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Catalysis Today 97 (2004) 277–282

CATALYSIS TODAY

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Conversion of naphthenes to a high value steamcracker feedstock using H-ZSM-5 based catalysts in the second step of the ARINO®-process

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Abstract

Future regulations for the limitation of sulfur and aromatics in fuels driven by the European Auto Oil Program (AOP II) stimulate the need for an alternative utilization of the resulting surplus of pyrolysis gasoline (pygas). The conversion of heavy pyrolysis gasoline into valuable steam cracker feedstock with a maximum yield of C_2–C_4 *n*-alkanes is achieved via the ARINO® two-step process, jointly developed by Linde, VEBA Oil and Süd-Chemie. The first step involves a hydrogenation of aromatics to naphthenes followed by the subsequent ring opening and cracking in the second step.

Süd-Chemie developed a new commercial cracking catalyst for the second step of the ARINO® process with the aim to maximize the yield of C_2–C_4 *n*-alkanes at low formation of methane and aromatics. The ring opening and cracking reaction of naphthenes was studied in a bench scale tubular reactor over extruded H-ZSM-5 based zeolite catalysts.

In a series of screening tests using a commercial, hydrogenated and desulphurized heavy pyrolysis gasoline, the influence of the preparation parameters such as zeolite acidity, palladium content as well as the type of binder were investigated. Furthermore, the influence of the process conditions space velocity and temperature was studied.

High yields of C_2–C_4 *n*-alkanes at low formation of undesired methane and aromatics were achieved over an alumina bound zeolite with medium Brønsted acidity loaded with palladium.

The reduction of the space velocity resulted in an increase in the C_2–C_4 *n*-alkane yield and lower formation of aromatics, but a simultaneous increase in the methane make. Raising the temperature from 280 to 370 °C significantly increased the catalyst activity.

Keywords: ARINO®-process; Heavy pyrolysis gasoline; Naphthene cracking; Pd/H-ZSM-5-cracking catalyst; C_2–C_4 *n*-alkanes

1. Introduction

The European Community agreed in the Auto Oil Program (AOP II) to reduce the total aromatics content in motor gasoline from 42 vol.% at present down to 35 vol.% in 2005 [1] (see Table 1).

The announced legislation rises a challenging scenario for European refineries. A surplus of C_7/C_8 aromatics of about 4–5 million tonnes per year (tpy) will result because the current average concentration of aromatics in the European gasoline production is about 39 vol.% [2].

One main source of aromatics is the so-called heavy pyrolysis gasoline, a by-product of the production of ethylene and propylene by steam cracking of naphtha. The use of pygas as a blending stock for motor gasoline will be reduced considerably by the AOP II, however, the predicted worldwide increasing demand of ethylene [3,4] and propylene [3,5] will increase the surplus of heavy pyrolysis gasoline and a loss of the heavy pygas value is obvious. This post AOP II scenario will be even worse if refiners follow the suggestion to meet the aromatic specification by dilution with light naphtha isomerisate. The removal of light naphtha from the steamcracker feedstock pool further increases the heavy pygas to ethylene product ratio because the amount of pygas produced depends on the feedstock type. The resulting

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2004.07.004

Table 1
European 2005 gasoline specification

Gasoline specification (maximum)	
Olefin content (vol.%)	10
Aromatics (vol.%)	35
Benzene (vol.%)	1
Oxygen (vol.%)	2.7
Sulfur (wt. ppm)	10

European Auto Oil Program (AOP II), January 2005.

surplus of pygas stimulates the need for other economical and technical solutions.

An innovative technology for upgrading heavy pyrolysis gasoline has been jointly developed by Linde, VEBA Oil and Süd-Chemie. The Aromatic RINg Opening (ARINO$^{®}$) concept converts heavy pyrolysis gasoline into a valuable steam cracker feedstock with high amounts of C_2–C_4 *n*-alkanes according to a two-step reaction concept.

