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NiMo/Al_2O_3–MgO (*x*) catalysts: the effect of the prolonged exposure to ambient air on the textural and catalytic properties

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Abstract

In the search to obtain stable catalysts for selective elimination of sulfur from gasoline, maintaining octane number, NiMo catalysts supported on Al–Mg mixed oxides were prepared by the sol–gel method and evaluated after 6-month storage in contact with ambient air, the results were compared with the freshly prepared samples. Both, freshly prepared and aged samples were characterized by nitrogen physisorption measurements (S_{BET}), infrared spectroscopy (FT-IR) and X-ray powder diffraction (XRD) and high-resolution electron microscopy (HREM), they were tested in the thiophene hydrodesulfurization reaction.

The results indicate that the incorporation of small amounts of magnesia (5 mol%) into the alumina support, leads to the catalyst with low hydrogenation function and appropriate stability during prolonged contact with ambient conditions.

Keywords: NiMo catalyst; Hydrodesulfurization; Alumina magnesia; Characterization; Textural stability

1. Introduction

The demand for reformulated gasoline with low sulfur content, explains the necessity to eliminate sulfur from streams that contribute to the pool of gasoline. Most sulfur in a typical refinery comes from the fluid catalytic cracking (FCC) gasoline, which contains several unsaturated compounds, with high octane number. Hydrodesulfurization (HDS) of gasoline with NiMo/Al_2O_3 conventional catalyst is accompanied by hydrogenation of unsaturated compounds leading to some loss in gasoline quality (RON). Therefore, there is a need to develop highly selective hydrodesulfurization catalysts with high activity towards hydrogenolysis reactions and a low hydrogenation (HYD) function.

To achieve selective HDS, the effect of the support on catalyst selectivity was studied on the HDS of dibenzothiophene by Shimada et al. [1]. It was found that unpromoted Mo catalysts, supported in different oxides, gave a decreasing hydrogenation function according to the following order: $Al_2O_3 > TiO_2 > MgO > SiO_2$, which was observed by comparing the cyclohexylbenzene to biphenyl ratio. Hillerová et al [2] and Bertolacini and Sue-A-Quan [3] also reported that the highest hydrogenolysis selectivity was achieved on the catalyst supported in oxides with low acidity, such as MgO. Klicpera and Zdrazil [4] and Cinibulk et al. [5] reported that the non-aqueous impregnation and low-temperature calcination produce high-activity Co(Ni)Mo/MgO catalytic structures, and they proposed that magnesia should be considered as a new promising support for Co(Ni)Mo sulfide catalysts. However, its sensivity to adsorb water and propensity to form solid solutions with CoO and NiO must be taken into consideration in the catalyst preparation.

Supports of pure magnesia, after a prolonged exposition to ambient conditions and after the aqueous impregnation, have a low textural and structural stability. The low textural stability was attributed to the structural change. The magnesia structure collapses when it is exposed during prolonged time to ambient conditions or during aqueous impregnation, due to the easy transformation from magnesium oxide to the mixture of magnesium hydroxide and magnesium carbonate compounds with very low surface

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area. Similar changes have also been reported before, for highly hygroscopic materials like MgO, CaO, ZnO and others [6]. However, structural and textural properties of NiMo or CoMo catalysts supported on texturally unstable materials after prolonged contact with ambient conditions or aqueous impregnated have not been studied in detail.

Recently, Zdrazil [7] reported that the basicity of magnesia is an advantage as compared with neutral or acidic supports. Oxide and sulfide Mo species are acidic and thus the basic support should keep them in highly dispersed form. Surface basicity should keep down cocking, which is intensive on alumina-supported catalysts and deactivates them. However, the problem is to find out a proper preparation procedure that maintains textural stability during the storage in ambient conditions and during the aqueous impregnation.

