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Catalysis Today 130 (2008) 190–194

CATALYSIS TODAY

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Gasoline desulfurization by catalytic alkylation over silica-supported heteropolyacids: From model reaction to real feed conversion

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Available online 4 October 2007

Abstract

In FCC gasoline, the alkylation of sulfur compounds with olefins present in the feed, followed by a distillation to eliminate them, could be a good alternative for the desulfurization. Acidic materials (zeolites, supported acids) were screened for the alkylation of 3-methylthiophene (3MT) with 2-methyl-2-butene (2M2B), used as model reaction. Results showed that the silica-supported 12-phosphotungstic (HPW) and 12-silicotungstic (HSiW) acids are the best catalysts among zeolites and other supported acids. The performance of 40HPW/SiO_2 was then studied in a real feed of FCC gasoline. The production of heavier sulfur compounds was obtained with high conversion, and this catalyst still showed some activity after 50 h of reaction, as compared to the silica-supported phosphoric acid (SPA-11), used as a reference. Moreover the deactivation could be reduced by increasing the reaction temperature.

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Keywords: Thiophenic compounds; Desulfurization; Alkylation; Heteropolyacids; Gasoline

1. Introduction

Petroleum contains impurities such as sulfur, which after refining remains in the gasoline (if no further treatment is performed) and poisons car's catalytic converters. For this reason, environmental legislations have been implanted to reduce the sulfur content in the gasolines to less than 10 ppm of sulfur by 2009. In order to reach such an objective, research has been devoted on enhancing the performance and selectivity of the hydrodesulfurization (HDS) process and studying other alternative processes such as the olefinic alkylation of thiophenic sulfur (OATS) process [1] patented by British Petroleum. This rather attractive process consists of weighing down the sulfur compounds by catalytic alkylation with olefins present in the feed followed by distillation. Levels of desulfurization of 99.5% with a minimal octane loss (less than two points) have been reported. This is advantageous compared to a classical HDS: for the same level of desulfurization, an octane loss of 6–10 points has usually been observed [2,3].

Previous works undertaken in our group, have been focused on studying the kinetics and reaction scheme for the alkylation of 3-methylthiophene (3MT) with 2-methyl-2-butene (2M2B) both representative of sulfur compounds and olefins of a FCC feed. Two catalysts have shown moderate activity: USY zeolite and silica-supported phosphoric acid (SPA-11), the latter showing lower activity but better stability [4,5].

The aim of the present study was to screen others potentially interesting heterogeneous catalysts for the alkylation of 3MT with 2M2B taken as a model reaction, and evaluate the performance of the best catalysts in real feed. For this study, we worked with acidic solids, already used in several acid-catalyzed reactions, such as the H-Beta zeolites [6] and the MCM-22 [7,8]. We have also investigated the supported heteropolyacids, used for many heterogeneous reactions like Friedel-Crafts acylation [9], alkylation of aromatics [10,11] and isoparaffins [12,13] or esterification [14] and which are well known to possess Brønsted acidity.

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doi:10.1016/j.cattod.2007.08.017

2. Experimental

SPA-11 (11 wt.% of phosphorus) was synthesized as indicated in literature [5] by a conventional impregnation technique using H_3PO_4 solution on silica (Grace Davison 432, 320 m^2/g) and activated under air stream at 573 K (10 K/min). The USY zeolite (silica/alumina: 10.7) was provided by Tosoh Co., and used after calcination under air flow at 673 K (1 K/min) for 4 h. MCM-22 zeolite was prepared as previously reported [15] and activated under air stream until 853 K (1 K/min). H-Beta is obtained by a procedure described in literature [16] and then calcined under air stream at 823 K (10 K/min) for 5 h. Supported heteropolyacids referred to 40HPW and 40HSiW (40% of 12-phosphotungstic and 12-silicotungstic acids on SiO_2, respectively) were prepared by impregnation of appropriate quantities of hydrated $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW) over a mesoporous silica (Grace Davison 432, 320 m^2/g), using methanol as solvent. After impregnation, maturation and drying, calcination was performed under air stream at 473 K (10 K/min) for 2 h. Chemical analysis afforded W content of 26.7 wt.%, corresponding to 36% of HPW/SiO_2 as final loading.

