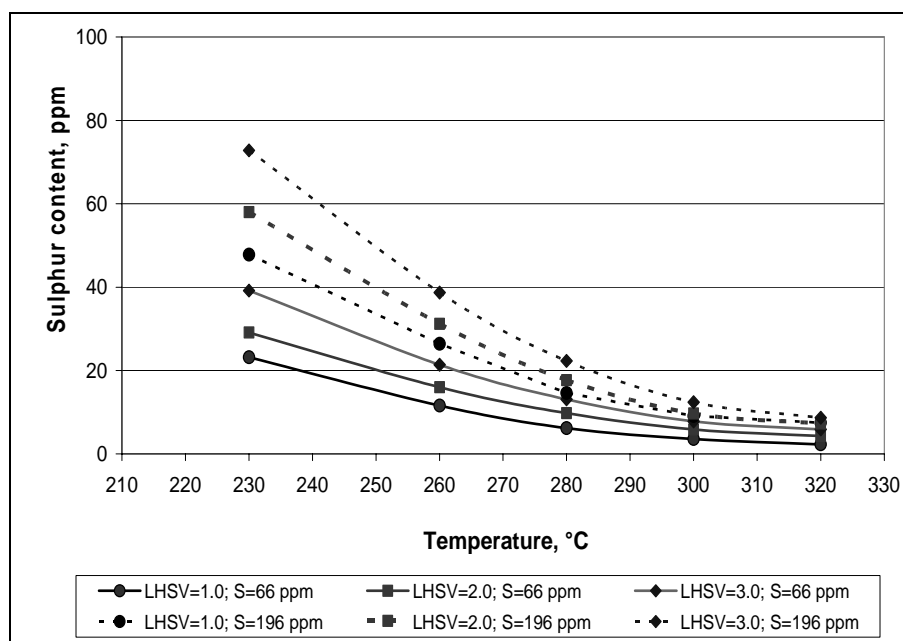


Figure 4. Sulphur content of the products at different LHSVs as a function of temperature (catalyst: PtPd/USY-zeolite)

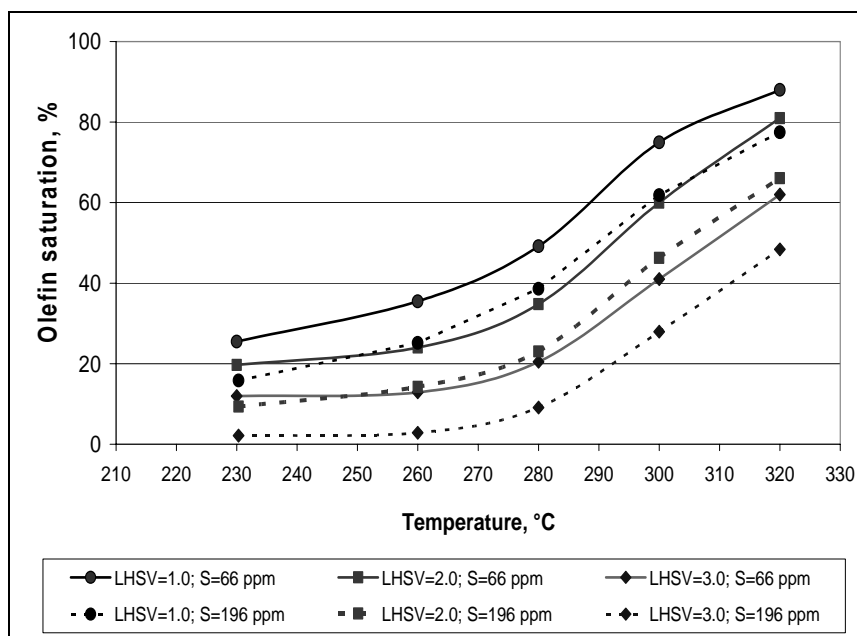


Figure 5. Olefin saturation at different LHSV as a function of temperature (catalyst: PtPd/USY-zeolite)

