

GAS AND LIQUID PHASE FUELS DESULPHURISATION FOR HYDROGEN PRODUCTION VIA REFORMING PROCESSES

Supprimé : DESULFURIZATI
ON MATERIALS FOR MULTI-
FUEL PROCESSORS FOR
HYDROGEN PRODUCTION

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ABSTRACT:

This paper focuses on the development of efficient desulphurization processes for multi-fuel processors for hydrogen production. Two processes are studied: liquid hydrocarbons desulphurization and H₂S removal from reformat gases. For each process specially designed materials in terms of chemical composition and microporous structure were synthesized. In terms of liquid desulphurization, the adsorption of sulphur compounds of diesel fuel under ambient conditions was studied on zeolite-based materials: Na-Y, metals ion-exchanged Na-Y (using the liquid ion-exchange technique) and H-Y. Some materials, in addition to exhibiting excellent performance with model diesel reducing sulphur to near zero levels, also showed promising results with commercial diesel. The gas phase desulphurization experiments involved zinc oxide powders (commercial and in-house synthesised) as well as Zn-Fe, Zn-Fe mixed oxides synthesised by non-conventional (combustion synthesis) techniques characterized by very short synthesis times. The preliminary results showed comparable or better performance of the in-house materials compared to the commercial powders.

KEYWORDS: desulphurization, diesel, H₂S, adsorption, zeolites

1 Introduction

Conventional transportation fuels, i.e. diesel and gasoline, are currently considered as ideal hydrogen sources due to their high energy density, their availability, as well as their relatively secure transportation and storage. Thus, the development of multi-fuel reformers, capable of converting a variety of liquid fuels into hydrogen, has become one of the most prominent technological challenges. One of the main disadvantages of the above fuels is that they contain sulphur compounds, which - even at minor quantities - can cause severe poisoning of catalysts used "downstream" in the liquid fuels processing, such as reformers and water gas shift reactors or in fuel cells anodes. According to the global fuel reforming process used, sulphur can be removed in the liquid phase or in the gas phase; the present work investigates both possibilities. Despite the fact that traditional refinery processes can achieve liquid fuels desulphurization down to several ppm, there is an ongoing need for the development of new, more efficient and economical methods that will offer the ability of further sulphur reduction down to ppb levels. The adsorption of sulphur compounds of liquid hydrocarbons on materials such as activated carbon, activated alumina, zeolites, silica-based materials as well as on mesoporous materials is currently under study with some of these materials exhibiting very interesting results [1]. The main purpose of the current work is the design of adsorption systems that will promote the selective adsorption of heavy aromatic sulphur hydrocarbons contained in both diesel and gasoline, including commercial fuels containing less than 10ppmw sulphur that will be in compliance with future EU legislation. In this perspective, several zeolite-based materials were studied, i.e.

commercial Na-Y and H-Y zeolites as well as several metal-ion-exchanged Na-Y zeolites. Concerning H₂S removal, as reformat gases are in most cases a reductive mixture, zinc oxide is usually considered as the state-of-art sorbent. In the present study, six zinc-oxide-based powders were evaluated and compared in terms of their activity in gas desulphurization in the range of 300-400°C: commercial and in-house ZnO, as well as four specially synthesized mixed oxide materials. In order to evaluate these adsorbents, an autonomous test bench was constructed.

2 Liquid Phase desulphurisation

2.1 Sorbents Synthesis and Characterization

The commercial zeolites Na-Y and H-Y were provided by Zeolyst International and have a SiO₂/Al₂O₃ mole ratio of 5.1 and 80 respectively. Utilizing Na-Y as the precursor, a variety of different zeolites, namely Pr-Na-Y, Gd-Na-Y, Nd-Na-Y, Y-Na-Y, La-Na-Y, Ce-Na-Y and Ce-Na-Y-2 have been prepared by the liquid ion-exchange method. The ion-exchange process between the metal ion and the sodium cation of the zeolite was conducted under ambient conditions. The respective metal nitrates (for instance Ce(NO₃)₃.6H₂O for cerium) were mixed and stirred with the Na-Y zeolite for 48 hours; this process was followed by filtration, washing and drying of the resulting sorbents. In order to achieve the highest possible ion exchange while ensuring the removal of any remaining nitrates, the sorbents were calcined at temperatures between 400°C and 600°C. The optimum calcination temperature was determined by evaluating the performance of the above zeolites and was found to be 400°C for Ce-Na-Y and Ce-Na-Y-2, and 500°C for all the others. We have also performed a second ion-exchange with ceria: starting from the first ion-exchanged powder (not calcined) we have repeated the procedure to insert more ceria in the zeolite (sample Ce-Na-Y-2). Ce represents 10% (weight basis) of the zeolite in sample Ce-Na-Y and approximately 15% in sample Ce-Na-Y-2.

