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Organic nitrogen compounds in gas oil blends, their hydrotreated products and the importance to hydrotreatment

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Abstract

In the pretreatment of feeds for catalytic cracking and for HDA, the primary objective is to reduce the amount of organic sulfur and nitrogen compounds in the feedstock [Catal. Rev.-Sci. Eng. 36 (1994) 75] [1]. Organic nitrogen compounds have a significantly negative kinetic effect on hydrotreating reactions. The distribution of the organic nitrogen compounds in feed and hydrotreated products is discussed. Alkyl-substituted carbazoles are found to be the dominant and most refractive organic nitrogen compound in the feed. Our results show that indoles and quinolines are very reactive as compared with carbazoles. From the characterization of the pyrrole benzologues, it is concluded that the more the substituents, the lesser the reactivity. It is well known that conversion of organic sulfur occurs via two different mechanistic routes: the direct and the hydrogenation route [J. Catal. 61 (1981) 523; AIChE J. 27 (1981) 663; J. Catal. 97 (1986) 52; Catal. Today, in press; Polyhedron 16 (1997) 3213] [2–6]. The hydrogenation route converts the most refractive S-molecules and plays a very important role in the conversion of N-compounds. N-containing molecules often show a very low reactivity as compared with the analogous sulfur compounds. Several studies using model feedstocks show that nitrogen-containing molecules, and in particular, basic organic nitrogen compounds inhibit the HDS reaction [Appl. Catal. A 170 (1998) 1] [7]. In this study, real feed experiments have demonstrated that even though carbazoles are slow to react and are among the predominant N-compounds, it is the basic N-compounds that are the major inhibiting species in diesel fuels.

Keywords: Diesel feed; N-compounds; Inhibition; Hydrotreating

1. Introduction

The oil industry is under increased pressure from legislators to improve the quality of diesel fuel with a view of reducing exhaust emissions. Organic nitrogen is removed catalytically by the hydrodenitrogenation (HDN) process. Removal of nitrogen is essential to many different refinery processes. Generally, HDN is the most difficult hydrotreatment reaction, and little is known about which N-compounds are the most problematic or about the kinetics of their conversion during HDN processes.

In this paper, we use a novel method to obtain quantitative results for the content of individual N-compounds in a diesel oil and in a severely hydrotreated product. Furthermore, we show how the different N-compound classes affect the hydrotreatment of sulfur.

2. Identification and reactivity of nitrogen compounds in diesel oil

In this study, a typical diesel feed and its hydrotreated product were investigated. The feedstock was a blend of a straight run Kuwait gas oil and

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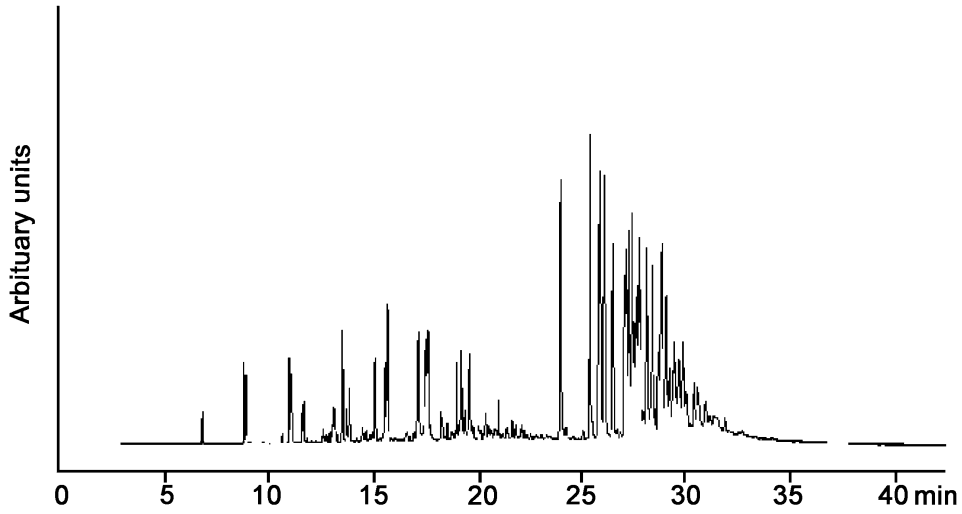


Fig. 1. GC/AED nitrogen chromatogram of the feed.

an LCO from a North Sea Crude. The blend ratio was 33/67% (v/v). The feed was treated in an isothermal bench-scale down-flow reactor at 350°C, pressure = 30 bar, LHSV = 1.0 h^{-1}. The feed contained 302 μg/ml of nitrogen and 0.627 wt.% sulfur, whereas the product contained 70 μg/ml of nitrogen and 10 ppm of sulfur. An analysis of the sulfur compounds was conducted using gas chromatography with sulfur specific chemiluminescence detection. The total nitrogen content was determined by oxidative combustion and chemiluminescence detection (ASTM D4629-91).

