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Resistance to poisoning by nitrogen compounds of NiMo/Al-MCM-41 hydrocracking catalysts

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Abstract

A series of MCM-41 of different compositions (silica/alumina ratios of 32, 49, 66 and infinite) was prepared and characterized by several techniques: XRD, N_2 adsorption, NMR (MAS) of ^{27}Al and ^{29}Si and FTIR of adsorbed pyridine. NiMo catalysts were prepared by impregnation and tested for cumene hydrocracking in the presence and absence of quinoline. The comparison of the results obtained in both conditions indicates that these catalysts are resistant to the poisoning by basic nitrogen compounds. Therefore, these materials are highly interesting to the development of hydrocracking catalysts better suited to the processing of nitrogen-rich brazilian crudes.

Keywords: Hydrocracking catalysts; Hydrodenitrogenation; Nitrogen compounds; Poisoning

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1. Introduction

Brazilian crudes coming from the 'Bacia de Campos', especially those from the field called 'Marlim', present a peculiar composition—low sulphur contents (0.75 wt.%), but very high nitrogen contents (0.45 wt.%). It is a heavy oil (21.5 vol.% of gasoil and 33 vol.% of heavier residues), which needs to be submitted to processes like fluid catalytic cracking (FCC) or hydrocracking (HCK) to convert the heavy fractions into lighter more valuable products [1].

Typical hydrocracking catalysts incorporate two functions—a hydrogenating-dehydrogenating function represented by a combination of two metals from Groups VIII and VI, usually Ni (or Co) and Mo (or W) and an acidic function, represented by the support, generally doped alumina, silica-alumina or zeolites, responsible for the cracking via a carbenium ion mechanism [1–4]. However, many organic nitrogen compounds are poisons to those acidic materials [1]. One possible solution to overcome this problem is the development of HCK catalysts resistant to poisoning, either to be used in one-stage processes or to allow less severe hydrotreating conditions in two-stage processes.

In the early 1990's a novel mesoporous molecular sieve, MCM-41, was synthesized [5,6]. Its pore system is constituted of uniform parallel channels, whose diameter can be adjusted between 15 Å and 100 Å varying the synthesis conditions, allowing the diffusion of bulky molecules. Aluminum can be incorporated in the structure, developing acidic sites of medium strength, comparable to a silica-alumina [7]. The large surface areas, wide pore diameters and mild acidity make these materials an interesting alternative as supports for hydroprocessing catalysts. They have already been tested for several reactions, including mild hydrocracking (MHC) [8,9], hydrogenation of aromatics [10], hydrodesulphurization (HDS) [11–13] and hydrodenitrogenation (HDN) [8]. Moreover, some previous works indicate that MCM-41 based catalysts present some resistance to poisoning by basic nitrogen compounds [8,14].

Apelian et al. [14] claimed that a NiW–MCM-41–Al_2O_3 catalyst is capable of hydrocracking a heavy distillate feed

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(initial boiling point of 680 K) containing high levels of sulphur (0.72 wt.%) and nitrogen (1500 ppm; 466 ppm of basic nitrogen). It was also shown that this catalyst was able to simultaneously remove sulphur and nitrogen compounds from a shale oil containing 2.2 wt.% of N (reduced to ca. 2 ppm) and 0.69 wt.% of S (reduced to ca. 0.5 wt.%) and eliminate metals like Fe and Ni.

Corma et al. [8] observed that NiMo–MCM-41 catalysts presented higher HDS, HDN and MHC conversions and better selectivity to middle distillates when processing an untreated vacuum gasoil (2.53 wt.% of S and 2900 ppm of N) than similar catalysts supported on USY zeolite or silica-alumina. When the feed was pretreated to remove half of its nitrogen, the MCM-41 catalyst showed a lower MHC activity than the USY, but higher than the silica-alumina, while maintaining its better selectivity to middle distillates.

Those features suggest that MCM-41 could be useful as a support for HCK catalysts, particularly in the processing of heavy nitrogen-rich brazilian crudes. In order to evaluate this hypothesis, we have compared the cumene HCK activity of NiMo–MCM-41 catalysts in the absence and in the presence of basic nitrogen compounds.