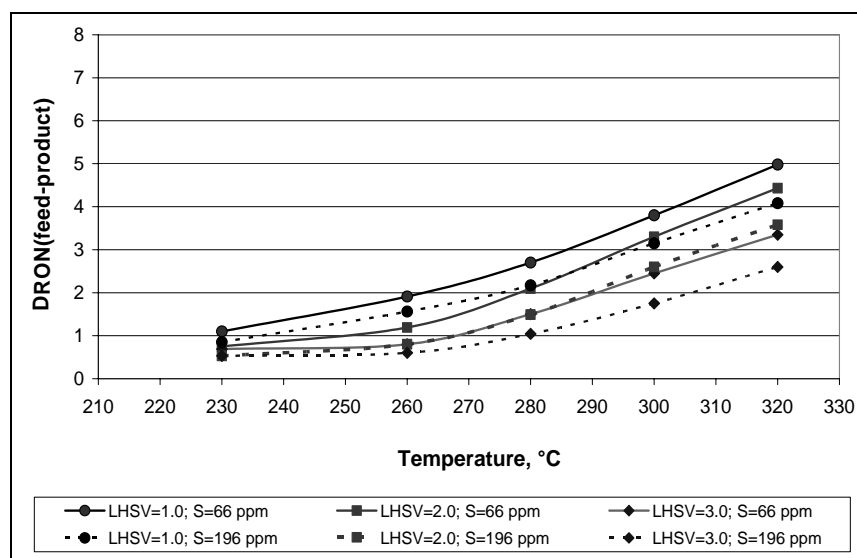


Figure 6. Loss of research octane number at different LHSV as a function of temperature (catalyst: PtPd/USY-zeolite)

The numerical characteristics of the products obtained over CoMo/Al₂O₃ and PtPd/USY-zeolite having ca. 10 ppm sulphur content are compared in Table 6. These data also confirm the superior performance of the zeolite supported catalyst against the conventional CoMo.

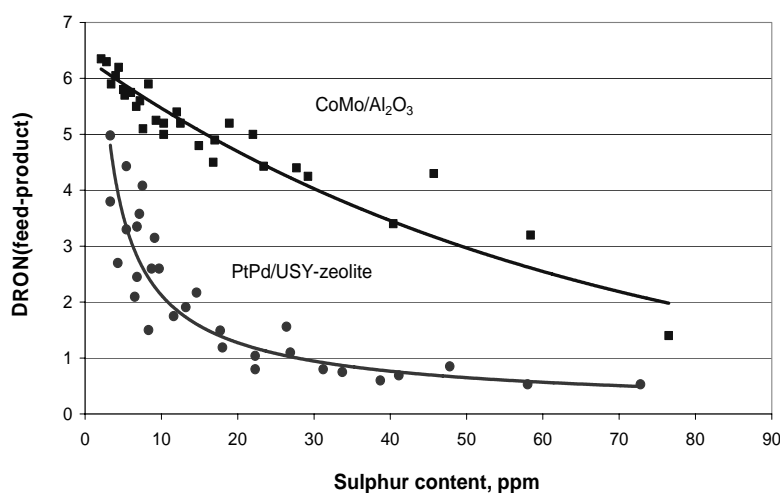


Figure 7. Loss of RON as a function of sulphur content of the products

Table 6. Main properties of the products at ~10 ppm sulphur content of the products

Characteristics	CoMo/Al ₂ O ₃		PtPd/USY-zeolite	
	66	196	66	196
Sulphur in feed, ppm	66	196	66	196
Operating conditions				
Temperature, °C	280	300	280	300
Pressure, barg	30	30	30	30
LHSV, h ⁻¹	3.0	2.0	2.0	2.0
H ₂ /HC, Nm ³ /m ³	300	300	200	200
Liquid products				
Yield, %	>99.5	>99.5	>99.5	>99.5
Density, g/cm ³	0.7420	0.7421	0.7436	0.7435
Sulphur content, ppm	~10	~10	~10	~10
Nitrogen content, ppm	<7	<5	<1	<1
Composition				
n-paraffins	12.13	13.13	7.14	8.04
i-paraffins	45.07	46.09	35.96	39.29
olefins	3.50	1.48	17.60	13.37
aromatics	30.66	30.13	29.89	29.96
naphthenes	8.64	9.17	9.41	9.34
RON	88.2	88.4	91.3	90.8
ΔRON (feed-product)	5.3	5.0	2.1	2.6
MON	77.4	77.4	80.6	79.9
ΔMON (feed-product)	4.3	4.3	1.1	1.8

Summary

Many refineries have a HDS or mild hydrocracking unit to pre-treat the feed of the fluid catalytic cracking unit. The sulphur content of such FCC gasoline is relatively low. Therefore, catalyst with limited sulphur tolerance may also be applied for upgrading it.

It was found that PtPd/USY-zeolite is suitable for selective desulphurization of FCC gasolines having relatively low sulphur content, i.e. <300 ppm. The experiments carried out with conventional CoMo/Al₂O₃ reference catalyst showed that hydrogenation activity of the proposed bimetallic zeolite catalyst was significantly lower relative to the reference catalyst. Consequently, the loss of RON through hydrodesulphurization of full range FCC gasoline (sulphur content: 66 and 196 ppm) was ca. 2.5-3.0 units lower than in the case of CoMo/alumina. The better selectivity of PtPd/USY-zeolite may be explained with the preferential adsorption of sulphur compounds on the catalyst thereby inhibiting hydrogenation reactions.

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