Catalytic model reaction was carried out in a 300 mL stirred slurry tank reactor charged with 0.02 mol of 3MT (2 mL) and 0.09 mol of 2M2B (10 mL) in 0.67 mol (100 mL) of heptane as solvent and with decane (2 mL) used as internal standard for the GC analysis. Freshly calcined catalyst was added to the reaction mixture. After N_2 introduction in the reactor (0.5 MPa), the mixture was stirred at 700 rpm and heated up from room temperature to reaction temperature (358 K). Time zero for the catalytic reaction was taken when this temperature was reached. Under these conditions, only 10% of 2M2B (reactant in excess) is in the gas phase (Cerius simulation).

Deactivation was measured in a continuous trickle bed reactor (micro-pilot), using the same feed composition at a spatial velocity of 74 h^{-1}, 358 K under 0,01 MPa. The liquid and gas flows were chosen in order to keep the reactants mostly in the liquid phase. In both cases, the samples were analyzed with a HP5890 gas chromatograph equipped with FID and with a CPSIL 5 column $[(50 \times 3.2 \times 10^{-4}) \times (5 \times 10^{-6}\ \mathrm{m})]$. Blank runs were carried out for both tank and continuous reactors and showed no activity and no diffusion problems.

The real feed experiments (FCC gasoline, 340 ppm S) were carried out in Japan (AIST, Tsukuba), using a continuous trickle bed reactor at 338–396 K, under 0.5 MPa of N_2 in order to avoid compounds oxidation. The spatial velocity (WHSV) was 4.5 h^{-1}, and the gasoline and nitrogen flows were 4.5 g/h and 43 N cm^3/min, respectively. The reactor was charged with 1 g of catalyst (powder). Samples were collected after 50 min of accumulation in the condenser which was maintained at 273 K by a cryostat. The sulfur compounds were analyzed using a GC-SCD (sulfur compound detector) with HP1 column $[(30 \times 3.2 \times 10^{-4}) \times (2.5 \times 10^{-7}\ \mathrm{m})]$. The total sulfur content was determined by elemental analysis with a TS-100V Mitsubishi Chemicals Co. The FCC gasoline contained only heavy fractions of the whole range FCC gasoline which was obtained from the Japanese refinery. It was analyzed by GC (Agilent 5890) installed with a gasoline peak identification software (GPI system, Agilent) to obtain the data of GC-RON, density, average molecular weight, and the hydrocarbon compositions, such as paraffins, isoparaffins, olefins, naphtenes, and aromatics (PIONA).

3. Results and discussion

3.1. Catalysts screening in model reaction and deactivation

The initial catalytic activities observed in batch reactor for the various catalytic materials are displayed in Fig. 1. It can be seen that silica-supported heteropolyacids are the most active catalysts. The H-Beta sample presents the highest activity among the considered zeolitic materials, therefore the 40HPW and 40HSiW catalysts are respectively 4 and 27 times more active than USY and SPA-11 materials which have been previously shortlisted as the more promising catalysts [4,5].

The alkylation of 3-methylthiophene (3MT) with 2-methyl-2-butene (2M2B) gives mono- and di-alkylated compounds by successive reactions (Scheme 1). However, a reaction of olefin dimerization occurs in parallel (in our case 2M2B) giving the formation of hydrocarbons compounds containing mainly 10 carbon atoms. Of course this side-reaction has to be avoided as much as possible to keep a high octane number. Nevertheless, the product distribution depends on the nature of the catalyst as it can be seen in Figs. 2 and 3. Less active catalysts like SPA-11 and MCM-22 showed high selectivity in products of mono-alkylation similarly to H-Beta zeolite and on the contrary supported heteropolyacids (40HPW and 40HSiW) and USY materials lead preferentially to products of dialkylation. Such a distribution could be associated to shape selectivity coming from the ratio between the size of the products and the size of solid cavities. Indeed the size of the monoalkylated molecules (1, 2, 3) has been estimated with Cerius^2 software [17] to be approximately 8 × 5 Å and the dialkylated molecule (4) size is approximately 10 × 5 Å. According to these sizes, all the products could easily diffuse inside the three-dimensional USY cavities (11 Å) but the maximal diameter for H-Beta and MCM-22 cavities are respectively 6.6 and 9.6 Å which only