Hydrotreatment was carried out with a commercial sulfided CoMo catalyst, TK-554, from Topsøe. The product was extensively characterized using a state-of-the-art technique for N-compound analysis. This procedure has been reported elsewhere [8]. In brief, the method consists of a novel pre-concentration step for the N-compounds on a silica SPE column followed by recovery of the N-compounds. The GC analysis was performed on a Hewlett-Packard 6890 equipped with an AED detector model G2350A. In most cases, more than 60% of the N-containing molecules in feed and product can be accounted for, and all major peaks identified.

The GC analysis of the SPE extract of the feedstock and the product using the nitrogen specific detector (AED) is shown in Figs. 1 and 2, respectively. Visually, the nitrogen specific chromatogram can be divided into two fractions, one before and one after a retention time of 23 min. The fraction eluting after 23 min accounts for the major part of the total nitrogen in the sample.

An analysis of carbazole and methyl-substituted carbazole standards and verification of the masses by GC/MS showed that compounds, which eluted after 23 min, were predominantly methyl-substituted carbazoles. The compounds that eluted before 23 min (Fig. 1) were identified as indole, quinoline, aniline and their methyl-substituted derivatives.

In the chromatograms, also minor amounts of isoquinolines, benzoquinolines, naphthylamines and diphenylamines were identified. Lists of the identified N-compounds in their absolute amounts in the feedstock and the hydrotreated product shown in Figs. 1 and 2 are reported elsewhere [8]. The exact positions of the alkyl groups were identified for most, but not all, of these compounds.

Most of the basic nitrogen compounds that were identified in reasonable amounts were present in the fraction eluting earlier than that of the carbazoles, and these were quite reactive in the hydrotreating process. The carbazoles were more refractory, and the reactivity of the various carbazole derivatives varied

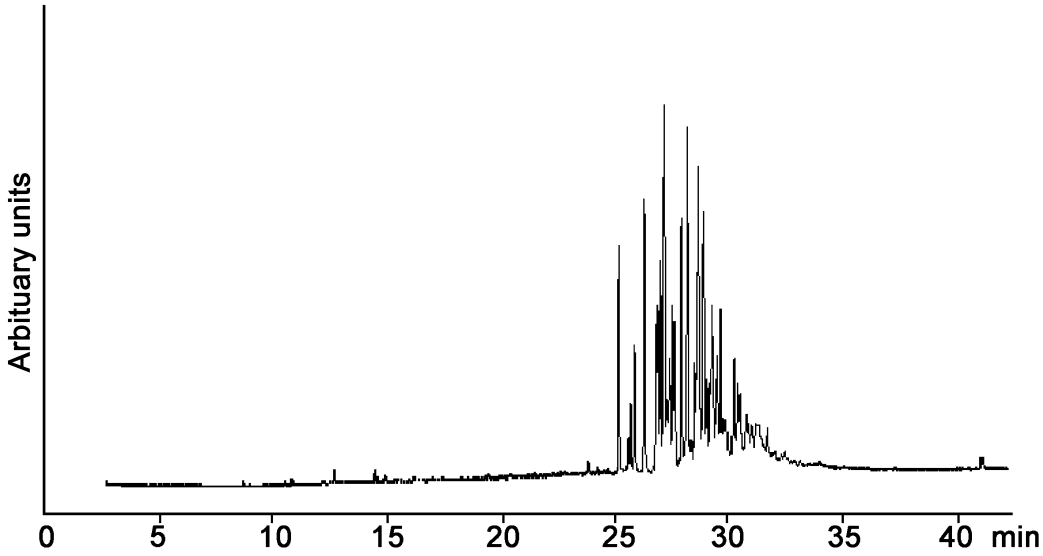
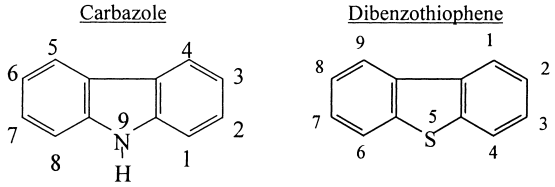


Fig. 2. GC/AED nitrogen chromatogram of the product.

substantially with the position and number of alkyl substituents on the carbazole nucleus. Alkyl dibenzothiophenes behave in the same way, as will be discussed later.