All the resulting zeolites have been characterized in order to check the efficiency of the ion-exchange process: the metal concentration in the sorbents was measured with the aid of Inductively Coupled Plasma (ICP) Spectrometry, their specific surface areas (BET) were determined by nitrogen porosimetry while the phase composition and the crystallinity of these materials were studied by X-Ray Diffraction (XRD). From the ICP analysis it was found that the concentration of metals in the zeolite was in accordance with our calculations. The nitrogen isothermal adsorption-desorption curves of the zeolites were the typical ones for mesoporous materials, while their specific surface area (864m²/gr for the Na-Y zeolite) seemed to decrease slightly with the insertion of the exchanged metal in the zeolite. The resemblance among the XRD spectra of the calcined zeolites - despite the reduction in the intensity of the characteristic peaks - indicated clearly that after the ion-exchange process the zeolites retain their initial structure and crystallinity, since no observable single-phase metal oxides formation occurred after calcination.

2.2 Experimental

To evaluate these zeolites, three commercial diesel samples having different sulphur concentrations were utilized: a High Sulphur Diesel (abbreviation HS) (163ppmw), a Medium Sulphur Diesel (abbreviation MS) (38ppmw) and a Low Sulphur Diesel (abbreviation LS) (5ppmw). Additionally, a standard Model Diesel, having a total sulphur concentration of 146ppmw, was prepared by using three model sulphur compounds commonly found in diesel fuel, namely benzothiophene, dibenzothiophene and 4,6-dimethyl-dibenzothiophene, diluted in hexadecane. The adsorption experiments were conducted by applying two different methods: 1. Batch Method (Static Experiments), according to which 2gr of the sorbent under study is diluted into 10 ml of diesel and the resulting slurry is stirred under ambient conditions (a stirring time of 30 min was found adequate for the adsorbent to become saturated with the diesel sulphur compounds), followed by filtration for the separation of the solid from the liquid phase. 2. Dynamic Experiments performed in a fixed bed reactor. In this case, the experimental apparatus consists of a vertical quartz tube reactor, having an internal diameter of 4mm and a length of 300mm and loaded with 0.5gr of sorbent. Prior to the dynamic experiments, the powder was dried at 130°C for 40 min and the sorbent bed was washed with heptane. The effluent diesel was collected at specified intervals and analyzed in order to determine its weight sulphur concentration with the aid of UV Fluorescence (analyzer Antek 9000).

2.3 Results and Discussion

The Na-Y zeolite was utilized as reference material for both the comparative evaluation of the results as well as for the determination of the optimal experimental conditions in the batch and fixed bed experiments described above.

The adsorption mechanism of sulphur-containing aromatics is based on the interaction of their π -electrons of the aromatic ring with the substitution metal ion of the zeolite, as well as on the direct bonding (σ -bond) between the metal and sulphur (S-M) [2]. Hence, it is possible that all the aromatics in diesel inhibit the former interaction. Therefore, in order to clarify the role of zeolites on the direct adsorption mechanism, experiments by utilizing the model diesel were conducted. According to Table 1, the sulphur reduction is in each case very close to 100% and demonstrates the high ability for Na-Y and its doped products to adsorb all sulphur compounds. Most research attempts focus on the investigation of a substitution metal that will mainly enhance the direct S-M mechanism.

Table 1: Sulphur reduction in the Model Diesel for selected powders (% w.t.)

