Reactivity of several olefins in the HDS of full boiling range FCC gasoline over sulphided CoMo/Al_2O_3

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Deep desulphurization of olefinic fluid catalytically cracked naphtha fractions (hereafter FCC gasolines) is essential for the crude oil refineries in order to meet stringent sulphur limits (e.g. <10 mg/kg in the EU beginning with 2009) of engine gasolines. The olefins in FCC gasolines are subjected to hydrogenation under deep hydrodesulphurization (HDS) conditions. The aim of this study was to investigate the reactivity of several olefins contained in a full boiling range FCC gasoline matrix during HDS over a new generation CoMo/Al_2O_3 catalyst. It was found that the isomerization of olefinic double bond is extremely fast under HDS conditions (230-280°C; 30 bar; LHSV: 2.0-5.0;H2/HC: 300 Nm^3/m^3). The composition of *n*-pentenes (1-pentene, *cis*-2-pentene and *trans*-2-pentene) was found to be practically constant in the LHSV range of 2.0-5.0 h^{-1}, indicating that conversion of double bond shift was practically equilibrium and the different hydrogenation rate of *n*-pentene isomers played a negligible role.

1. Introduction

Desulphurization of FCC gasoline is a key process in refineries blending gasoline of ultra low sulphur content. Among the main FCC gasoline sulphur reduction options (pre-treating, in-situ sulphur reduction in the FCC unit by using catalyst additives, post-treating), hydrotreatment of cracked naphtha is still the most preferred method. Hydrodesulphurization (HDS) on conventional CoMo/Al_2O_3 catalysts results in significant olefin saturation and high H_2 consumption making this process unsuitable for cracked naphtha upgrading. Numerous methods have been developed to overcome this problem. These options are reviewed in several papers (Babich and Moulijn, 2003; Brunet at al., 2005; Song, C., 2003).
The dissimilar reactivity of various olefins can have a significant effect on the octane number of the products, because the difference in the RON or MON between a certain olefin and its saturated paraffin derivative can greatly depend on its structure and carbon number. This is well represented in Table 1.
A number of researchers studied the effect of the carbon number or structure of olefins on their reactivity under the conditions typical for FCC gasoline HDS. Meerbott and Hinds presumed already in 1955 that n-olefins may hydrogenate faster than isoolefns during FCC gasoline HDS. Lebedev's rule, based on the liquid phase hydrogenation of

Table 1. Difference between the average RON or MON of various olefin groups and their paraffin derivatives

Olefins	Paraffins	ΔRON	ΔMON
n-pentenes	n-pentane	26.0	13.8
n-hexenes	n-hexane	62.9	48.8
n-heptenes	n-heptane	72.6	66.3
methyl-butenes	methyl-butane	4.7	-9.4
methyl-pentenes	methyl-pentanes	23.7	9.0
methyl-hexenes	methyl-hexanes	41.3	26.2
dimethyl-butenes	dimethyl-butanes	-4.9	-12.5
dimethyl-pentenes	dimethyl-pentanes	7.9	-5.2
dimethyl-hexenes	dimethyl-hexanes	23.4	2.5

ΔRON: average RON of an olefin group minus average RON of a paraffin group

olefin couples over Pt/Al_2O_3 catalyst at 20°C states that hydrogenation rate of olefins decreases with the number of substituents on the double bond. However, it is difficult to obtain similar results in gas phase reactions, where extensive double-bond migration takes place, transforming each olefin in a mixture of isomers (Germain, 1969). In a recent study, Toba et al. (2007) found that the conversion of *trans*-olefins is lower that those of *cis*-olefins and the conversion of internal olefins is lower than those of terminal olefins during the HDS of FCC gasoline over sulphided $CoMo/Al_2O_3$. They suggested that the lower conversion of *trans*-olefins and internal olefins is caused by their lower hydrogenation rate because of the steric hindrance of the double bond.
The aim of this study, was to try to clarify the behaviour of several olefins in the hydrodesulphurization of a full boiling range FCC gasoline.

2. Experimental

2.1. HDS pilot-unit

The tests were carried out in a pilot scale HDS unit. The effective volume of the down-flow HDS reactor is 100 cm^3. The test system contained all the equipments and devices (pumps, separators, heat exchanger as well as temperature, pressure and gas flow controllers), which are applied in full-scale commercial gasoline desulphurization units. The tests were carried out in continuous operation.

2.2. Feedstock

Full boiling range FCC gasoline was used as a feedstock of the HDS tests. The feed was supplied by a local refinery processing Russian crude oil. Its main characteristics are as summarized in Table 1. The concentration of several olefins contained in the FCC gasoline is given in Table 2.

2.3. Catalysts

The catalyst was a new generation $CoMo/Al_2O_3$, which was used in sulphided form. It is currently used for the selective HDS of FCC gasolines on industrial scale. Catalyst properties are confidential.

