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Removal of nitrogen compounds from liquid hydrocarbon streams by selective sorption on metal-organic framework MIL-101

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High sorption capability and selectivity towards N-containing compounds were observed for metal-organic framework MIL-101 under the sorption from light cycle oil and model mixtures.

Hydrodesulfurization (HDS) is a conventional method employed by refineries to produce low-sulfur fuels.[1,2] Organic nitrogen compounds typically found in middle-distillate oil inhibit the HDS of organosulfur compounds through competitive adsorption on the catalytic sites.[3–5] It was shown that the removal of nitrogen compounds from the middle-distillate oil significantly improve HDS performance, allowing one to achieve an ultra deep HDS under mild conditions using conventional catalysts.[6] The removal of nitrogen compounds by adsorption at ambient temperature is a promising approach. The adsorption of nitrogen compounds by well-known porous materials such as activated carbons,[7–9] activated alumina,[8,9] silica-based adsorbents[10,11] and zeolite-based materials[12,13] was studied (Table 1). The best results were achieved for activated carbons with the highest surface area, pore volume and percentage of mesoporosity.[7,8]

Table 1 Adsorption capacities of porous materials for total nitrogen.

Sorbent	Adsorption capacity[a]/mg of nitrogen per gram of sorbent	Reference
Activated carbon	15–19	8, 9
Silica-based adsorbents	8	10
Activated alumina	5–6	8, 9
Zeolite-based materials	3	12

[a] Total nitrogen content in hydrocarbon streams is 200–300 ppmw.

Therefore, the mesoporous metal-organic framework MIL-101 (where MIL – Materials of Institute Lavoisier) with extra-large Langmuir surface area (for N_2, 5900±300 $m^2\,g^{-1}$)[14] is a promising material for this application. This coordination polymer is built from Cr_3O triangular cluster complexes, bridged by linear terephthalate linkers into a regular porous framework with MTN (Mobil Thirty Nine) zeolite topology. Another important feature of MIL-101 is unsaturated coordination environment of the Cr^{III} cations, which makes them strong binding sites for organic substrates. In the present study, the denitrogenation of model mixtures and middle-distillate hydrocarbon streams by MIL-101 sorbent was investigated.

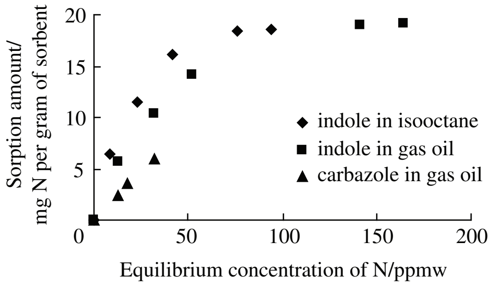

Figure 1 Adsorption isotherms for indole and carbazole for MIL-101 from model mixtures (carbazole is poorly soluble in isooctane or hydrotreated SRGO).

The straight run gas oil (SRGO) and cracked products of heavier feedstocks (light cycle oil), as well as the model mixtures of nitrogen compounds in isooctane, were used for the sorption experiments. Light cycle oil (LCO) has higher nitrogen concentration, so it is especially important to remove organic nitrogen compounds from LCO. Most of the nitrogen compounds found in LCO and SRGO are present as aromatic heterocycles with multiple rings (indole, carbazole and their alkyl derivatives).[15]

First, we examined the sorption of individual nitrogen-containing compounds on porous material MIL-101. For producing the adsorption isotherms, the solutions of nitrogen compounds in isooctane and in preliminary hydrotreated straight run gas oil with negligible nitrogen content were used (Figure 1). MIL-101 showed a remarkable sorption capability towards indole and carbazole. Interestingly, the sorption capability changes weakly when sorption occurs from hydrotreated SRGO instead of isooctane in spite of the presence of substantial amounts of aromatic compounds in the gas oil. Thus, MIL-101 is able to separate nitrogen-containing compounds from middle distillates with high selectivity.[†]

The adsorption of nitrogen compounds from the commercial samples of SRGO and LCO using metal-organic framework MIL-101 was also studied. It was demonstrated in our experiments that MIL-101 (10 mg) can adsorb 9.0 mg of nitrogen per gram of sorbent from SRGO containing 131 ppmw N. The total nitrogen content after sorption was almost halved to 78 ppmw. Sorption from LCO under the same conditions leads to a decrease of total nitrogen content from 498 to 395 ppmw N. This corresponds to a very high sorption capacity of 19.6 mg nitrogen per gram of MIL-101 sorbent.

