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A new material for selective removal of nitrogen compounds from gasoils towards more efficient HDS processes

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A selective removal of nitrogen compounds from gasoils is proposed, using a recyclable sorbent capable of forming charge-transfer complexes;[1] the selective elimination of nitrogen compounds strongly improves the hydrodesulfurization (HDS) of denitrogenated feed.

Nitrogen compounds poison hydrotreating catalysts,[2,3] drastically decreasing[4] their activity and lifetime. Therefore, their elimination is very important in order to reach the low sulfur levels that will be allowable in future in gasoils. Extraction of nitrogen compounds from petroleum fractions has been investigated for many years. Several methods were used such as solvent extraction,[5,6] ion exchange-, coordination- and adsorption-chromatography[7] to remove N-compounds from oils, but none of them seemed to be selective or efficient enough to for total removal.

Previous studies[8,9] indicated that alkyldibenzothiophenes could be removed from oil fractions by formation of charge-transfer complexes (CTC) and subsequent elimination by filtration. From the structural similarities between dibenzothiophene and carbazole, it was expected that nitrogen compounds could form CTC with π-acceptors. Furthermore, donor–acceptor complexes with N-molecules, such as carbazole,[10] indole[10] and *N*,*N*-dimethylaniline[11] have already been described.

Investigations led us to choose 2,4,5,7-tetranitrofluorenone (TENF) as π-acceptor for its good characteristics: a high rate and good yield of complexation in synthetic solutions. The elimination of nitrogen compounds by formation of CTC proved however to be non-selective by introducing TENF as a suspension in gasoils. Indeed, GC-MS analysis (Fig. 1) of the trapped compounds from an Iranian Straight Run showed that sulfur compounds and aromatics without heteroatoms were preferentially complexed. Only derivatives of carbazole and acridine could be detected as traces. This is probably due to the important differences in concentration between these polyaromatic compounds. Indeed, sulfur derivatives are 20 times more concentrated than nitrogen compounds in the initial feed.

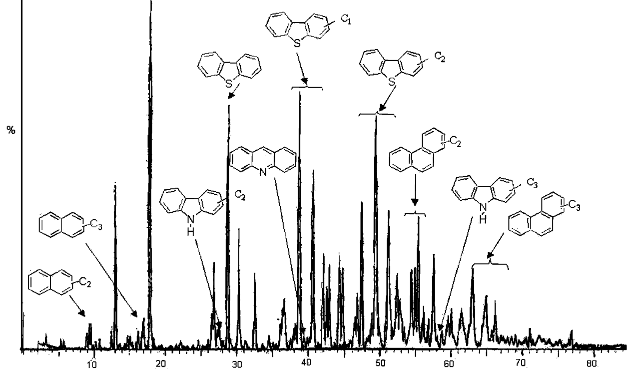

Fig. 1 GC-MS of aromatic compounds complexed by TENF in an Iranian Straight Run.

A way to achieve a selective complexation of N-compounds is to synthesize a polar polymer with electron-deficient sites. Indeed, nitrogen compounds are more polar than S-containing molecules and it was expected that such an environment near the CTC sites would favour the selective complexation of the nitrogen species.

Polyglycidylmethacrylate was chosen as cheap, easily available and polar support for the acceptor. Polyglycidylmethacrylate beads were synthesized by using the method described by Svec and colleagues.[12] Introduction of TENF was performed in two steps *via* its carbonyl group (Fig. 2): substitution of the epoxide functionalities with acetone oxime followed by coupling of TENF on the oxime function gave a polar polymer with electron-deficient sites (0.2 mmol of TENF per gram of resin, determined by elemental analysis). The presence of TENF on the polymer was detected by IR spectroscopy, which showed absorptions due to asymmetrical and symmetrical stretching of NO_2 groups, at 1550 cm^{-1} and 1390 cm^{-1} respectively.

The activity and selectivity of this polymer were firstly tested on a synthetic solution: equimolar amounts of aniline, quinoline, acridine, indole, carbazole and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were dissolved in a heptane–toluene (15%-wt) mixture. The polymer was added to this solution, which was stirred mechanically. Activity and selectivity were evaluated by GC-analysis (internal standard method). It was noticed that N-containing molecules were rapidly complexed (between 50 and 90% of their initial amount) in one hour, whereas only *ca.* 10% of 4,6-DMDBT was removed by the polymer. The selectivity towards the elimination of N-compounds of the modified polyglycidylmethacrylate was thus evidenced.

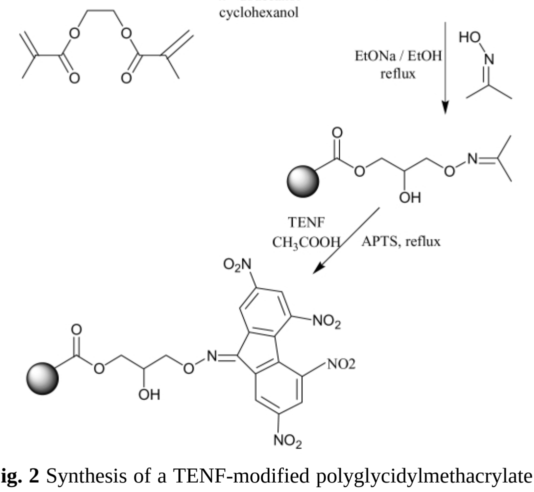

Fig. 2 Synthesis of a TENF-modified polyglycidylmethacrylate.