2. Experimental

2.1. Synthesis

MCM-41 of different silica/alumina molar ratios (SAR) were prepared from aqueous mixtures of silica (Gasil Aerojet), sodium aluminate (Carlo Erba, p.a.), sodium hydroxyde (Merck, p.a.) and cetyltrymethylammonium (CTMA) chloride (Aldrich). The molar compositions of the reaction mixtures were SiO_2, 1.0; Na_2O, 0.1; CTMA, 0.3; H_2O, 26, and Al_2O_3, 0.025, 0.033, 0.05 and 0 for SAR values of 40, 30, 20 and infinite (no Al), respectively. The solids obtained after heating at 423 K for 48 h were washed with water and then dried overnight at 393 K and calcined at 813 K, 1 h in a flow of nitrogen and 5 h in air. Ni–Mo catalysts (3.4 wt.% NiO and 10 wt.% MoO_3) were prepared by incipient wetness impregnation in two consecutive steps, using aqueous solutions of ammonium heptamolybdate and nickel nitrate. After each impregnation step the samples were dried overnight at 393 K and then calcined at 773 K for 3 h.

2.2. Characterization

Elemental analysis (ICP/AES) was carried out with a Perkin-Elmer P-1000 spectrometer. The samples (approximately 0.10 g) were dissolved in a mixture of nitric and fluoridric acid at 353 K for 30 min.

X-ray diffraction patterns were measured with a Miniflex–Rigaku powder diffractometer (Cu Kα, 30 kV, 15 mA) between 1.2° and 10° (2θ) in steps of 0.02° and a step time of 2 s.

Nitrogen physisorption was measured at 77 K with a Quantachrome Autosorb 1C apparatus. The surface area and the pore size distribution were determined using the BET and BJH methods, respectively.

Solid-state ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Varian Inova-300 spectrometer with a VT-CP/MAS probe for solid samples. For ^{27}Al, the frequency was 78.4 MHz, the rotor was spun at 6.2 kHz and 6000 scans were acquired, using $AlCl_3{\cdot}6H_2O$ as a reference. The samples were previously hydrated for 48 h. For ^{29}Si, the frequency was 59.6 MHz, the rotor was spun at 3.1 kHz and 500 scans were acquired, using kaolin (91.5 ppm) as a reference.

FTIR spectra of adsorbed pyridine were obtained on a Nicolet Magna 760 spectrometer using self-supported wafers of 10 mg cm^{-2}, treated in a vaccuum cell at 753 K for 3 h. Pyridine was admitted at room temperature, and after saturation the samples were degassed at 423 K for 2 h.

2.3. Catalytic tests

The catalytic activity of NiMo–MCM-41 catalysts for the hydrocracking of cumene was determined using 0.3 g of sample in a continuous-flow tubular reactor at 51.7 bar (750 psig) and 673 K. The H_2 and liquid feed (76.5% [molar] *n*-hexane, 20% cumene, 2% *n*-decane and 1.5% dimethyldisulphide) flow rates were 450 mL min^{-1} and 12.5 mL h^{-1}, respectively. Quinoline was added to the feed (0.14%, i.e. 150 ppm of N) to assess the resistance to poisoning by nitrogen. A commercial catalyst (NiMo–SiO_2–Al_2O_3; 3.5 wt.% NiO and 10 wt.% MoO_3; 300 $m^2\,g^{-1}$) was tested under the same conditions for comparison.

3. Results and discussion

3.1. Elemental composition

The elemental analysis of the pure molecular sieves showed SAR values superior to the theoretical ones, indicating that part of the aluminum was not incorporated into the structure. The results obtained were 66, 49 and 32, instead of 40, 30 and 20, respectively. Ni and Mo contents of the catalysts were always close to the expected. SAR values were not altered by the impregnation procedure.

3.2. X-ray diffraction

The X-ray diffractograms obtained (Fig. 1) are typical of MCM-41 [15,16]. A very strong band appears at a low angle (about 2°), corresponding to the 100 reflection line, whose intensity decreases with increasing aluminum content. A large weaker band is observed at higher angles (between 3° and 5°), probably formed by a combination of the 110 and 200 lines. The decrease in intensity of the main band and the

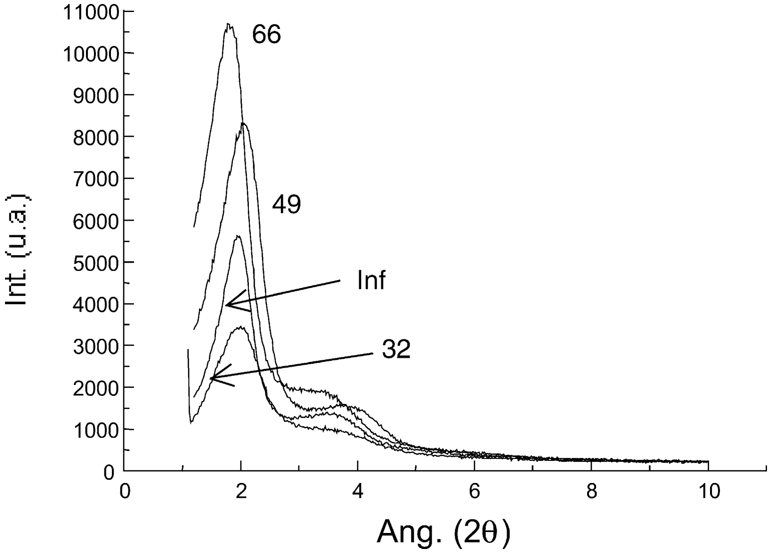

Fig. 1. X-ray diffraction patterns of calcined MCM-41.