The detailed analysis of the nitrogen compounds in the LCO before and after adsorption allowed us to conclude that the sorption treatment leads to a decrease in the concentration of all N-containing components (Figure 2, Table 2). The high sorption capacity of MIL-101 for nitrogen-containing compounds can be attributed to the coordination of nitrogen atoms to the unsaturated Cr^{III} centres. In that connection, the better steric accessibility of N atom of the substrate molecule, the higher

Table 2 Composition of nitrogen compounds in LCO before and after sorption on MIL-101.

Compound	Before sorption/ μg N cm^{-3}	After sorption/ μg N cm^{-3}	Conversion (%)
Indole derivatives	25	17	32
Carbazole	20	15	25
1-Methylcarbazole	32	24	23
3-Methylcarbazole	17	13	23
2-Methylcarbazole	21	16	23
4-Methylcarbazole	19	15	23
1,8-Dimethylcarbazole	12	10	21
1,3-Dimethylcarbazole	12	9	22
1,6-Dimethylcarbazole	14	11	21
1,7-Dimethylcarbazole	16	13	21
1,4- and 1,5-Dimethylcarbazole	33	26	22
3,6-, 2,6-, 3,5-, 2,7-, 2,4-, 1,2-, 2,5-Dimethylcarbazole	62	47	24
2,3- and 3,4-Dimethylcarbazole and C$_3$-carbazoles	113	93	18
C$_4$-carbazoles	21	17	21
Sum of peaks	420	328	22
Total N (by ASTM D5762)	473 (498 ppmw)	375 (395 ppmw)	21

sorption performance of MIL-101 toward this substrate. Indeed, indole and its derivatives show higher sorption values, whereas carbazoles with two methyl groups at 1- and 8-positions possess the worst sorption properties among all other substrates due to the steric hindrances caused by the methyl groups. The sorption selectivity for nitrogen compounds in middle-distillate oil over the MIL-101 increases in the order 1,8-dimethylcarbazole < < carbazole < indole derivatives < indole (Table 2, Figure 1).

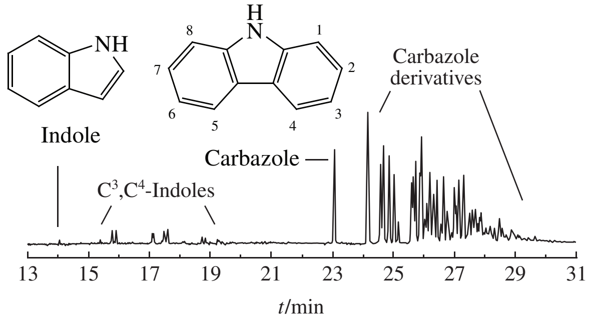

Figure 2 GC-AED nitrogen chromatogram of LCO.

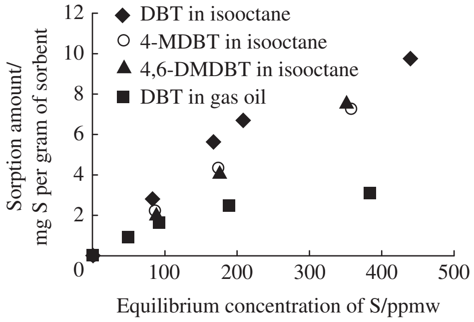

Figure 3 Adsorption isotherms for dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) for MIL-101 from model mixtures.

The sorption of other aromatic molecules apparently occurs due to π–π stacking interactions with terephthalate bridges of metal-organic framework. For example, the sorption capacity of MIL-101 for dibenzothiophene derivative is low (Figure 3) and strongly decreases when sorption experiments are carried out in the hydrotreated SRGO instead of isooctane. This behaviour indicates competitive sorption between sulfur-containing and other aromatic compounds.