It should be noted that there is, in addition to the sharp individual peaks, a substantial broad hump of unresolved N-species that must be considered. The identification of all the minor peaks constituting the broad hump will be the subject of future research work. By integrating the whole spectrum including the broad hump, the total nitrogen content detected by GC/AED was found to be 90–110% of the total nitrogen analysis determined by ASTM D4629-91. Table 1 lists the carbazole and derivatives found in the feed and product. The concentration of these was determined by integration of the areas of the peaks above the broad hump. Detailed peak identification is found in [8]. The compositions shown and discussed in [8] compare well with previous literature, however, the new procedure described in [8] gives a more quantitative assessment of the content of the individual species and how these change during processing.

For reference, the chemical structures and the nomenclature of carbazole and its sulfur analog dibenzothiophene are shown.



Carbazole and mono-methyl-substituted carbazoles account for about 27% of the total amount of the carbazole fraction in this feed. The data show that 1-methyl carbazole was the most predominant compound in the feedstock. Of the di- and tri-methyl carbazoles, substitution at position 1 was observed to be the most predominant. The high relative concentrations of 1-substituted carbazoles in natural crudes were attributed to preferential migration of nitrogen compounds having sterically shielded N-centers. The shielded N-centers have low adsorptive interactions with the clay minerals through which the crude has migrated [9]. The high relative concentrations of 1-substituted carbazoles in the products were attributed to a lower reactivity of these species as will be discussed later.

The conditions used for the hydrotreatment of the diesel oil were quite severe. Supplementary analyses of the sulfur species remaining in the hydrotreated product showed that the sulfur content had been

Table 1
Feed and HDT product compositions and relative rate constants

Compound name	Concentration		Percent conversion	Relative 1st order constant[a]
	Feed (μg N/ml)	Product (μg N/ml)		
Carbazole	7.6	0.2	97	100
1-Methylcarbazole	11.1	1.8	84	49
3-Methylcarbazole	6.0	0.2	96	87
2-Methylcarbazole	7.7	0.5	93	73
4-Methylcarbazole	7.5	1.1	86	53
1,8-Dimethylcarbazole	5.7	2.3	59	24
1,3-Dimethylcarbazole	4.5	1.2	74	37
1,6-Dimethylcarbazole	5.0	1.3	73	36
1,7-Dimethylcarbazole	6.0	1.9	69	32
1,4- + 1,5-Dimethylcarbazole	10.6	4.7	56	22
3,6-Dimethylcarbazole	2.9	0.6	79	43
2,6- + 3,5- + 2,7-Dimethylcarbazole	7.9	1.5	81	45
2,4- + 1,2-Dimethylcarbazole	5.8	1.4	75	38
2,5-Dimethylcarbazole	3.8	1.2	68	31
2,3-Dimethylcarbazole	5.2	2.1	60	25
3,4-Dimethylcarbazole	2.2	0.9	61	25
1,4,8-Trimethylcarbazole	7.2	3.5	52	20
1,3,5-Trimethylcarbazole	8.8	4.0	54	21
1,5,7-Trimethylcarbazole	5.1	3.1	40	14
2,4,6-Trimethylcarbazole	1.4	0.6	58	24
1,3,4- + 2,4,7-Trimethylcarbazole	4.4	1.9	57	23
1,4,5- + 2,3,6- + 2,3,5-Trimethylcarbazole	2.8	1.3	54	21
3,4,6-Trimethylcarbazole	2.5	1.5	41	
C3-carbazole	1.2	0.7	40	
C4-carbazole	1.4	1.0	28	
C4-carbazole	1.3	0.7	45	
C4-carbazole	1.2	0.7	42	
C4-carbazole	1.1	0.6	50	
C4-carbazole	3.2	2.7	17	

[a] All rate constants are relative to carbazole $k = 100$.

reduced from 0.627 wt.% S to about 10 ppm S, corresponding to 99.8% hydrodesulfurization. The remaining 10 ppm S primarily consisted of highly substituted dibenzothiophenes, and specifically only 1.2 ppm S was detected as 4,6-dimethyldibenzothiophene. The feedstock was found to contain 52.2 ppm S as 4,6-dimethyldibenzothiophene. Thus, even this highly refractory S-compound was 97.7% converted.