unresolved secondary bands can be attributed to distortions in the structure caused by the insertion of Al atoms, since the Al–O bonding length (1.75 Å) is higher than the Si–O (1.60 Å) [15]. The Si-MCM-41 sample (SAR Inf.) shows a similar pattern, whose intensity is between those of SAR 32 and 49 samples, despite the absence of Al, indicating that this structure is not as well organized as one could expect.

3.3. Nitrogen adsorption

The N_2 physisorption isotherms are of type IV, according to IUPAC classification [16], with no noticeable hysteresis loop, typical of mesoporous structures with fairly uniform pores. They are reversible and exhibit a sharp step, due to capillary condensation within the mesopores, at relative pressures around 0.35, corresponding to an average pore diameter close to 40 Å. The calculated pore size distributions present limited variation around the average value, showing that the pores are quite homogeneous. The results obtained with pure supports are summarized in Table 1. The values from samples with SAR 66 and 49 are very similar, but SAR 32 presents lower surface area and pore volume. This could be explained by a less organized structure, due to the distortions caused by the presence of higher amounts of Al, which is in agreement with the results from XRD, since surface areas vary with SAR in the same way of the intensities of the 100 reflection lines. The textural results of Si-MCM-41 fit into this trend. Its surface area and pore volume are between those of SAR 32 and 49, like the intensity of the diffraction patterns.

Lower surface areas and pore volumes are observed after the impregnation of Ni and Mo (Table 2), probably due to partial blockage of the pores.

Table 1
Textural properties of MCM-41 molecular sieves

SAR	Inf.	66	49	32
Surface area ($m^2\ g^{-1}$)	846	927	982	743
Pore volume ($cm^3\ g^{-1}$)	0.89	0.98	0.96	0.80
Pore diameter (Å)	45	42	38	43

3.4. NMR (MAS) of ^{27}Al and ^{29}Si

The ^{27}Al NMR spectra of pure MCM-41 presented peaks around 0 ppm, corresponding to octahedral aluminum (extra-framework Al), and 50 ppm, attributed to tetrahedral aluminum (Al that was incorporated into the molecular sieve framework by isomorphic substitution of Si atoms).

The ^{29}Si spectra showed peaks around shifts of -92, -102 and -110 ppm, corresponding to silicon in structures known as Q_2 (groups $(\text{-O-})_2\text{Si-(OH)}_2$), Q_3 (groups $(\text{-O-})_3\text{Si-OH}$) and Q_4 (groups $(\text{-O-})_4\text{Si}$), respectively [17].

Table 3 shows the relative amounts of all those species, determined by the areas of the corresponding peaks. The proportion of tetrahedral Al grows with increasing aluminum content, in accordance with previous results obtained by Reddy and Song [15]. The Si-MCM-41 presented the highest proportion of Q_2 species, confirming that the structure of this sample was not very well organized. The SAR 66 sample has the highest proportion of Q_4 species (and the lowest Q_3/Q_4 ratio), indicating that this structure is the most polymerized.

Table 2
Textural properties of NiMo–MCM-41 catalysts

SAR	Inf.	66	49	32
Surface area ($m^2\ g^{-1}$)	489	704	727	521
Pore volume ($cm^3\ g^{-1}$)	0.56	0.73	0.69	0.56

Table 3
NMR (MAS) of ^{27}Al and ^{29}Si

SAR	Inf.	66	49	32
% Tetrahedral Al	–	28.2	35.2	40.8
% Octahedral Al	–	71.8	64.8	59.2
% Q_2 Si	9.3	5.3	7.5	7.3
% Q_3 Si	42.5	35.7	37.1	37.5
% Q_4 Si	48.2	59.0	55.3	55.1
Q_3/Q_4	0.88	0.60	0.67	0.68

3.5. FTIR of adsorbed pyridine

The results obtained by FTIR of adsorbed pyridine are shown in Table 4. The amounts of Brønsted and Lewis sites were determined by the areas of the peaks at 1546 and 1450 cm^{-1}, respectively. The Si-MCM-41 sample presented no Brønsted sites. The amounts of Brønsted and Lewis sites of SAR 49 sample were lower than those of SAR 66 and 32.