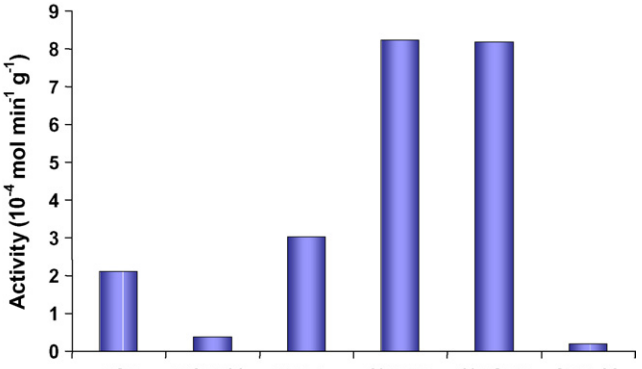
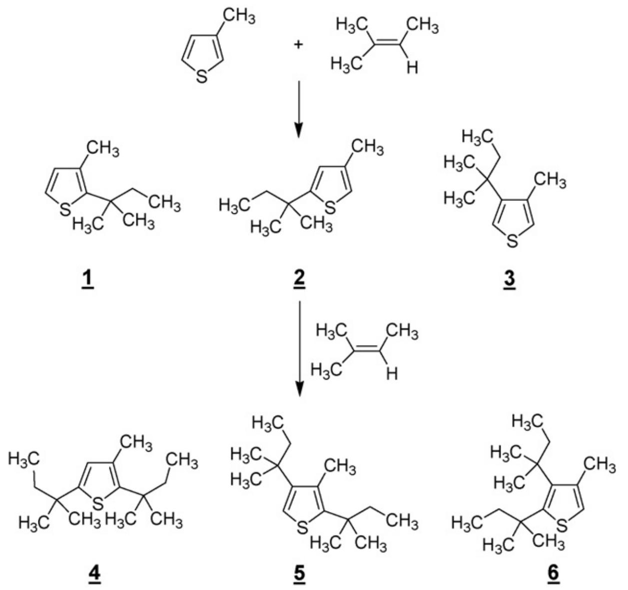


Fig. 1. Initial activities in the alkylation of 3MT with 2M2B (batch reactor, 358 K, $P(N_2) = 0.5$ MPa, 700 rpm).



Scheme 1. Reaction scheme of the alkylation of 3MT with 2M2B.

allows the monoalkylated products to diffuse. For SPA, such a pore size effect could also be considered since an important loss of mesoporosity has been reported after impregnation of the active phase [5]. The selectivity found for the supported heteropolyacids is in agreement with the conservation of the mesoporosity observed after impregnation and calcination of the silica. H-Beta zeolite allowed a medium activity but could be preferred according to the selectivity to economize olefins and preserve the octane number. The ratio dimerization/alkylation is also advantageous for this zeolitic material just as the supported heteropolyacids.

Differences in selectivities toward alkylation and dimerization of the olefin, previously observed for USY and SPA-11, have been explained by change in the surface mechanism (Langmuir Hinshelwood or Eley Rideal mechanism) [4,5]. Therefore, the high selectivity toward the alkylation reaction (as compared to the dimerization reaction) observed for 40HPW and 40HSiW, suggests a high interaction between the thiophenic compound and the catalytic surface. Adsorption experiments (not reported here) confirmed this assumption. All these catalysts have been tested in a continuous flow unit, at 358 K. First of all, these experiments have confirmed both the activities and selectivities already observed in the batch mode. Secondly, evolution of 3MT conversion with time showed that H-Beta was rapidly deactivated and that only supported heteropolyacids (40HPW and 40HSiW) could maintain a good activity after 15 h on stream. Therefore, 40HPW catalyst has been chosen for real feed experiments and compared to the SPA-11 sample.

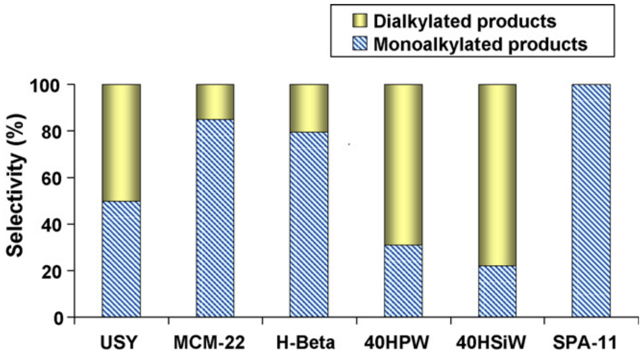


Fig. 2. Dialkylated and monoalkylated products selectivity in the alkylation of 3MT with 2M2B (at 30% of 3MT conversion, 358 K, $P(N_2) = 0.5$ MPa, 700 rpm).