In order to avoid the disadvantages of pure magnesia as a catalytic support, and obtain a selective hydrodesulfuration catalyst, magnesia can be incorporated into an alumina support [4,8]. CoMo catalysts, supported on Al–Mg mixed oxides, produced from the thermal decomposition of a crystalline hydrotalcite-like compound of formula $Mg_{4.5}\cdot Al_2(OH)_{13}CO_{3.3}\cdot 5H_2O$, gave some selectivity advantages, equal to a decrease of 10–40% in the olefin hydrogenation at 80% of HDS conversion. Bertolacini and Sue-A-Quan [3] and Yu and Myers [9] suggested the use of magnesia or mixtures of MgO with other refractory inorganic oxides as selective catalysts with low hydrogenation function for hydrodesulfurization of cracked naphtha. Kukes et al. [10,11] reported the use of magnesia doped with an alkali metal in order to obtain low hydrogenation activity with respect to the sulfur elimination. Jacquin et al. [12] reported the use of a support with low surface area and low acidity in order to maintain a selective hydrodesulfurization of cracked naphtha.

Previously, we have reported the use of magnesia-alumina mixed oxides [13]. The previous results showed that the catalysts modified with MgO have a higher catalytic activity towards hydrogenolysis than the conventional catalyst, giving a low loss in octane number in the desulfurized fraction and maintaining the liquid yield. However, the effect of incorporation of different amounts of magnesia on textural and structural stability of the NiMo/Al_2O_3–MgO (x) catalysts during prolonged exposition to ambient conditions have not been reported in detail before. The aim of the present work is to analyze the textural and structural stability of the NiMo catalysts supported on MgO and Al_2O_3–MgO (x) mixed oxides with different molar ratios after prolonged contact with ambient air.

2. Experimental

2.1. Support and catalyst preparation

A series of magnesia and Al_2O_3–MgO (x) mixed oxides were prepared with different molar ratios x = MgO/[MgO + Al_2O_3] by the sol–gel method, where x = 0.0, 0.05, 0.25, 0.50 and 1.0. Aluminum isopropoxide (Al(i-PrO)$_3$; Aldrich 99%) and magnesium ethoxide (Mg(OEt)$_2$; Aldrich 98%) as precursors and n-propyl alcohol as solvent were used in the preparation and have been described previously [13]. Mo and NiMo/Al_2O_3–MgO (x) catalysts were prepared by a standard incipient wetness technique. The calcined supports were impregnated successively with the aqueous solutions of ammonium heptamolybdate and nickel nitrate according to the required Mo and Ni loading: 2.8 at/nm^2 of molybdenum and a nickel content corresponding to an atomic ratio r = 0.3, where r = Ni/(Ni+Mo). After each impregnation, the solids were dried at 373 K (12 h) and calcinated at 773 K (4 h). The catalysts characterized and tested in thiophene hydrodesulfurization reaction at recent preparation time were called freshly prepared catalysts. The 6-month exposed catalysts are prepared in order to study the effect of the exposure to ambient conditions for 6-month period, supports and catalysts were stored with exposition to air from ambient conditions and then characterized and tested in thiophene HDS again.

2.2. Catalytic activity

Prior to the catalytic activity tests the catalysts were sulfided in situ in a stream of 15% volume of H_2S in H_2 for 4 h at 673 K.

Catalytic activities were evaluated in the thiophene hydrodesulfurization reaction at steady state conditions, after a 12 h stabilization period using a micro-flow reactor operating at atmospheric pressure. In all the experiments, the feed rate of thiophene was 1.53 mmol h^{-1} and the feed rate of hydrogen was 50 mmol h^{-1}. The thiophene conversion was sequentially determined at four temperatures from 533 to 623 K in steps of 30 K. HDS of thiophene reaction was followed by means of gas chromatography (GC), identifying compounds such as thiophene, 1-butene, *cis*- and *trans*-2-butene and the hydrogenated butane product. So, to evaluate the hydrogenation function, the conversion to butane was determined, which was defined as moles of butane in the products per mole of thiophene in the feed. The HDS function was evaluated by means of the thiophene conversion.