Sorbent	Na-Y	Nd-Na-Y	Y-Na-Y	La-Na-Y	Ce-Na-Y
Sulphur reduction	99.4	97.8	98.5	97.3	99.7

Then the adsorption ability of the materials was investigated, still with the batch method, by testing the sulphur removal from the HS, the MS and the LS diesel. The results are presented in Figure 1. It can be seen that the ion-exchange zeolites give better adsorption results than Na-Y, indicating that the insertion of the different metals is efficient for all three fuels. Interestingly, the sulphur removal in the HS diesel ranges from 30 to approximately 60% depending on the sorbent - significantly lower values than the ones achieved with the Model Diesel. Although the capability of these materials for sulphur reduction is promising for further applications, it highlights the inhibition phenomenon caused by the competitive adsorption of aromatic hydrocarbons contained in the "real" diesels as demonstrated in other studies [3]. In addition, a common phenomenon in this plot is that the sulphur reduction capacity decreases for all powders (apart for La-Na-Y and Ce-Na-Y-2) with the decrease of initial sulphur content in the diesel feed. This behaviour is attributed to the fact that the lower the initial sulphur content in the fuel the most difficult the adsorption of the sulphur compounds becomes, since these are mainly comprised of heavier alkylated polyaromatics which have been found to be extremely resilient to both traditional and alternative desulphurization methods. However, La-Na-Y and Ce-Na-Y-2 zeolites look quite promising as they seem to retain most of their efficiency on low sulphur feed, indicating that the insertion of lanthanum and cerium has a positive effect on the adsorption of the heavy sulphur aromatics in a real diesel feed. The reasons are currently under investigation: for the Ce-Na-Y-2, a possible explanation is the advantage of the higher Ce content (via the second ion-exchange step) on the adsorption. Very recently, an attempt has been made to utilize a more acidic sorbent (a property that could lead to the enhancement of the direct S-M bond) like the H-Y zeolite. According to Figure 1, the results are encouraging as H-Y leads to a sulphur reduction substantially higher than the single Na-Y for HS and MS diesels: 59 and 43% reduction respectively. These values for the single H-Y are also superior to all the ion-exchanged Na-Y zeolites, so the future ion-exchange synthesis using H-Y as a basis may yield even superior adsorption capabilities.

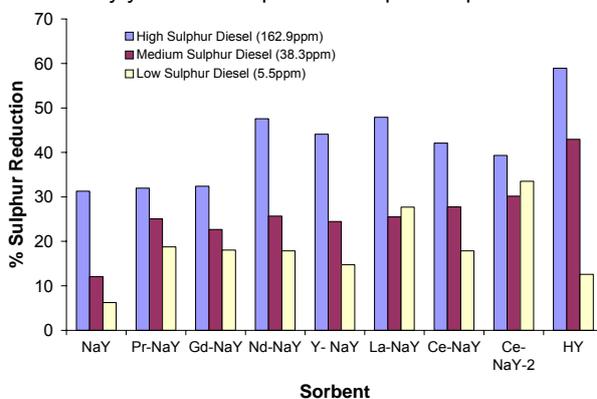


Figure 1: Sulphur reduction of the three commercial diesel (%wt) using different zeolites, at room conditions

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Dynamic experiments in a fixed bed reactor have also been launched; the results of several compounds are reported in Figures 2 and 3. In Figure 2 the Model Diesel has been processed and the sulphur reduction appears to stay stable at almost 100% for a high cumulative amount of treated diesel, confirming the ability of the selected materials to remove the sulphur from a simple mixture. On

this model, further experiments will be performed to determine the maximum sulphur uptake capacity (g/g) of the powders. Figure 3 shows the results for the dynamic experiments using the MS diesel. Also, in this case, the initial sulphur reduction, in accordance with the batch experiments values, is significantly lower than in the case of Model Diesel and it decreases with the amount of diesel processed. This decrease is justified by the progressive saturation of the sorbent by the sulphur compounds and, mostly, by the aromatics. It can also be concluded that the three ion-exchanged zeolites studied show clearly higher sulphur reduction capability than Na-Y.