By comparison, only about 77% of the nitrogen compounds were converted. Thus, many of the N-compounds present in this feed are considerably less reactive than hindered dialkyldibenzothiophenes, the most refractive N-compounds being methylated carbazoles.

Most of the lower boiling N-compounds identified in the feedstock are converted under these rather severe hydrotreating conditions into ammonia and hydrocarbons. Essentially, no basic compounds were observed in this severely hydrotreated product as separate peaks in the chromatogram. This means that indole, quinoline, aniline and their methylated derivatives have a higher reactivity than the carbazoles. Most of the compounds in the product that did elute earlier than 23 min were new compounds not present in the feed. These were identified as aniline

derivatives and are believed to be reaction intermediates in the HDN of the carbazoles.

Basic organo-nitrogen compounds have often been described as the strongest inhibitors of the HDS reaction, and have therefore been the most studied model nitrogen compounds [7,10,11]. However, only few quantitative inhibition effects have been reported.

In the present study, we investigated the reactivity of the individual carbazole derivatives by comparing the amounts present in the feed with those present in the product. Assuming simple first order kinetics, we estimated the relative rate constants of the individual compounds by using carbazole as reference ($k = 100$). It should be noted that the accuracy of these calculations is somewhat questionable for many of the compounds as the peaks are not fully resolved. These estimated rate constants are presented in Table 1.

Comparing the chromatograms of feed and product, it can be seen that the relative abundance of the various compounds changes considerably during hydrotreatment. In the feed, carbazole and mono-methylcarbazoles were the most predominant species, whereas in the product, the di- and tri-methylcarbazoles were the dominant species. This shows that as the degree of substitution increased, the reactivity decreased. In the feedstock, carbazole and mono-methylcarbazoles accounted for 27% of the nitrogen, whereas in the product, they only accounted for 8%. The reason for the specific increased resistance of these non-basic N-compounds to HDN appears to be related to the position of the alkyl-substituents on the aromatic nuclei. This is quite similar to the behavior of alkyldibenzothiophenes in that substitution adjacent to the heteroatom lowers the reactivity substantially [10].

3. Catalytic removal of sulfur and nitrogen

In the literature, it is concluded that hydrotreated products contain high amounts of 1-substituted carbazoles [12–14]. Our results confirm those results and provide additional kinetic data on the relative reactivity of carbazoles substituted at different positions. The difference in reactivity of the different methyl-substituted carbazoles is, however, not quite as pronounced as for the dibenzothiophene analogs. The most refractive sulfur compounds are higher molecular weight dibenzothiophenes that contain side chains at positions close to the sulfur atom. It is well known that 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene are among the most refractory sulfur compounds. Relative differences in reactivity according to Gates and Topsøe [6] are as follows: DBT:4-MDBT:4,6-DMDBT is 10:3:1. This difference in reactivity was proposed to be due to sterical hindrance.

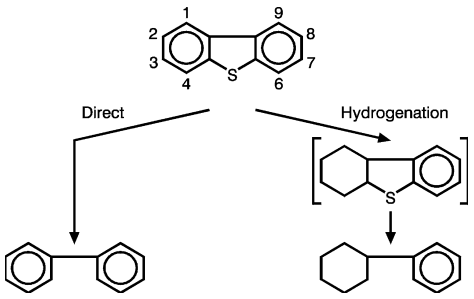


Fig. 3. Reaction pathways for HDS of DBT.

We were able to estimate the first order rate constant for HDS of 4,6-dimethyldibenzothiophene in our present HDN studies. The rate constant for HDS of 4,6-DMDBT was observed to be almost the same as the rate constant for HDN of carbazole. Thus, alkyl-substituted carbazoles appear to react at rates about $\frac{1}{10}$ of those of alkyldibenzothiophenes of comparable structures. Surprisingly, it can be seen in Table 1 that alkyl-substitution at position 4 of carbazoles lowers the reactivity almost as much as substitution at position 1 (adjacent to the N-heteroatom). From the data in Table 1, it can be seen that the cause of this lower reactivity is not solely due to steric effects. Work is in progress to clarify this.

It is well known that there are two reaction pathways for HDS of dibenzothiophene and alkyl-substituted dibenzothiophenes as shown in Fig. 3 [15]. One route involves hydrogenation of one aromatic ring prior to removal of the sulfur atom (hydrogenation route), and the other route involves direct extraction of the sulfur atom without ring hydrogenation (direct route). It was shown that the rate of the hydrogenation route is

not substantially affected by the position or number of alkyl-substituents on dibenzothiophene, whereas the rate of the direct route is strongly reduced by substituents adjacent to the sulfur atom [6]. CoMo-based catalysts primarily operate via the direct HDS route, thus for the sulfided CoMo catalyst used in the present study, it is not unlikely that the 4,6-DMDBT reacts more slowly.