2.3. Catalyst characterization

In order to compare the freshly prepared catalysts and those exposed to ambient conditions for six months, both of them were characterized by nitrogen physisorption measurements, characterizing the surface area (S_{BET}), pore diameter (D_p) and pore volume (V_p), infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) and high resolution electron microscopy (HREM). The surface area and pore characteristics of the supports and catalysts (in their oxided state) were obtained using a Micromeritics ASAP 2000 system. Prior to the physisorption measurements, all samples were outgassed for 3 h at 523 K. In general, the errors found in repeated measurements of surface area determinations were within 2–3% of the total surface area. FTIR measurements were performed with a Nicolet 510 spectrometer. Dehydration of the freshly prepared samples was achieved by heating the pressed disks under vacuum at 523 K for 1 h. Only 6-month exposed to ambient conditions samples were pressed in disks. The IR spectra were recorded at room temperature, with 300 scans and 4 cm^{-1} resolution. X-ray diffraction patterns were recorded in the range $3^\circ \leq 2\theta \leq 80^\circ$ in a Philips PW 1050/25 diffractometer, using Fe-filtered Cu Kα radiation (λ = 1.5418 Å) and a goniometer speed of 2° (2θ) min^{-1}. High-resolution transmission electron microscopy characterizations of sulfided catalysts were performed using a Jeol 2010 microscope (with point to point resolution of 1.9 Å). The solids were ultrasonically dispersed in heptane and the suspension was collected on carbon-coated copper grids.

3. Results and discussion

Textural properties on catalysts with different magnesia contents are shown in Table 1. According to this table, BET surface areas on freshly prepared catalysts with low magnesia contents (molar ratio of x = 0.0–0.05) are higher than those found on catalysts supported on Al_2O_3–MgO with x = 0.25, 1.0. The catalyst with the lowest MgO content (x = 0.05) maintains a surface area of 247 m^2 g^{-1} even after prolonged exposure to ambient conditions (six months). However, for higher MgO contents ($x \geq 0.25$) the loss of surface area increases with MgO content. It seems that the dispersion of magnesia into the alumina matrix helps in maintaining the textural properties in catalysts containing magnesia. Low stability is observed when the magnesia content is beyond $x \geq 0.25$.

According to the XRD results, obtained in a previous work [13], the appearance of the diffraction lines corresponding to periclase crystalline phase is observed at magnesia contents above $x \geq 0.25$. An interesting fact observed when comparing the diffractograms (Fig. 1) of supports with those of the unpromoted and nickel-promoted samples is that the incorporation of molybdenum to the support induces a loss in the crystallinity of the magnesia species whose signals become now broader and less intense. This decrease of the intensity of the diffraction lines (Fig. 1b) of periclase phase (◆) has been related with molybdenum aqueous impregnation, with subsequent thermal treatment. In contrast, the incorporation of Ni to the catalyst produces a recovery of the magnesia phase crystallinity (Fig. 1c). After 6-month storage of the sample in contact with ambient air, X-ray diffraction patterns are changed (Fig. 2). Some new diffraction lines appear, that correspond to the Brucite phase (*), ($Mg(OH)_2$). However, diffraction lines corresponding to the Periclase phase are still observed. Unpromoted Mo catalyst supported on magnesia shows diffraction lines that correspond to the periclase phase; however, these lines have less intensity after storage as a consequence of the crystallinity loss. For promoted NiMo catalyst supported on magnesia, we observed that the diffraction lines do not change a lot with respect to the support, which is due to the system stability, probably by the interaction between metallic phases and the magnesia support. It is important to note that the brucite phase ($Mg(OH)_2$) has a very low surface area. It can be concluded, therefore, that magnesia containing samples have structural and textural stability at low magnesia content, x = 0.05.

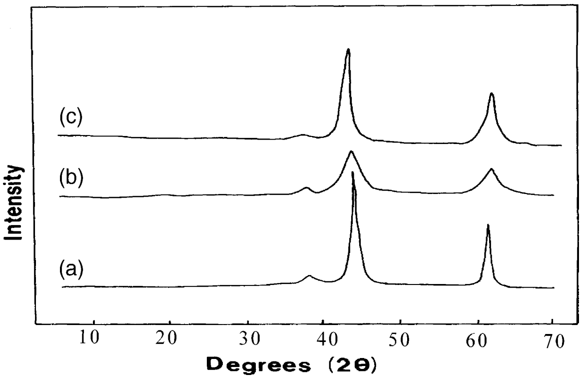

Fig. 1. X-ray diffraction patterns of freshly prepared samples: (a) Al_2O_3–MgO (1.0) support; (b) Mo/Al_2O_3–MgO (1.0); and (c) NiMo/Al_2O_3–MgO (1.0).