In summary, metal-organic framework MIL-101 shows a remarkable sorption capability and selectivity towards N-containing compounds during the sorption from liquid hydrocarbon streams (SRGO and LCO) and model mixtures. This observations can be explained by coordination of nitrogen atoms to Cr^{III} centers of metal-organic framework whereas sorption of other aromatics occurs mainly due to the stacking interaction.

References

1 H. Topsoe, B. S. Clausen and F. E. Massoth, *Hydrotreating Catalysis. Science and Technology*, Springer-Verlag, Berlin, 1996.

2 S. K. Bej, S. K. Maity and U. T. Turaga, *Energy Fuels*, 2004, **18**, 1227.

3 M. Egorova and R. Prins, *J. Catal.*, 2004, **221**, 11.

4 S. D. S. Murti, H. Yang, K.-H. Choi, Y. Korai and I. Mochida, *Appl. Catal. A*, 2003, **252**, 331.

5 T. C. Ho, *J. Catal.*, 2003, **219**, 442.

6 M. Macaud, M. Sevignon, A. Favre-Reguillon, M. Lemaire, E. Schulz and M. Vrinat, *Ind. Eng. Chem. Res.*, 2004, **43**, 7843.

7 Y. Sano, K.-H. Choi, Y. Korai and I. Mochida, *Appl. Catal. B*, 2004, **49**, 219.

8 M. Almarri, X. Ma and C. Song, *Ind. Eng. Chem. Res.*, 2009, **48**, 951.

9 J. H. Kim, X. Ma, A. Zhou and C. Song, *Catal. Today*, 2006, **111**, 74.

10 J.-M. Kwon, J.-H. Moon, Y.-S. Bae, D.-G. Lee, H.-C. Sohn and C.-H. Lee, *ChemSusChem*, 2008, **1**, 307.

11 Y.-S. Bae, M.-B. Kim, H.-J. Lee, C.-H. Lee and J. W. Ryu, *AIChE J.*, 2006, **52**, 510.

12 A. J. Hernandez-Maldonado and R. T. Yang, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 1004.

13 Y. Shiraishi, A. Yamada and T. Hirai, *Energy Fuels*, 2004, **18**, 1400.

14 G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2005, **309**, 2040.

15 P. Wiwel, K. Knudsen, P. Zeuthen and D. Whitehurst, *Ind. Eng. Chem. Res.*, 2000, **39**, 533.

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† Indole (99%) and carbazole (96%) were purchased from Acros. Straight run gas oil (10500 ppmw S, total aromatic content 30.9 wt% and 131 ppmw N) and light cycle oil (3000 ppmw S, total aromatic content 69.2 wt% and 498 ppmw N) used in this study were provided by a Russian commercial refinery of Urals crude oil. The coordination polymer MIL-101 was prepared as described by Ferey *et al.*[14] The XRD data confirm the phase purity of MIL-101.[14] A commercial CoMo/Al$_2$O$_3$ catalyst was used to produce hydrotreated SRGO with negligible nitrogen/sulfur content (10.8 ppmw N; 8.5 ppmw S, total aromatic content 25.0 wt%). Nitrogen and sulfur compounds were monitored by gas chromatography (Agilent 6890N Instrument equipped with a 19091J-413 HP-5 capillary column, 30 m×0.32 mm×0.25 μm, and a JAS atomic emission detector). Identification of indole and carbazole derivatives in LCO was performed according to literature data.[15] The total nitrogen content was determined by chemiluminescence using an Antek 9000 NS (ASTM D5762) instrument.

The individual organonitrogen or organosulfur compounds were dissolved in isooctane or hydrotreated SRGO (2 ml), and MIL-101 (10 mg) was added to the solution. Under the sorption from hydrocarbon feed MIL-101 (10 mg) was added to 2 ml of SRGO or LCO. After stirring the mixture for 16 h at room temperature, the sorbent was collected by filtration. The filtrate was analyzed by GC. MIL-101 is stable under the experimental conditions. After the sorption experiments, the mesoporous metal-organic framework could be regenerated by extracting the N-containing compounds by acetone, dried and reused in the next cycles of sorption experiments, without appreciable loss of its sorption capability.