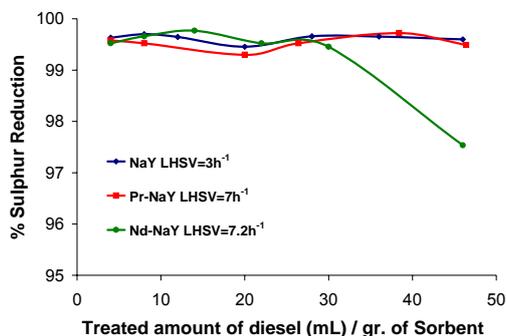


Figure 2: Dynamic sulphur removal experiments with Model Diesel

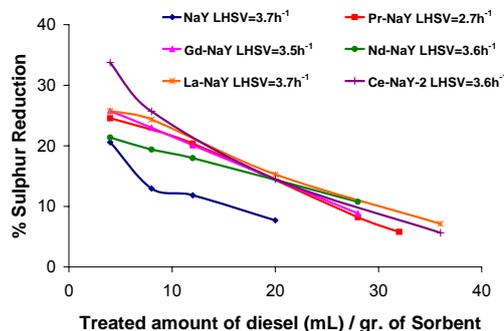


Figure 3: Dynamic sulphur removal experiments with MS Diesel

3 Gas Phase desulphurisation

3.1 Sorption materials

A commercial zinc oxide (HP grade – Purity > 99.99%), provided by Umicore (ref ZnO-HP), was used in these experiments as a reference material. It has been compared with a ZnO powder (ref ZnO-NP) synthesised in our laboratory. Additionally, some mixed oxides were also employed: two mixed zinc-iron oxides of the general formula $Zn_xFe_yO_z$, denoted as ZnFe -L and -S respectively; and two zinc-iron mixed oxides doped with Mn and Ce denoted as ZnFeMn and ZnFeCe respectively. All these mixed oxides have been synthesised within very short synthesis times via combustion reactions among liquid or solid precursor materials [4,5].

3.2 Experimental

The custom-made lab-scale unit, constructed to perform gas phase desulphurization (and sorbent regeneration) experiments, is presented in Figure 4. The unit is autonomous, mobile and consists of 2 programmable parallel three-zone furnaces (up to 1000°C) in order to allow its simultaneous operation under both desulphurization and regeneration mode. The control of the unit is achieved with the aid of Labview software. The feed gas is prepared using several mass flow controllers, that allow synthesis of mixtures comprising H_2S , steam and any diluent, including syngas mixtures representative of reformat gases. The unit includes an in-house water saturator (bubbler) made of Teflon for steam generation (steam content adjustable). Quartz reactors of 9mm ID are used and can be loaded either with sorbent powders or with small-size sorbent-coated substrates. Where necessary, lines are built with Sulfinert® materials to avoid H_2S losses and incorrect measurements. H_2S and SO_2 measurements are performed with an on-line mass spectrometer (V&F, Airsense 2000), capable of measuring down to ppb levels in a continuous way (SO_2 is monitored in order to check undesired reactions leading to SO_2 formation).

Two types of experiments have been performed using the sorbents described above:

- Net performance experiments: at 300°C, a 10ppmv H_2S mixture in N_2 was passed through the sorbent bed and the outlet H_2S was measured for a 30 minutes steady state period. The Gas Hourly Space Velocity (GHSV) was maintained constant at 12000h⁻¹. The inlet had low sulphur concentration (10ppmv), as requested to be close to representative commercial diesel reformat H_2S content. The goal was to preliminary screen the materials by investigating the maximum sulphur reduction achievable from the various powders; that is why dry mixture was used at this stage.
- Breakthrough experiments: since sulphur saturation of the powders, using 10ppmv H_2S mixture, can take an extremely long time, a high-sulphur-concentration H_2S mixture

(5000ppmv in He) has been used to characterize the sulphur capacity of the sorbents. Using a sorbent volume of 1mL, the H₂S outlet concentration was monitored as a function of time. The breakthrough time (BT) was defined as the time when this concentration reached 10 % of the initial one, i.e. 500ppmv.



Figure 4: Test unit for gas phase desulphurisation experiments

3.3 Results and Discussion

The net performance of the sorbents tested is compared in Figure 5. The steady-state outlet concentrations are all in the range 15-30ppbv (note: the analyser detection limit is 10ppbv) with slightly decreasing performance in the order of ZnFeCe>ZnFe-L>ZnO-HP>ZnFeMn>ZnFe-S. Although these differences have to be noticed, we can consider that all powders have almost the same performance and that in-house synthesised materials including zinc-, iron-, ceria- and manganese- doped appear to reach as low outlet values as the commercial ZnO.