Table 1
Textural properties of freshly prepared and 6-month exposed to ambient conditions NiMo/Al-Mg (x) catalysts

Catalyst		Textural properties			Surface area loss (%)
		S_{BET} (m^2/g)	V_p (cc/g)	D_p (Å)	
NiMo/Al_2O_3–MgO(0.0)	Freshly prepared	187	0.33	70	0
	6-month exposed	187	0.33	70	
NiMo/Al_2O_3–MgO(0.05)	Freshly prepared	246	0.25	40	
	6-month exposed	247	0.24	40	0
NiMo/Al_2O_3–MgO(0.25)	Freshly prepared	192	0.21	44	
	6-month exposed	147	0.20	46	23
NiMo/Al_2O_3–MgO(1.0)	Freshly prepared	154	0.58	150	
	6-month exposed	84	0.41	182	45

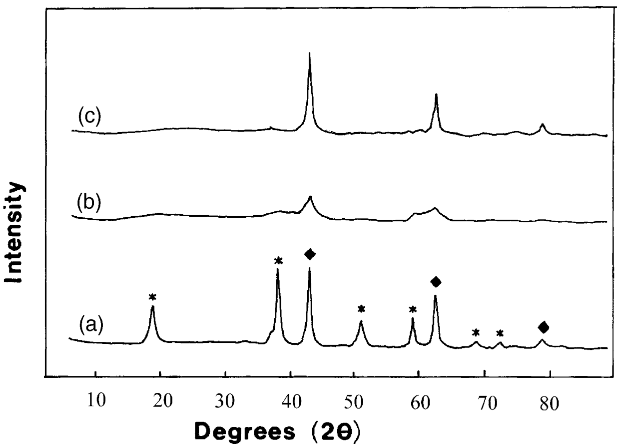

Fig. 2. X-ray diffraction pattern of 6-month exposed to ambient conditions samples: (a) magnesia support; (b) Mo/Al_2O_3–MgO (1.0); and (c) NiMo/Al_2O_3–MgO (1.0); (◆) Periclase, MgO; (*) Brucite, $Mg(OH)_2$.

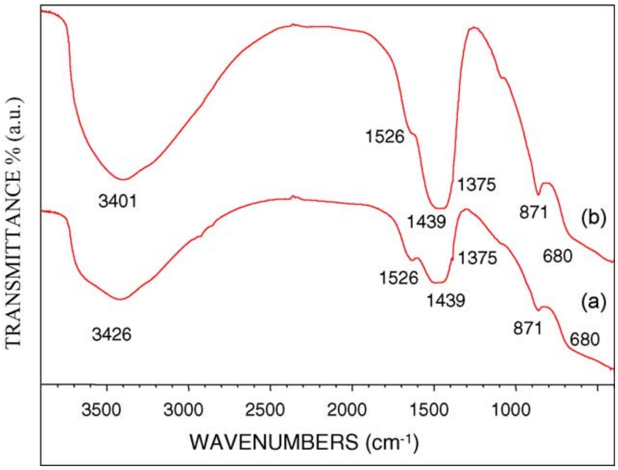

Fig. 4. FTIR spectra of the Al_2O_3–MgO (0.05) support: (a) freshly prepared sample and (b) 6-month exposed to ambient air sample.

In the previous work [13], the change observed with MgO containing supports x = 0.0, 0.05, 0.25, 0.50, 0.75 and 1.0 after Ni and Mo deposition were discussed. In this work, the stability of supports and catalysts was evaluated after prolonged contact with ambient air. It was observed that the magnitude of the textural and structural changes in supports and catalysts depends on the MgO/Al_2O_3 ratio, as well as on the presence of Mo and Ni species in the sample. In order to clarify the reason of these changes, IR characterization of the samples was carried out. Figs. 3–5, show the infrared spectra of NiMo/Al_2O_3–MgO (x = 0.05, 0.50 and 1.0) fresh catalysts and of the ones exposed to ambient conditions. The molar ratios x = 0.05, 0.50 and 1.0 were selected in order to characterize the change in the IR spectra of samples with different composition (Mg/Al ratios). Catalyst with molar ratio x = 0.50 (Fig. 4) shows the appearance of bands that correspond to carbonates (bands corresponding to ionic CO_3^{2-} carbonate to 1439 cm^{-1}, physisorbed CO_2 at 1526 cm^{-1} and monodentated –O-CO_2 carbonate at 1375 cm^{-1}), catalyst with content of magnesia x = 1.0 (Fig. 5) shows the bands related to carbonate species and also absorb H_2O during the exposure to ambient conditions, that is the reason for the appearance of the bands located at 1640 and 3690 cm^{-1} that are assigned to physisorbed water (Fig. 5b). In the fundamental region at 500–900 cm^{-1}, sample with molar ratio x = 0.05 shows two broad bands assigned to vibrations Al–O of tetrahedral (800 cm^{-1}) and octahedral (603 cm^{-1}) aluminum. These results are in line with the XRD diffractograms, where the transformation from Periclase to Brucite phase was observed for samples with magnesia molar ratios beyond x = 0.5. IR characterizations confirm that structural and textural stability are obtained when magnesia content in the sample is $x < 0.25$.