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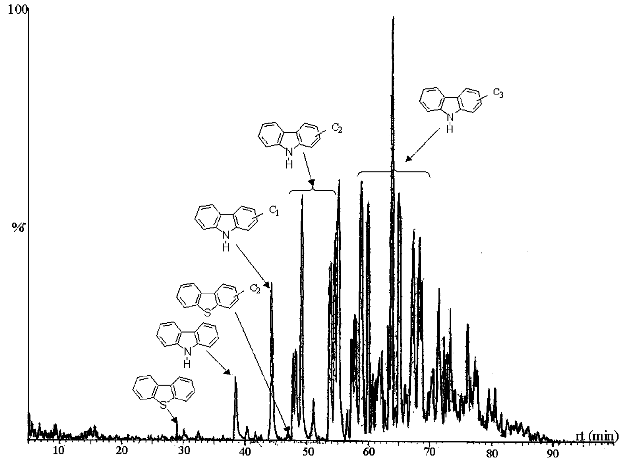

Fig. 3 GC-MS of the compounds trapped by a TENF modified polyglycidylmethacrylate in an Iranian Straight Run.

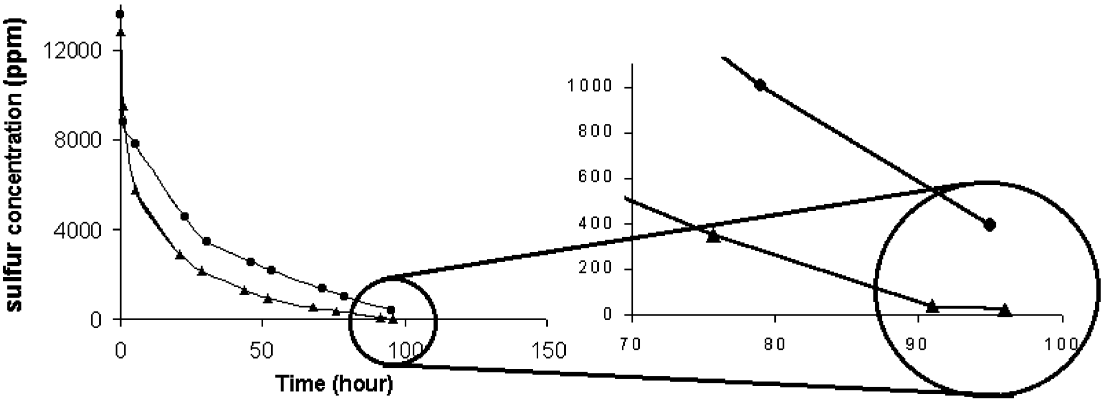

Fig. 4 Comparative hydrodesulfurization conversion between a denitrogenated straight run feed (▲) and an untreated one (●). Batch reactor, NiMo catalyst, 643 K, 50 MPa H_2.

This affinity for N-containing molecules was extended to gasoils. The gasoil and the complexing polymer were stirred at room temperature, leading to the formation of CTC. After filtration, the nitrogen level of the treated gasoil was determined by chemiluminescence (ANTEK 9000 apparatus). A measure of the sulfur level was performed by X-ray fluorescence (Sulfur in oil analyser – HORIBA SLFA1800) in order to determine the selectivity factor α[13] [eqn. (1)] of the polymer. Regeneration was performed by washing the solid with toluene. The structures of the trapped compounds were then analysed by GC-MS.

$$\alpha = \frac{\%\text{Nadsorbed} \cdot \%\text{Ssolution}}{\%\text{Nsolution} \cdot \%\text{Sadsorbed}} \qquad (1)$$

An Iranian Straight Run (SR) feed which contained 360 ppm N and 13600 ppm S was treated with the TENF-polyglycidylmethacrylate. The mass ratio gasoil/polymer was 8:1 and the separation factor α was calculated in order to quantify the selectivity of the sorbent towards nitrogen compounds.

Firstly, the treatment with the TENF modified polymer led to an efficient removal of the nitrogen compounds: the decrease of the total nitrogen level was about 50%, whereas the sulfur level dropped by only 5%. Determination of the α factor highlighted the selectivity of the polymer: despite the difference of initial concentrations between nitrogen and sulfur compounds in the feed, a value of 20 was calculated for the Iranian Straight Run.

These results were confirmed by analyses of the trapped compounds by GC-MS (Fig. 3): it is obvious from the chromatogram, that nitrogen species are predominant in the mixture of the aromatic compounds trapped by formation of charge-transfer complexes. More precisely, derivatives of carbazole are the most extracted class of compounds from the studied feed. Sulfur derivatives and polyaromatics without heteroatoms are present as traces. Moreover, the polymer proved to be recyclable: after several washings with toluene, it was reused without loss of activity or selectivity.

A three-CTC-step pretreatment on the Iranian Straight Run proved furthermore to be efficient for obtaining low nitrogen level feed. Nitrogen elimination reached 90%, whereas sulfur removal was limited to 5%, leading to a new Iranian Straight Run feed containing 25 ppm of nitrogen and 12800 ppm of sulfur.

HDS of this CTC treated feed was compared with the untreated one: hydrodesulfurization was performed on a commercial NiMo catalyst, in a batch reactor at 643 K and under 5 MPa of hydrogen.

Results showed (Fig. 4) that such an elimination of nitrogen compounds as a pretreatment improved drastically the HDS conversion. While HDS of untreated SRGO resulted in a 400 ppm S effluent, ultra low sulfur feed, containing only 25 ppm S, was obtained by hydrotreating the denitrogenated feed.

We have thus demonstrated that nitrogen compounds contained in gasoils were selectively removed by formation of charge-transfer complexes. Introduction of π-acceptors on a polar polymer led to a very selective complexation of nitrogen compounds towards other polyaromatic molecules. Development of such complexing materials is of great importance for the improvement of hydrotreating processes and allows obtention of low sulfur concentration, in respect of the future low sulfur legislation for gasoils.

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