1. In the first step the *aromatics are saturated* to naphthenes under medium pressure and at moderate temperature using a commercially available nickel or precious metal based hydrogenation catalyst.
2. In the second step the *naphthenic rings are opened* and the molecules are cracked to smaller paraffins in the presence of hydrogen. A suitable catalyst for this step is a H-ZSM-5 based catalyst loaded with palladium [6–8], which is in contrast to such typical bifunctional catalysts characterized by a palladium content of only maximum 0.1 wt.% [7].

Within an R&D project Süd-Chemie designed a new commercial catalyst for the second step (ring opening and cracking reaction of the ARINO$^{®}$ process) in order to maximize the yield of C_2–C_4 *n*-alkanes at low formation of methane and aromatics with regard to the following preparation and process parameters.

- Palladium content
- Zeolite acidity
- Binder type
- Weight hourly space velocity (WHSV)
- Temperature

2. Experimental

The ring opening and cracking reaction was investigated with a commercial, hydrogenated and desulphurized heavy pyrolysis gasoline consisting of naphthenes (predominantly C_7–C_9 naphthenes) as well as smaller amounts of poly-naphthenes, olefins, aromatics and paraffins. Screening tests were carried out over a catalyst as fixed bed in a bench scale tubular reactor (Fig. 1a) at 60 bar (g), a gas inlet temperature of 370 °C, a WHSV of 2 kg/(kg h) and at a hydrogen to oil ratio of 700 Nl/kg. During the tests the reference inlet temperature 30 mm in front of the catalyst bed was kept constant (see Fig. 1b).

In each test a sample of 20 g catalyst (extrusions, particle size: 1.59 mm diameter and 2–3 mm length) was diluted with SiC in the weight ratio 1:6, in order to minimize the temperature gradient caused by the strong exothermal reaction within the catalyst bed. The activation of the catalyst was carried out with hydrogen at 400 °C and atmospheric pressure.

The gas phase was analyzed online by a Agilent Refinery Gas Analyser (Micro GC) equipped with thermal conductivity detectors. The C_1–C_2 hydrocarbons were separated by a PoraPlot column, the C_3–C_4 hydrocarbons