Table 1. Main characteristics of the full boiling range FCC gasoline feed

Characteristics	Full range FCC gasoline feed
Density, g/cm^3	0.7371
Sulphur content, mg/kg	525
Nitrogen content, mg/kg	34
Hydrocarbon composition, wt%	
n-paraffins	5.1
i-paraffins	32.2
olefins	23.2
naphthenes	9.2
aromatics	28.0
Research octane number	92.4
Motor octane number	81.2

2.4. Analytical methods

Composition of feedstocks and liquid products were also determined by gas chromatography according to a modified version of NF M07-086 method. Octane numbers were calculated from the compositions using CARBURANE software. Sulphur and nitrogen contents were measured according to ISO 20846 and ASTM-D 6366-99, respectively (Multi EA 3100).

2.5. Test conditions

The process conditions of the test were typical for gasoline HDS: temperature: 230-290°C; pressure: 30 bar; ratio of H_2/hydrocarbons: 150 Nm^3/m^3 and liquid hourly space velocities (LHSV): 2.0-5.0.

Results and discussion

The results showed that the rate of olefin hydrogenation under the conditions of gasoline HDS decreases with the carbon number of the olefin (Figure 1.). Although hydrogenation of *n*-pentenes is significantly faster than those of methyl butenes, the conversion of *n*-hexenes is barely higher than those of methyl pentenes. These findings are in accordance with Lebedev's rule.

Table 2. Concentration of several olefins in the FCC gasoline feed

Olefin	Conc., wt%	Olefin	Conc., wt%
1-butene	0.62	3-methyl-1-pentene	0.20
trans-2-butene	0.49	1-hexene	0.29
cis-2-butene	0.57	trans-3-hexene	0.31
3-methyl-1-butene	0.49	cis-3-hexene	0.10
1-pentene	1.79	2-methyl-2-pentene	0.73
2-methyl-1-butene	1.91	3-methyl-trans-2-pentene	0.68
trans-2-pentene	2.06	3-methyl-cis-2-pentene	0.95
cis-2-pentene	1.14	trans-2-hexene	0.63
2-methyl-2-butene	2.96	cis-2-hexene	0.42
4-methyl-1-pentene	0.22		

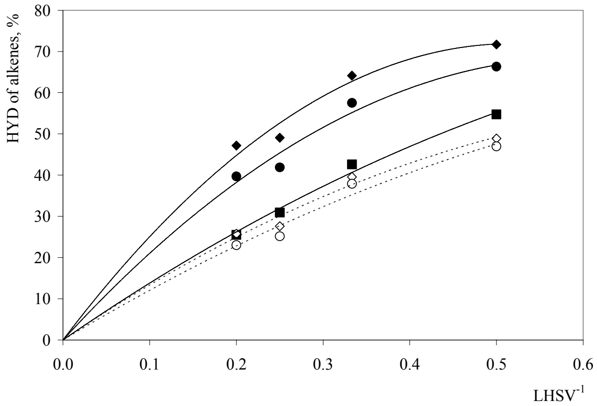

Figure 1. Hydrogenation of n-alkenes and methyl alkenes vs. contact time (reaction temperature: 290°C; ◆ *n-butenes* ● *n-pentenes* ■ *n-hexenes* ◇ *methyl butenes* ○ *methyl pentenes)*

Our results also showed that double-bond migration took place during the HDS of the FCC gasoline feed, because the conversion of certain olefins (e.g. *trans*-2-pentene and 2-methyl-2-butene) was negative (Figure 2), indicating that more of these olefins formed from other olefin isomers, than they were consumed in their saturation to paraffins. Similarly to the results of Toba et al. (2007), conversion of terminal olefins was much higher than those of internal ones also in our tests.

Figure 3 shows the composition of *n*-pentene isomers (1-pentene, *cis*-2-pentene and *trans*-2-pentene) as a function of apparent contact time, (LHSV^{-1}). It can be seen that the initial composition of *n*-pentenes in the feed (36 wt% 1-pentene; 23 wt% *cis*-2-pentene and 41 wt% *trans*-2-pentene) significantly alters even in case of a relatively short contact time, where the conversion (hydrogenation) of *n*-pentenes is quite low.

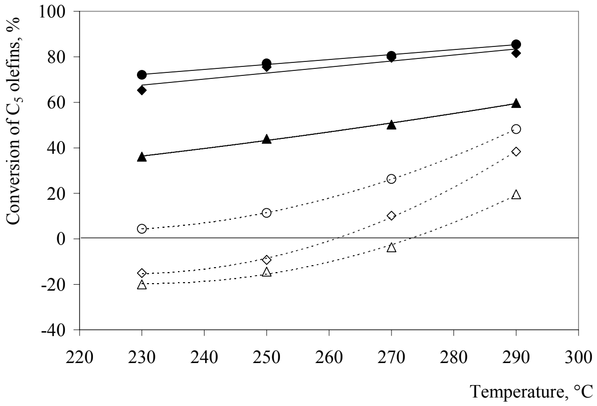

Figure 2. Conversion of C_5 olefins as a function of reaction temperature (LHSV=3.0; ● *1-pentene* ○ *cis-2-pentene* ◇ *trans-2-pentene* ▲ *2-methyl-1-butene* △ *2-methyl-2-butene* ◆ *3-methyl-1-butene*)