Changes occurring in the catalytic support upon contact with ambient air can also affect the characteristics of the MoS_2 active phase. The sulfided active phase was characterized by means of high-resolution electron microscopy, (Figs. 6–8). In the alumina-supported catalyst, the

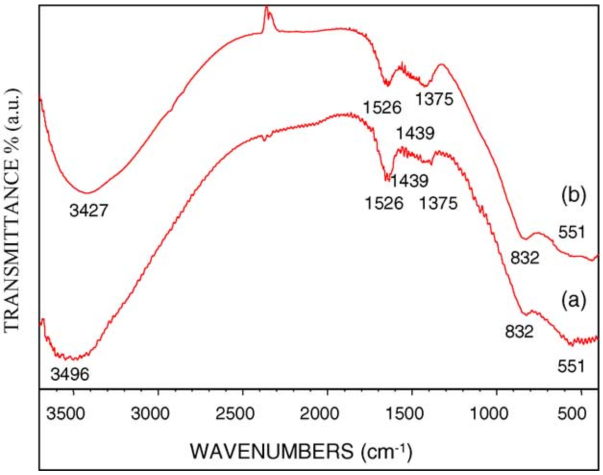

Fig. 3. FTIR spectra of freshly prepared (a) and 6-month exposed to ambient air and (b) NiMo/Al_2O_3–MgO (0.05) catalysts.

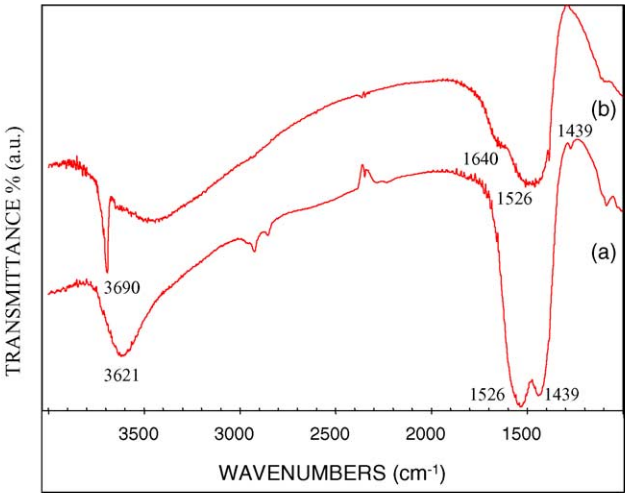

Fig. 5. FTIR spectra of freshly prepared (a) and 6-month exposed to ambient air (b) NiMo/Al_2O_3–MgO (1.0) catalysts.