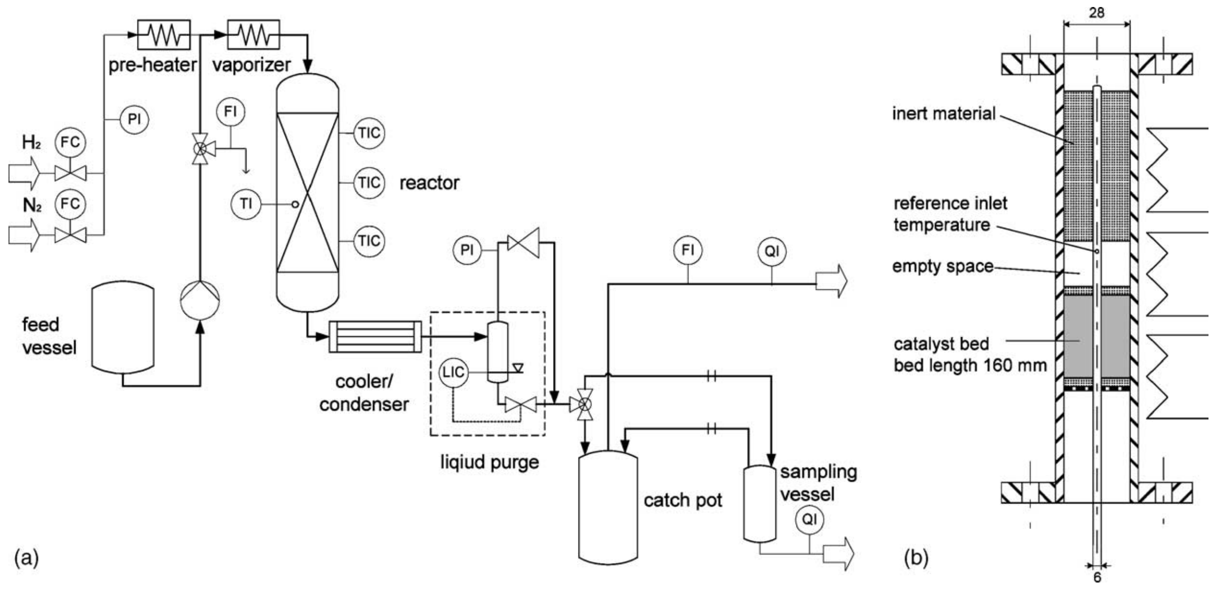

Fig. 1. Test unit (a) and reactor loading scheme (b).

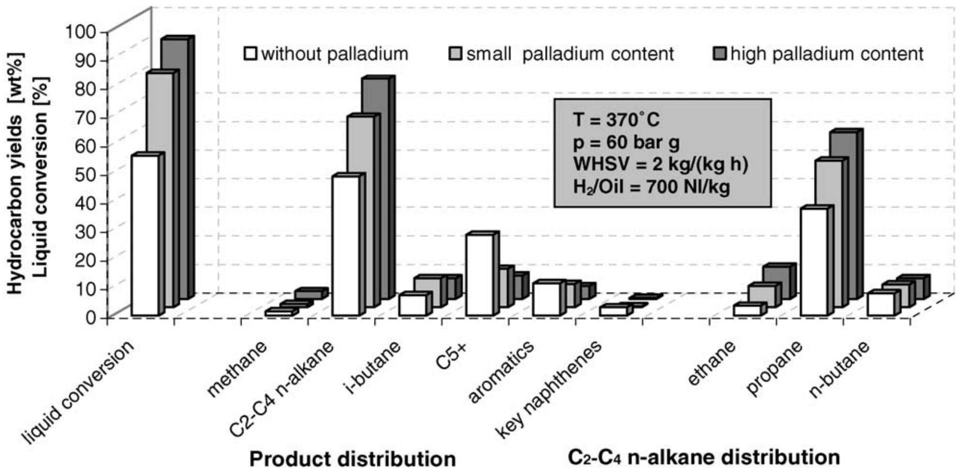

Fig. 2. Influence of the palladium content on the liquid conversion and the product distribution over an alumina bound medium acidic H-ZSM-5.

by a AluminaPlot column and the C_5–C_6 hydrocarbons by a OV-1 column. The content of aromatics in the liquid phase was determined offline by HPLC. The solved gaseous components and selected naphthenes were analyzed by GC equipped with a RTX-1 column and a flame ionization detector. Due to the complex composition of the commercial feedstock, a simple liquid conversion rate was used for the evaluation of the activity. The liquid conversion was calculated from the liquid amount before and after the reaction at atmospheric conditions. The presented key naphthenes were methylcyclopentane, methylcyclohexane, ethylcyclohexane and *iso*-propylcyclohexane.

3. Results and discussion

3.1. Investigation of the preparation parameters

The effect of the preparation parameters palladium content, Brønsted acidity and binder type in the ring opening and cracking reaction will be discussed. In order to ensure the comparability between the catalyst samples, the presented results refer to activities after 72 h on stream.

The influence of palladium loading over an alumina bound medium acidic H-ZSM-5 is shown in Fig. 2.

The palladium free zeolite catalyst shows a low liquid conversion and poor C_2–C_4 *n*-alkane yield, which should be caused by the absence of the palladium. No signs of olefin formation were observed, which is attributed to the activation of the hydrogen by the acid sites [6,8].