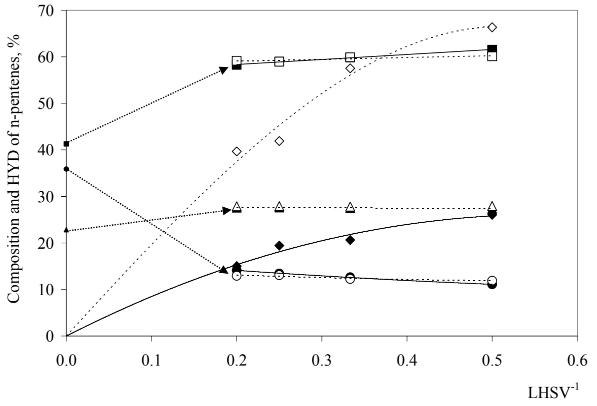

Figure 3. Composition and hydrogenation of n-pentenes vs. contact time (feedstock composition is plotted on axis Y; ● 1-pentene, 230°C; ○ 1-pentene, 290°C; ▲ cis-2-pentene, 230°C; △ cis-2-pentene, 290°C; ■ trans-2-pentene, 230°C; □ trans-2-pentene, 290°C; HYD of n-pentenes, 230°C; HYD of n-pentenes, 290°C)

It is interesting to note that after hydrogenation the composition of n-pentenes in the product does not seem to depend on the contact time; it remains almost constant (11-13 wt% 1-pentene; 27-28 wt% *trans*-2-pentene and 59-60 wt% *cis*-2-pentene) while their hydrogenation clearly increases. In fact, the composition of *n*-pentene isomers is also practically constant as function of the temperature in the investigated range of 230-290°C. This suggests that under gasoline HDS conditions the rate of double-bond shift is much more higher compared to that of hydrogenation leading to a near-equilibrium composition of olefins taking part in double-bond shift reactions.

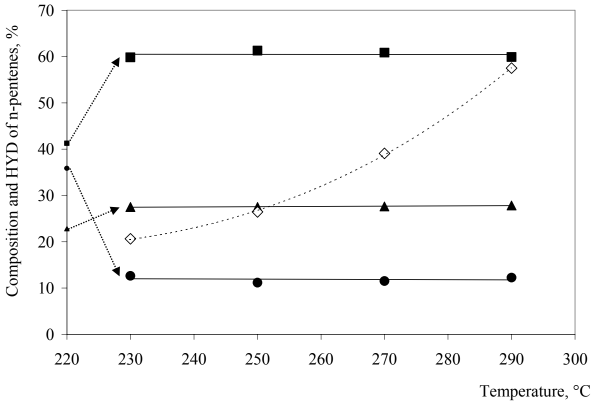

Figure 4. Composition and hydrogenation of n-pentenes vs. reaction temperature (LHSV= 3.0;feedstock composition is plotted on axis Y; ● 1-pentene ▲ cis-2-pentene ■ trans-2-pentene ◇ HYD of n-pentenes)

Consequently, the different conversion of olefin isomers can be originated to double-bond isomerization instead of the different hydrogenation rates.

Analogically, this phenomenon also applies for the methyl butenes isomers (Figure 5.). Composition of methyl butenes in the products is also practically constant in function of the tested values of temperature and LHSV.

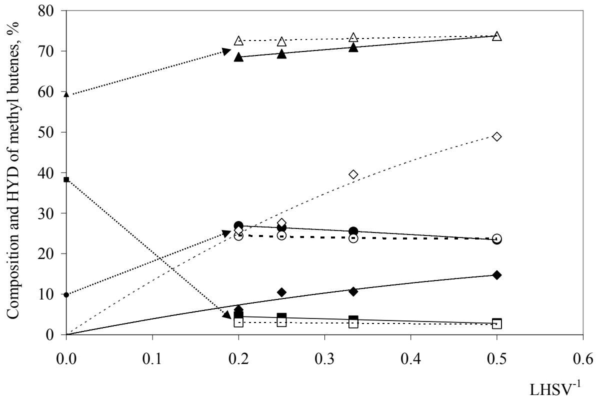

Figure 5. Composition and hydrogenation of methyl butenes vs. contact time (feedstock composition is plotted on axis Y; ● 2-methyl-1-butene, 230°C; ○ 2-methyl-1-butene, 290°C; ▲ 2-methyl-2-butene, 230°C; △ 2-methyl-2-butene, 290°C; ■ 3-methyl-1-butene, 230°C; □ 3-methyl-1-butene, 290°C; HYD of methyl butenes, 230°C; HYD of methyl butenes, 290°C)

Conclusions

Higher conversion of terminal olefins in FCC gasoline HDS is caused by their conversion to internal ones. Composition of olefin isomers (e.g. 1-pentene, *cis*-2-pentene and *trans*-2-pentene; analogically for methyl butenes) in the products follows the equilibrium conversion and it is not easy to observe any differences in the hydrogenation rate of olefin isomers in these conditions due to fast double-bond shift.

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