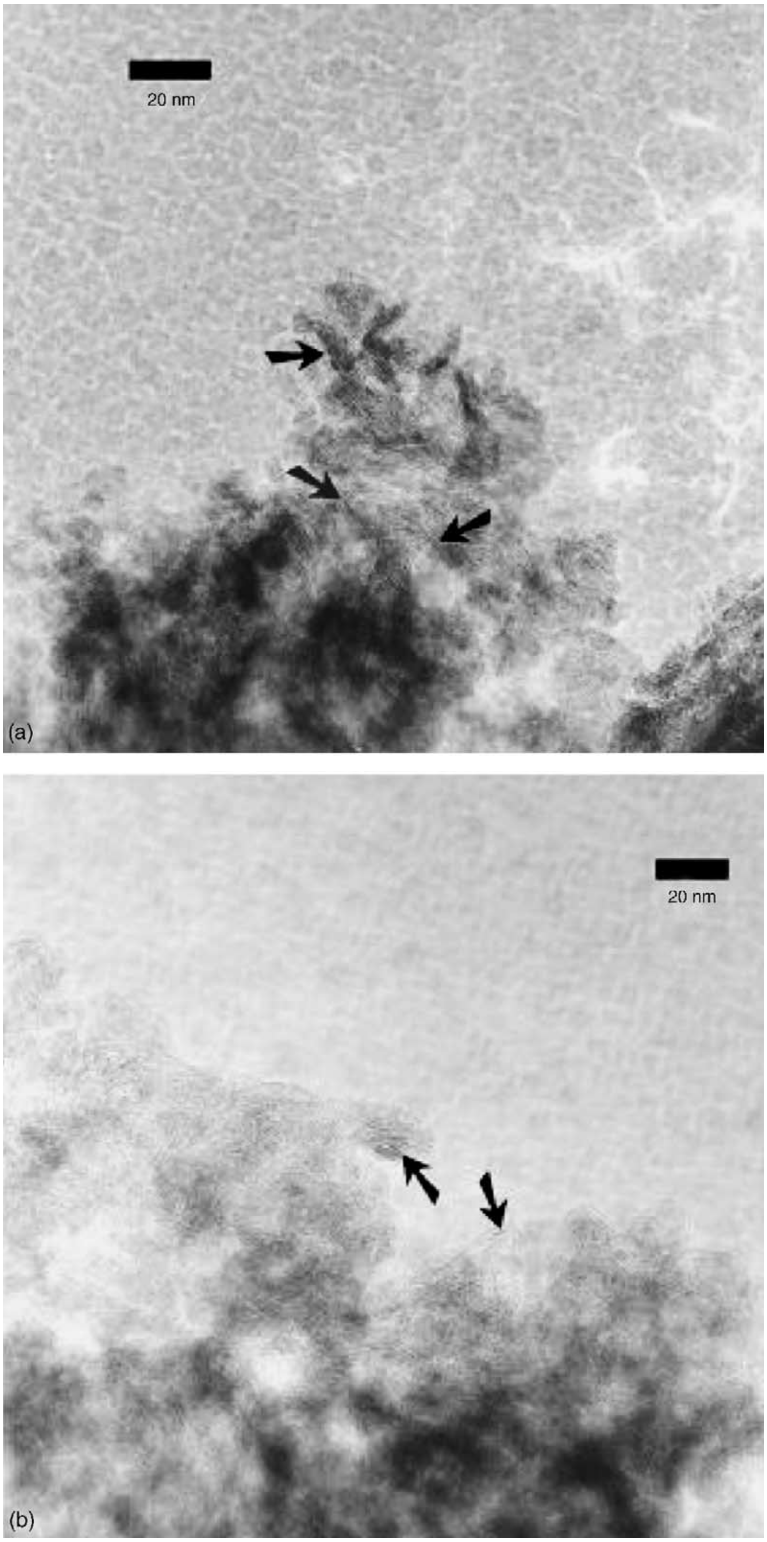

Fig. 6. HREM micrographs of NiMo/Al_2O_3–MgO (0.0) catalysts: (a) sulfided after preparation and (b) sulfided after 6 months exposure to ambient conditions.

electron microscopy results of the catalysts show the typical fringes due to MoS_2 crystallites with 6.2 Å interplanar distances. MoS_2 crystallites with average lengths of about 40 Å and stacking of about one to three layers are observed (Fig. 6a). The morphology of MoS_2 phase on alumina supported catalysts is not changed after 6-month contact with ambient air (Fig. 6b). In contrast, in pure magnesia supported catalyst, the MoS_2 crystallites when