The performance of the pentasil type catalyst is significantly improved by loading the catalyst with palladium. Higher C_2–C_4 *n*-alkane yield at low formation of undesired by-products methane and aromatics were observed for a zeolite with small palladium content. A further increase of the palladium content, but still smaller than that of a typical bifunctional catalyst [7], result in an improvement of the liquid conversion up to 91% and a C_2–C_4 *n*-alkane yield up to 77% with simultaneous decrease of the aromatics yield below 5 wt.%. However, the higher palladium loading resulted in an slightly increased methane formation.

The C_2–C_4 *n*-alkane fraction presented in Fig. 2 consisted predominantly of propane as well as small amounts of

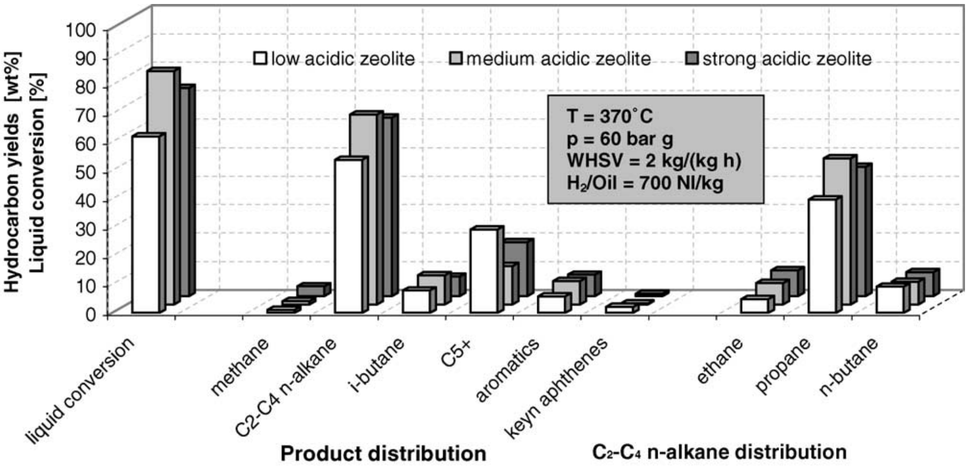

Fig. 3. Influence of the zeolite acidity on the liquid conversion and the product distribution over an alumina bound H-ZSM-5 with small Pd content.

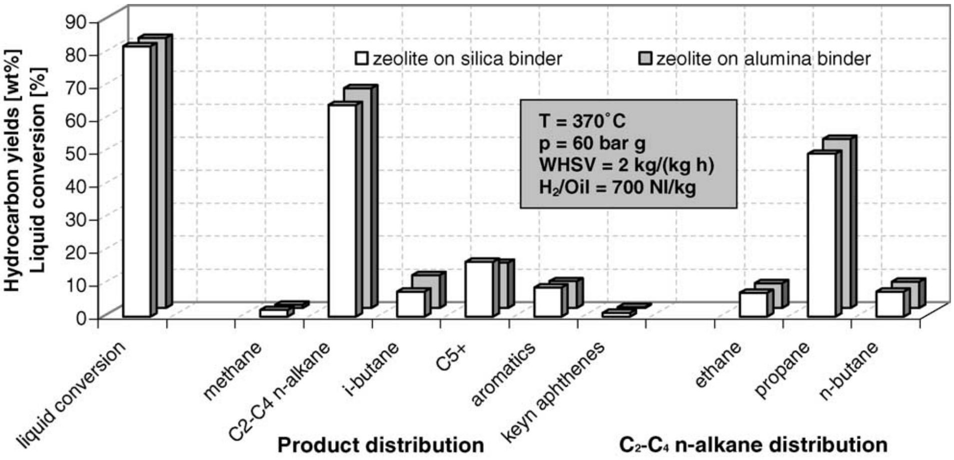

Fig. 4. Influence of the binder on the liquid conversion and the product distribution over a medium acidic H-ZSM-5 with small Pd content.

ethane and butane. Rising the palladium content increased the formation of ethane and propane, while no significant change in *n*-butane formation was observed.