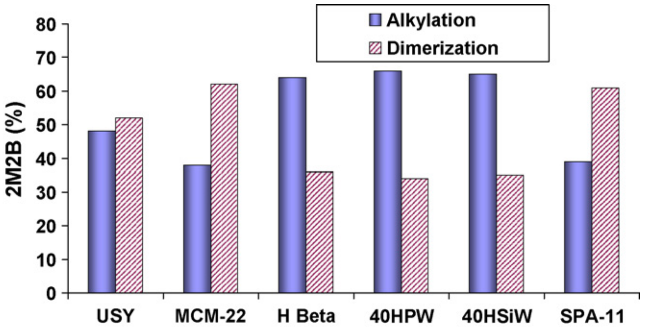


Fig. 3. Percentage of 2M2B involved in dimerization and alkylation reactions (358 K, $P(N_2) = 0.5$ MPa, 700 rpm).

3.2. Test in real feed: alkylation of sulfur compounds in gasoline

In addition to aromatics (33 wt.%), olefins (22 wt.%), paraffins (4.4 wt.%), isoparaffins (28.6 wt.%) naphtenes (12 wt.%), and sulfur compounds (340 ppm), the FCC feed used in this study contained also nitrogen compounds (19 ppm); the feed octane number was 89 (RON) and a molar weight of 109 g/mol (Table 1). According to the GC analyses, true boiling

Table 1
Properties of the FCC feed

Properties of the feed	
Density (15 °C)	0.765 g/cm3
Vapor pressure	16.3 kPa
Molar weight	109 g/mol
GC-RON	89
Nitrogen	19 ppm
Sulfur	340 ppm
Oxygen	0 ppm
Total C	86.7%wt
Distillation (°C)	
IBP	70.2
10 vol.%	88.6
30 vol.%	107.9
50 vol.%	116.2
70 vol.%	132.0
90 vol.%	173.4
FBP	206.8
PIONA analysis (vol.%)	
Paraffins	5.0
Isoparaffins	31.3
Olefins	23.3
Naphtenes	11.8
Aromatics	28.5

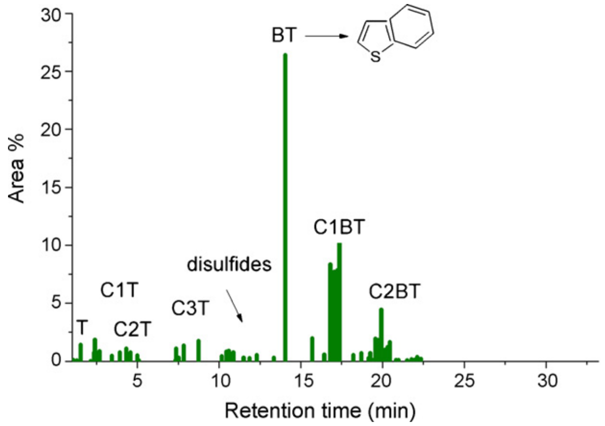
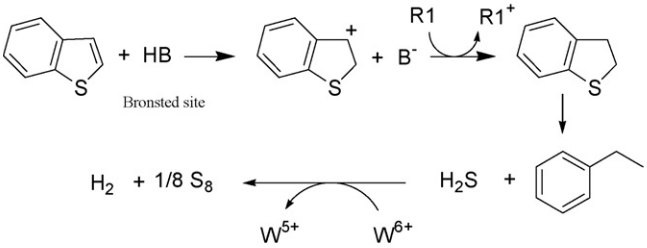


Fig. 4. Sulfur compounds observed by GC-SCD in the real feed.

curve (TBP) was obtained after rearranging the assigned components in the order of the boiling points and accumulating them in vol.%. The peak area assignment was more than 98.5%. These TBP data were correlated with the distillation data in Table 1 by ASTM D86. However, this distillation data is not strictly the same as the distillation data by ASTM D3710.