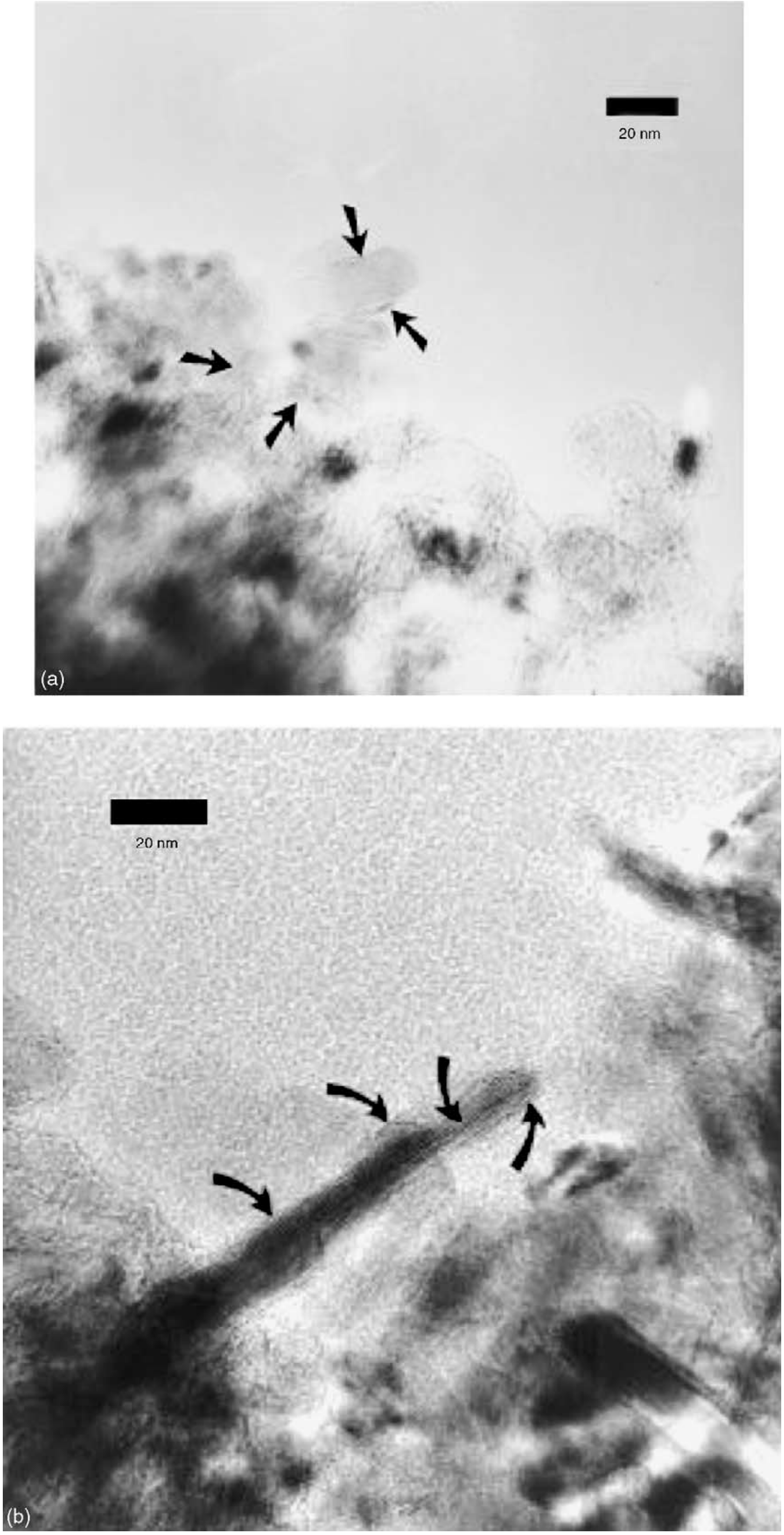

Fig. 7. HREM micrographs of NiMo/Al_2O_3–MgO (1.0) catalysts: (a) sulfided after recent preparation; (b) and (c) sulfided after 6-months exposure to ambient conditions.