Comparison of FTIR and NMR results from Al containing samples indicates an apparent contradiction, since the increase in the relative amount of tetrahedral Al was not followed by the amount of Brønsted sites. SAR 49 has an intermediate level of tetrahedral Al, but the lowest amount of Brønsted sites and SAR 32 has 45% more tetrahedral Al than SAR 66, but only 26% more Brønsted sites. Weglarski et al. [18] attributed a similar deficit of Brønsted sites when comparing results from the same techniques to partial dehydroxylation during the activation of the samples (heating under vacuum at 673 K) prior to pyridine adsorption. IR spectroscopy showed that Brønsted sites in MCM-41 were more susceptible to dehydroxylation than those of zeolites ZSM-5 [18] and (Na or H)-Y [19] and that this effect increased with the Al content. Brønsted sites would be progressively destroyed, generating Lewis sites, one per each two Brønsted sites.

3.6. Cumene hydrocracking

In the absence of nitrogen compounds, the cumene HCK activity (Table 5) of MCM-41 catalysts of SAR 66 and 49 was close to the conversion of the commercial catalyst. The Si–MCM-41 based catalyst was the less active, as expected due to the absence of Brønsted sites. The catalyst supported on SAR 32 presented an intermediate level of conversion.

When 150 ppm of nitrogen were added to the feed, the conversion of the commercial catalysts dropped 66% (from 94.6 to 30.8%, becoming the lowest of all samples), whereas the Al–MCM–41 based catalysts lost only 4% (SAR 32) to 7% (SAR 66 and 49) of their activity. The loss of activity in the Si–MCM-41 based catalyst was more pronounced (around 23%) than in the Al-containing samples but much lower than in the case of the commercial catalyst.

Table 4
Acid sites measured by FTIR of adsorbed pyridine

SAR	66	49	32
Brønsted[a]	0.31	0.22	0.39
Lewis[a]	3.43	2.53	3.02

[a] Arbitrary units.

Table 5
Cumene conversion (%) in the absence and in the presence of quinoline

N (ppm)	Commercial catalyst	SAR			
		66	49	32	Inf.
0	94.6	99.7	98.6	76.4	57.6
150	30.8	92.8	91.3	73.1	44.5

3.7. Activity versus characterization

There is no direct correlation between the cumene conversions of the Al–MCM-41 based catalysts and the number of Brønsted acid sites (presumably the active sites) or the amount of tetrahedral aluminum (responsible for their formation). Catalysts with SAR 66 and 49 present different amounts of Brønsted sites and tetrahedral aluminum but show almost the same conversions, in the presence or absence of nitrogen compounds. The catalyst with SAR 32 has the highest amounts of Brønsted sites and tetrahedral aluminum but the lowest conversions. One possible explanation to these discrepancies is the fact that those characterizations are carried out in conditions that are very different from the catalyst operating environment (heating under vacuum prior to pyridine adsorption experiments versus high hydrogen pressure during catalytic tests, for instance).

The parameter that seems to influence the level of conversion is the degree of structural order of the Al–MCM-41. Catalysts with SAR 66 and 49, which showed the highest surface areas and pore volumes and the most intense diffraction bands, indicating a better organized structure, are the most active. The catalyst with SAR 32, whose conversion was the lowest, presented smaller area and pore volume and less intense diffraction bands, which are indications of a lesser organized structure.

The resistance to poisoning by nitrogen compounds is most likely linked to the HDN capability of those catalysts, helped by the fact that their Brønsted sites are of medium strength [7,8]. If the sites were too weak, they would be less prone to poisoning but not so active for hydrocracking. Very strong sites would be active, but readily and irreversibly poisoned. Medium strength sites, while presenting fair HCK activity, should be able to adsorb basic nitrogen compounds and allow the desorption of the products formed after HDN reactions. As pointed out earlier in the text, Corma et al. [8] observed that in the presence of high nitrogen content (2900 ppm) NiMo–MCM-41 catalysts showed higher HCK and HDN activities than catalysts based on silica-alumina or USY zeolite. In the present work, additional HDN and HCK tests at different nitrogen contents will be necessary to have a more precise assessment of the resistance to poisoning by basic nitrogen compounds.

4. Conclusions

The observed resistance to poisoning by nitrogen compounds indicates that MCM-41 is a very interesting support for the development of hydrocracking catalysts suitable for processing heavy brazilian crudes, but further experiments will be necessary to fully understand that feature.

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