The SCD chromatograms of sulfur compounds present in the initial feed are shown in Fig. 4. In addition to thiophenic compounds, benzothiophenic derivatives (BT, C1-BT and C2-BT) are found to be the major sulfur compounds of this feed. The highest retention time for these reactants is 23 min.

After 2 h on stream on both 40HPW and SPA-11, the retention time of the sulfur compounds reached 33 min. This means that initial sulfur compounds have become much heavier. We can note that dibenzothiophene (DBT, bp = 333 °C) was eluted with a retention time of 25 min in the same conditions. The initial conversion of the real feed was 60% for 40HPW and 33% for SPA-11. After 10 h, the activity decreased but sulfur products with retention times higher than 23 min were still present (Fig. 5). It must also be mentioned that 40HPW allowed transformation of BT and C1-BT compounds rather than thiophenic compounds. After 50 h on stream, a feed conversion of 8% was still observed using 40HPW compared to 0.1% using SPA-11 catalyst.



Scheme 2. Reaction scheme for the formation of S_8.

For both catalysts, after 2 h on stream, a large peak appeared at 28 min of retention time and has been assigned to S_8 (identified by direct injection). The quantity of S_8 decreased after about 10 h of reaction and so catalytic activity. The production of S_8 (Scheme 2) could be explained by the oxidation of H_2S [18] formed by cracking reactions of sulfur compounds [19,20]. Although these cracking reactions have been reported at higher temperature they could be favored by the acidity of the catalyst. The effect of temperature on the deactivation is displayed in Fig. 6. At higher temperature

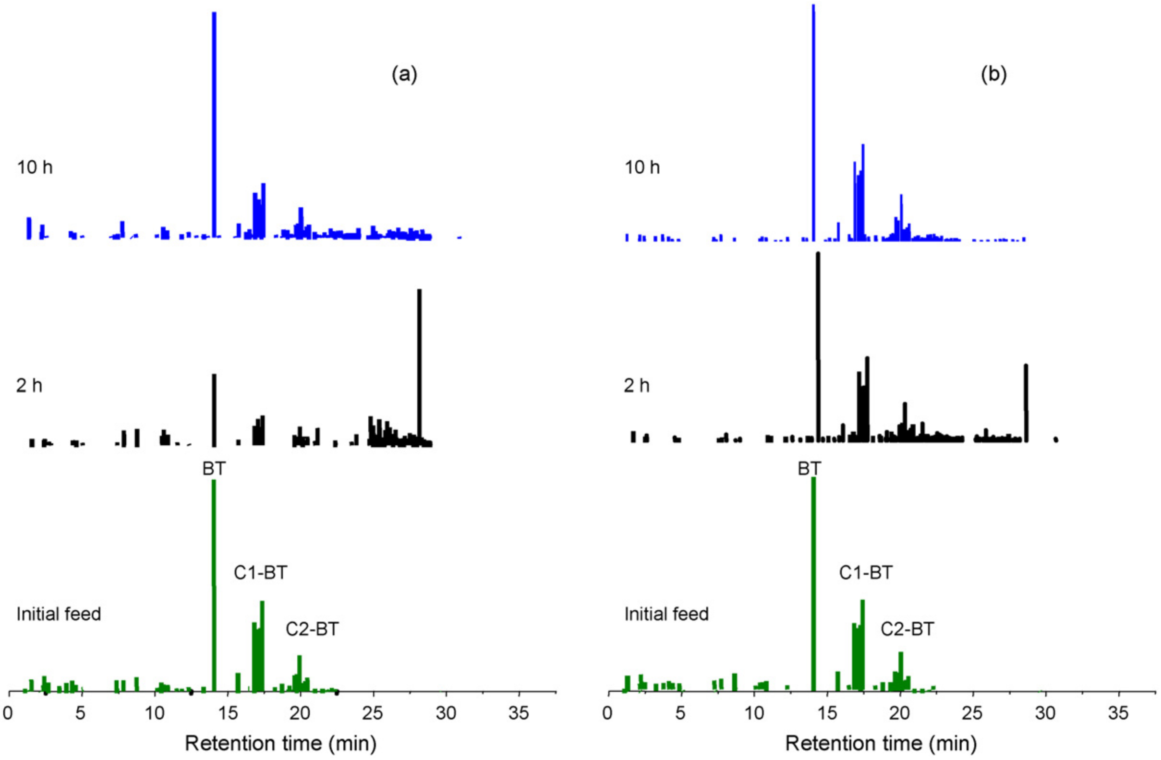


Fig. 5. GC-SCD analysis of the feed at initial time, and after 2 and 10 h with (a) 40HPW and (b) SPA-11.