Variation of the Brönstedt acidity (shown in Fig. 3) of an alumina bound H-ZSM-5 catalyst with low palladium content indicated that the best liquid conversion is achieved with the medium acidic zeolite (up to 82 wt.%). Excellent C_2–C_4 *n*-alkane yields as well as low formation of methane and C_{5+} products are found with this zeolite catalyst. This may be the result of a well balanced ratio of the concentration of the acid sites to the acid site strength, adjusted by a proper zeolite Si:Al ratio.

The C_2–C_4 *n*-alkane fraction indicated different yields of propane as well as ethane but no significant influence of zeolite acidity on the butane yield. With the medium acidic zeolite high yield of propane was observed. However, the strong acidic zeolite showed a high formation of ethane.

The influence of the binders—silica binder, respectively, alumina binder—investigated over a medium acidic H-ZSM-5 loaded with small palladium content is presented in Fig. 4. Both catalysts exhibit a comparable activity with a liquid conversion of about 82%. However, a slight difference was observed in the product distribution. The alumina bound zeolite showed a slightly better C_2–C_4 *n*-alkane yield at simultaneously lower formation of methane and aromatics most likely due to the increased acidity compared to the silica bound catalyst.

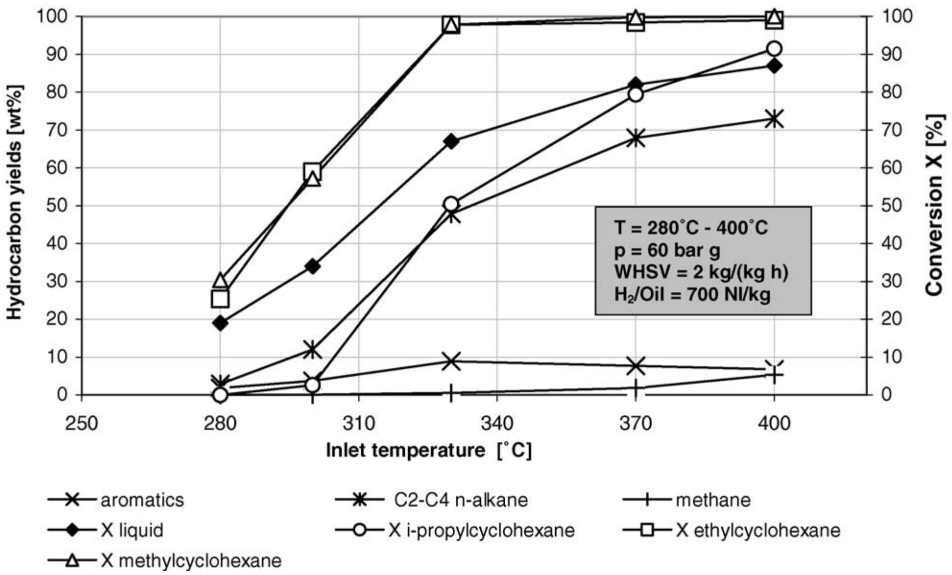

Fig. 5. Influence of the temperature on the naphthene conversions, liquid conversion, C_2–C_4 *n*-alkanes, methane and aromatics over an alumina bound medium acidic H-ZSM-5 with small palladium content.