4. Determination of inhibitors for the hydrogenation route

It has already been mentioned that the hydrogenation route is severely inhibited by nitrogen-containing compounds. It is thus important to understand which of the N-compounds are the most inhibiting, and how they interfere with the HDS reactions. Model compound studies have shown that some basic nitrogen-containing molecules (like acridine) are orders of magnitude more inhibiting than other N-containing molecules (like aniline and indole), and also more inhibiting than DBT itself [16]. There are therefore indications to the effect that some of the basic N-compounds are by far the worst inhibitors for HDS. The interesting results from these model compound tests called for additional real feed studies, where the inhibition of HDS in typical diesel fuels was investigated. In the following, the results of such real feed studies are described.

It was decided to simplify the inhibition studies by removing essentially all N-compounds from the diesel fuel and adding known model compounds from different classes of N-compounds. The diesel fuel used in this study was a blend of 25% LCO and 75% SR from Kuwait. In this way, a clear assessment of the relative effects of different classes of N-compounds in diesel fuels could be made. The selective removal of N-compounds, leaving all the sulfur compounds unaltered, was accomplished by preparative chromatography over silica gel. During the early stages of this chromatography, the aromatic sulfur compounds and polyaromatic hydrocarbons were also adsorbed, but they came into equilibrium with the column after about two bed volumes of diesel fuel had been passed through the column. Chromatography could then be continued for a significant volume of diesel fuel

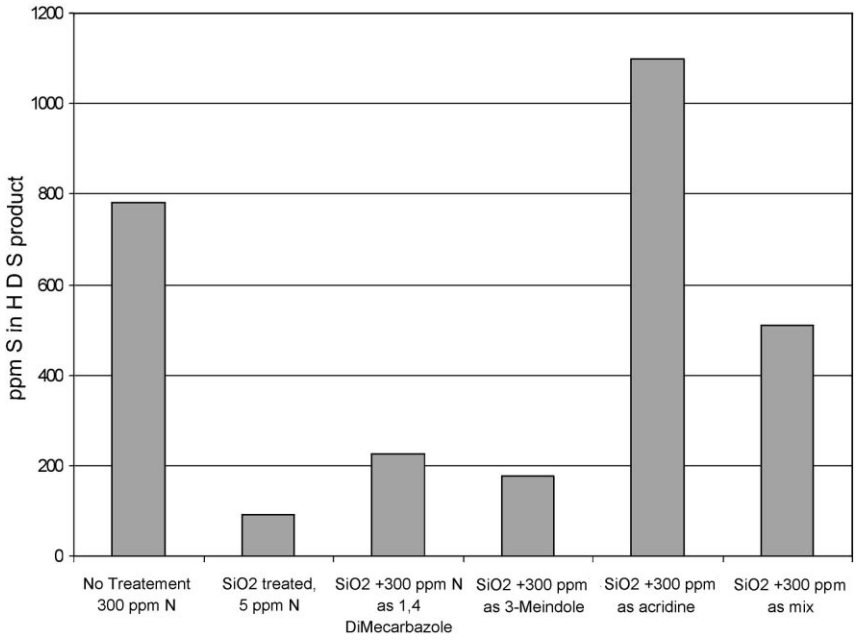


Fig. 4. Sensitivity of HDS of feed composition.

before N-compounds began to elute. The diesel fuel used for these studies contained 260 μg/ml of nitrogen and 1.5 wt.% sulfur. Four different 260 μg/ml N fuels were prepared using three different N-compound classes blended back into the N-free diesel fuels. The compounds chosen were 3-methylindole, 1,4-dimethylcarbazole and acridine. Acridine was added to the feed as representative of the basic N-compounds even though this specific compound is not found in our gas oil blends. In addition to this, a blend containing 87 μg/ml N from each compound was made with the N-free fuel. The modified diesel fuels were then hydrotreated, and the results were compared with those obtained from hydrotreatment of the untreated fuel. A commercial sulfided Ni–Mo catalyst on alumina, TK-573, from Topsøe was used in this study.