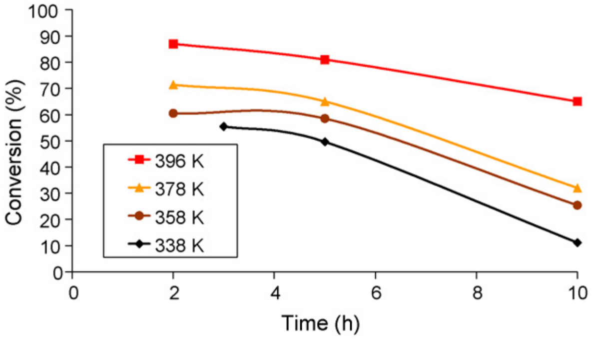


Fig. 6. Influence of the temperature on real feed conversion with 40HPW (VVH = 74 h^{-1}, 0.5 MPa).

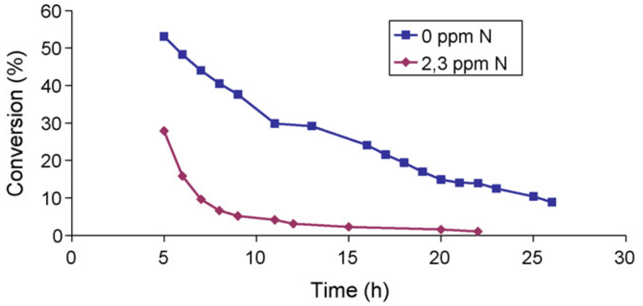


Fig. 7. Effect of *o*-toluidine in the model reaction with 40 HPW (358 K, VVH = 74 h^{-1}).

(396 K), the conversion of the real feed increased to almost 87% and the deactivation was drastically reduced. After 10 h at 396 K, the feed conversion was still 70% compared to 30% at 358 K. This behaviour was probably due to the lower adsorption strength of poisoning compounds (nitrogen compounds) at higher temperature of reaction. Deactivation of 40HPW with nitrogen compounds was confirmed during continuous and batch catalytic test using the model reaction and by adding a few ppm of *ortho*-toluidine, one of the typical nitrogen compounds present in FCC gasoline. The effect of *o*-toluidine addition on the activity of 40HPW/SiO_2 in alkylation of 3MT with 2M2B is displayed in Fig. 7. The distribution of the products in presence of *o*-toluidine did not change. On the other hand, the conversion of 3MT with addition of 2.3 ppm of *o*-toluidine decreased drastically compared to the conversion obtained without any nitrogen compound. This poisoning effect clearly came from the basicity of the N-compound (*o*-toluidine) and additional experiments have shown that the *o*-toluidine was adsorbed irreversibly onto the catalyst at 358 K. It can also be noticed the formation of much heavier sulfur compounds at 396 K than those found at 358 K with 40HPW. Compounds with retention times of 35 min were most probably formed by self-alkylation reactions [21].

4. Conclusions

The silica-supported heteropolyacids 40HPW and 40SiW were singled out as the most active catalysts in the model alkylation of 3MT with 2M2B. These catalysts lead selectively to products of dialkylation and proved to be less deactivated than the other solids in continuous tests. Then, they catalyzed efficiently the transformation of sulfur compounds in real feed of FCC gasoline under soft reaction conditions. In these experiments, benzothiophenic derivatives were preferentially converted than thiophenic compounds. Evidence for cracking reactions was found at the beginning of the catalytic test leading to the formation of S_8. Catalyst deactivation, probably mainly due to the poisoning by N-compounds and coke deposition at the beginning of the reaction, may be drastically reduced by increasing the temperature of the reaction.

Acknowledgments

M. Arias is grateful to Dr. A. Tuel (IRCELYON) for providing MCM-22 sample and to Dr. J. Blanchard (LRS, UPMC, Paris) for providing H-Beta zeolite. This work was generously supported by AIST and the CNRS.

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