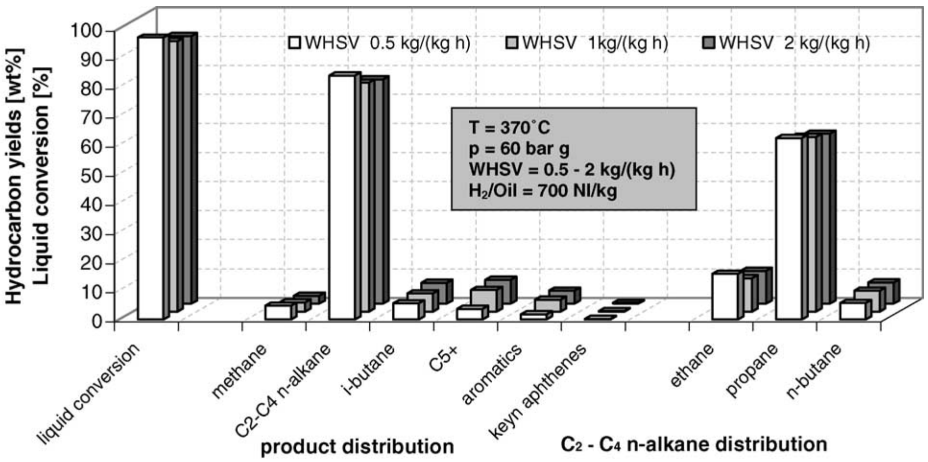

Fig. 6. Influence of the weight hourly space velocity on the liquid conversion and the product composition over an alumina bound medium acidic H-ZSM-5 with high palladium content.

3.2. Investigation of process conditions

The variations of temperature and space velocity were carried out.

The temperature influence was investigated over the range from 280 to 400 °C. The results are presented in Fig. 5.

In the range from 280 to 370 °C the liquid conversion increased rapidly from 20 to 80%. Above 370 °C only a slight increase was observed. With regard to C_2–C_4 *n*-alkane yield as well as low formation of methane and aromatics the best performance could be reached at 370 °C. At higher temperatures, the C_2–C_4 *n*-alkanes could be increased further at simultaneously lowering of the aromatics content. However, the methane make was significantly increased.

The conversion of the key naphthenes was studied as function of the temperature. The conversion profiles for methylcyclohexane and ethylcyclohexane were very similar. Above 330 °C, conversions of higher than 99% were observed. At lower temperature the conversions decreased rapidly. At 280 °C the conversion of methylcyclohexane and ethylcyclohexane were less than 30%. The *iso*-propylcyclohexane conversion was always lower compared to the conversion of methylcyclohexane and ethylcyclohexane, e.g. 92% compared to >99% at 400 °C. Reducing the temperature the *iso*-propylcyclohexane conversion decreased rapidly and at 280 °C no conversion was observed anymore.

The results of the variation of the weight hourly space velocity are presented in Fig. 6.

The decrease of the WHSV from 2 kg/(kg h) to 1 kg/(kg h) did not result in a visible change in cracking activity and selectivity. Only a further decrease to 0.5 kg/(kg h) resulted in a significant increase of the liquid conversion and C_2–C_4 *n*-alkane yields coupled with a decrease of the aromatics. However, this distinct reduction of the space velocity led to a stronger formation of methane. The reason of this effect is supposed to be an increase of secondary cracking reactions to form short chain alkanes caused by the prolonged residence time.

4. Conclusions

The conversion of heavy pyrolysis gasoline into a valuable steam cracker feedstock with high amounts of C_2–C_4 *n*-alkanes has been successfully demonstrated by the two-step ARINO® process concept.

Using a commercial, hydrogenated and desulphurized heavy pyrolysis gasoline for the second step of the ARINO® process, excellent performance, i.e. high yield of C_2–C_4 *n*-alkanes at low formation of methane and aromatics, is achieved over an alumina bound medium acidic H-ZSM-5 with high palladium content. The highest palladium value in the series of palladium loading investigated is even smaller than that of a typical bifunctional catalysts.

Furthermore the influence of the temperature and the space velocity was studied. For the examined hydrogenated heavy pyrolysis gasoline the best results with regard to high liquid conversion and C_2–C_4 *n*-alkane yields at a simultaneous low formation of methane and aromatics were observed at a temperature of 370 °C and a space velocity of 2 kg/(kg h). In general the exact operating conditions depend on the feedstock type and quality especially on the C_{9+} fraction of the hydrogenated pyrolysis gasoline.

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