Fig. 4 shows the results of these studies. It can clearly be seen from the figure that 3-methylindole and 1,4-dimethylcarbazole are not major inhibitors, whereas acridine is a major inhibitor. The three component blends behave essentially as a linear combination of the three different N-compounds. There are also indications to the effect that acridine strongly inhibits the conversion of 1,4-dimethylcarbazole. In the absence of acridine, even this low reactivity alkylcarbazole was converted to a high degree. Surprisingly, even though 1,4-dimethylcarbazole was present in the blend at concentrations similar to those of the alkylcarbazoles in the untreated diesel fuel, the degree of inhibition was much lower than that of the untreated diesel fuel. This indicates that alkylcarbazoles are not the major species of concern in HDS inhibition, even though they are the major species detected in hydrotreated diesel fuels. Thus, there may be some components of diesel fuels that inhibit both HDN of alkylcarbazoles and HDS of alkyldibenzothiophenes. To answer this question, additional studies were conducted on the N-free diesel fuel. This work is reported separately [17].

5. Conclusions

Using a novel analytical procedure, including pre-concentration of N-compounds and a GC analysis coupled with a highly sensitive and selective atomic emission detector, we identified most of the refractive organic nitrogen compounds present in a typical gas oil and its hydrotreated product.

Alkyl-substituted carbazoles were found in large amounts in the feed, and carbazole compounds substituted at position 1 were found to be the most abundant. 1-Methyl carbazole was the single most predominant species. Carbazoles were found to be the most refractory organic N-compounds in the feed towards HDN. Generally, the more the methyl substituents on the carbazole, the lower the reactivity. The cause of this lower reactivity is not solely due to steric effects.

The least reactive sulfur compounds in the diesel range are dibenzothiophenes with substituents at positions 4 and 6, e.g. 4,6-dimethyldibenzothiophene. It is the reactivity of these very refractive compounds that determine the overall desulfurization rate in ultra deep HDS. The results obtained by hydrotreating selectively altered diesel fuels and specific N-compounds added to diesel fuels show that basic compounds intrinsically found in diesel fuels are by far the worst inhibitors for HDS of refractory S-compounds, and that carbazoles are not serious inhibitors.

Although carbazoles are the dominant N-compounds in the product during severe hydrotreatment, it is certain that basic N-compounds cause inhibition of the sterically hindered sulfur compounds. This strongly suggests that the desulfurization of sterically hindered sulfur compounds and denitrogenation of carbazoles take place primarily via the hydrogenation route on the same type of site.

References

[1] A. Stanislaus, B.H. Cooper, Catal. Rev.-Sci. Eng. 36 (1) (1994) 75.
[2] M. Houalla, et al., J. Catal. 61 (1981) 523.
[3] D.H. Broderick, B.C. Gates, AIChE J. 27 (1981) 663.
[4] M. Nagai, T. Sato, A. Aiba, J. Catal. 97 (1986) 52.
[5] H. Topsøe, K.G. Knudsen, L.S. Byskov, J.K. Nørskov, B.S. Clausen, Studies in Surface Science and Catalysis 121 (13) (1999).
[6] B. Gates, H. Topsøe, Polyhedron 16 (1997) 3213.
[7] F. van Looij, et al., Appl. Catal. A 170 (1998) 1.
[8] P. Wiwel, K.G. Knudsen, P. Zeuthen, D.D. Whitehurst, I(E Proc. Res. 39 (2) (2000) 533.
[9] M. Li, S.R. Larter, D. Stoddart, Anal. Chem. 64 (1992) 1337–1344.
[10] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (9) (1991) 2021–2058.

[11] T.C. Ho, Catal. Rev.-Sci. Eng. 30 (1) (1988) 117–160.
[12] M. Dorbon, I. Igniatiadis, J.M. Schmitter, P. Arpino, G. Guiochon, H. Toulhout, A. Huc, Fuel 63 (1984) 565.
[13] J.M. Schmitter, I. Igniatiadis, M. Dorbon, P. Arpino, G. Guiochon, H. Toulhoat, A. Huc, Fuel 63 (1984) 557–564.
[14] I. Igniatiadis, M. Kuroki, P. Arpino, J. Chromatogr. 366 (1986) 251–260.
[15] K.G. Knudsen, H. Topsøe, B.H. Cooper, Appl. Catal. A 189 (1999) 205–215.
[16] D.D. Whitehurst, K.G. Knudsen, I.V. Nielsen, P. Wiwel, P. Zeuthen, Prepr. Pap. Am. Chem. Soc., Div. Pet. Chem. 45 (4) (2000) 692.
[17] K.G. Knudsen, D.D. Whitehurst, P. Zeuthen, Prepr. Pap. Am. Chem. Soc., Div. Pet. Chem. 45 (2) (2000) 367.