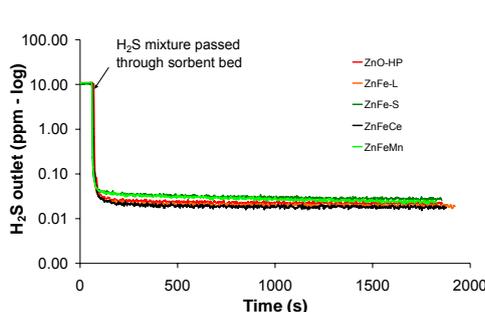


Figure 5: H₂S removal with commercial ZnO and mixed oxides materials

Inlet: 10ppmv H₂S/N₂, T=300°C, GHSV=12000h⁻¹

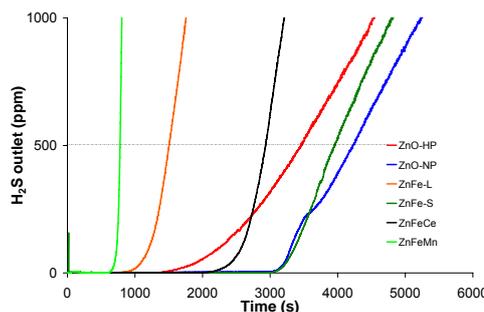


Figure 6: H₂S breakthrough curves with commercial ZnO and mixed oxides materials

Inlet: 5000ppmv H₂S/He, T=400°C, GHSV=12000h⁻¹

Typical breakthrough curves for the materials tested are shown in Figure 6. It can be observed that for all powders tested, the outlet H₂S concentration remains negligible for a significant amount of time. It appears that the ZnO-NP and the ZnFe-S sorbents exhibit the highest breakthrough time, allowing thus the highest time autonomy in desulphurization for a given volume. From these curves, the comparative material performance graph shown in Figure 7 was constructed, based on the saturation of 1mL of each sorbent with sulphur. It shows the comparison of the H₂S adsorption (uptake) per gram and per m² of surface area (BET) of sorbent during this breakthrough time. ZnO-NP has an H₂S uptake per gram and m² of sorbent very close to that of ZnO-HP. The ZnFe-L sample exhibits very high H₂S uptake per gram of sorbent, but shows a poor breakthrough time: this phenomenon is linked to the very low density of this powder. In the same time the ZnFe-S and, to a lower extent, the ZnFeCe materials, seem to be very efficient sorbents with long breakthrough time, and mostly, a very high H₂S uptake / m² of powder. This parameter, considering the importance of high space velocities favouring surface reaction preponderance, and a scaled-up configuration employing sorbent-coated porous substrates, is probably as interesting as the uptake per mass unit. In

addition to this interesting result, the potential positive influence of their modification with iron and cerium dopants for H₂S removal in steam and reformat mixtures is currently under evaluation.

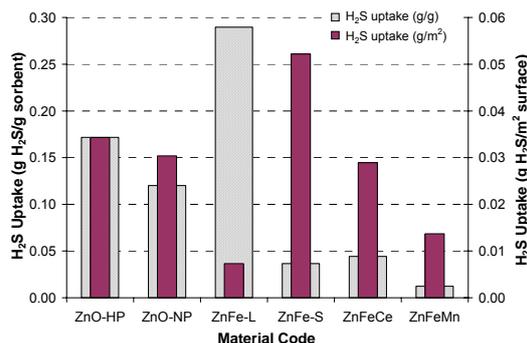


Figure 7: H₂S mass and surface ratios uptake

Inlet: H₂S 5000ppmv, T=400°C, GHSV = 12000h⁻¹, Sorbent bed = 1mL

4 Conclusions

Two desulphurization processes to be utilized in multi-fuel processors for hydrogen production were investigated: desulphurization of liquid hydrocarbons and H₂S removal from reformat gases. With respect to the liquid desulphurization process, it has been demonstrated that H-Y zeolite shows promising results in terms of reduction of sulphur compounds contained in diesel fuel, while the addition of lanthanides or transition metals inserted in Na-Y (ion-exchange) is able to further enhance the Na-Y initial performance. The presence of aromatic compounds in the fuel inhibits the selective adsorption of sulphur aromatics due to the prevalence of the π-bond adsorption mechanism, and combination of the above and new compounds is under investigation to reduce this effect. In terms of gas desulphurization, synthesised zinc oxide, zinc-iron, ceria and manganese oxide-based materials show promising and sometimes better results compared to commercial zinc oxide, at low temperatures and with simple mixtures. The advantages of these materials, in terms of composition and physical properties due to their synthesis methods, will be further investigated, particularly with more complex gaseous mixtures including steam and simulated reformat.

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