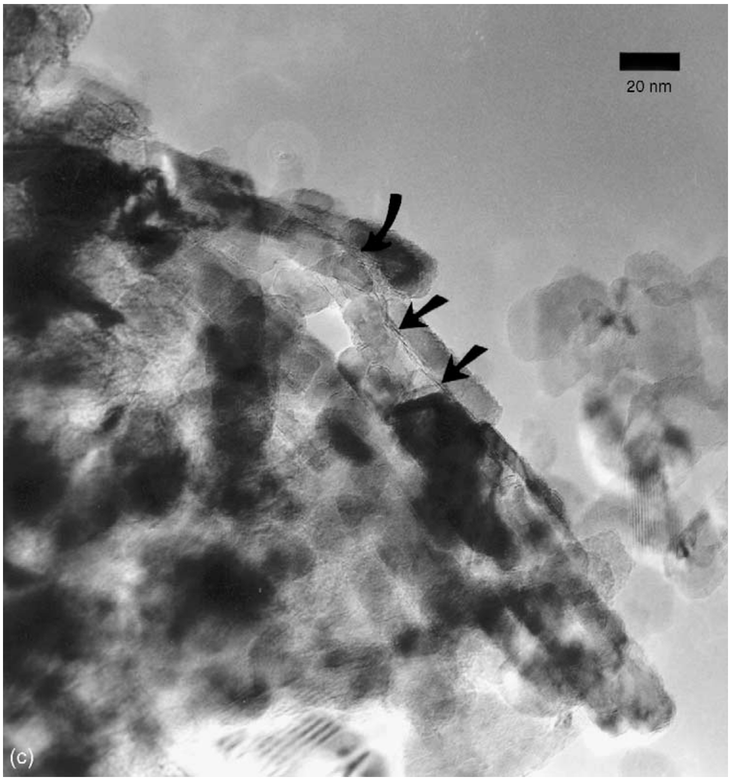

Fig. 7. (*Continued*).

are exposed to ambient conditions (Fig. 7a–c) show fringes with very different lengths and it was difficult to obtain a representative average length. In the samples with low magnesia content (x = 0.05), the morphology of MoS_2 crystallites is similar to the one observed on alumina, the MoS_2 fringes are well dispersed (Fig. 8a). Also, when the sample was exposed to ambient conditions for 6 months, there were no detectable changes in dispersion or average lengths of MoS_2 species (Fig. 8b) with $x = 0.05$, in line with the XRD, textural properties and FT-IR characterizations.

Catalysts with high magnesia content ($x \geq 0.25$) show a lower deactivation period (6–8 h) than those with low magnesia content or supported in alumina, where deactivation period was about 12 h. It seems that a decrease in catalytic activity decreases the deactivation time. The catalytic behavior of the freshly prepared and aged catalysts is shown in Table 2. Reaction rate was calculated at reaction temperatures of 533, 563, 593 and 623 K after the catalyst sulfidation at 673 K. Catalytic activity of freshly prepared catalysts changed with the magnesia addition to the support. An activity decrease is observed even at low magnesia content (x = 0.05), as it was described and discussed in details in the previous work [13]. However, catalysts (x = 0.05 and 0.25) exposed for 6 months have a slight increase on catalytic activity (1.1–1.2 times) than those freshly evaluated. Unexpectedly, catalytic activity of the 6-month exposed magnesia supported catalyst was 1.3–1.6 times higher than the one obtained on the freshly prepared sample (Table 2). This behavior is possibly due to a re-dispersion of the active phase during the catalyst activation, since in this step the surface area of the catalyst is reconstructed to values similar to the original freshly prepared catalyst.

Results from Table 2 show that samples supported on texturally and structurally stable Al_2O_3–MgO (x) mixed oxides (x = 0.0, 0.05) do not change a lot their catalytic behavior in thiophene HDS. On the contrary, supports with MgO content higher than $x = 0.25$ are not texturally stable. It appears that the catalytic supports with high MgO content deteriorate texturally upon contact with ambient air for a prolonged period of time and can achieve textural restructuration and redispersion of the Mo oxide phase during catalyst activation (at 673 K) and in part at reaction conditions (533–623 K).

The results in Table 3 show that the thiophene conversion percent increases when the catalysts are exposed to ambient conditions and in most cases the butane conversion percent as well. The increase in thiophene conversion and butane formation is more pronounced in catalysts supported in pure magnesia. However, it is clear that butane conversion percent does not increase as quickly as that of the thiophene, when the catalysts are supported in pure magnesia. Probably those changes are related to low magnesia stability after the exposure to ambient conditions and changes in morphology of the active sites.

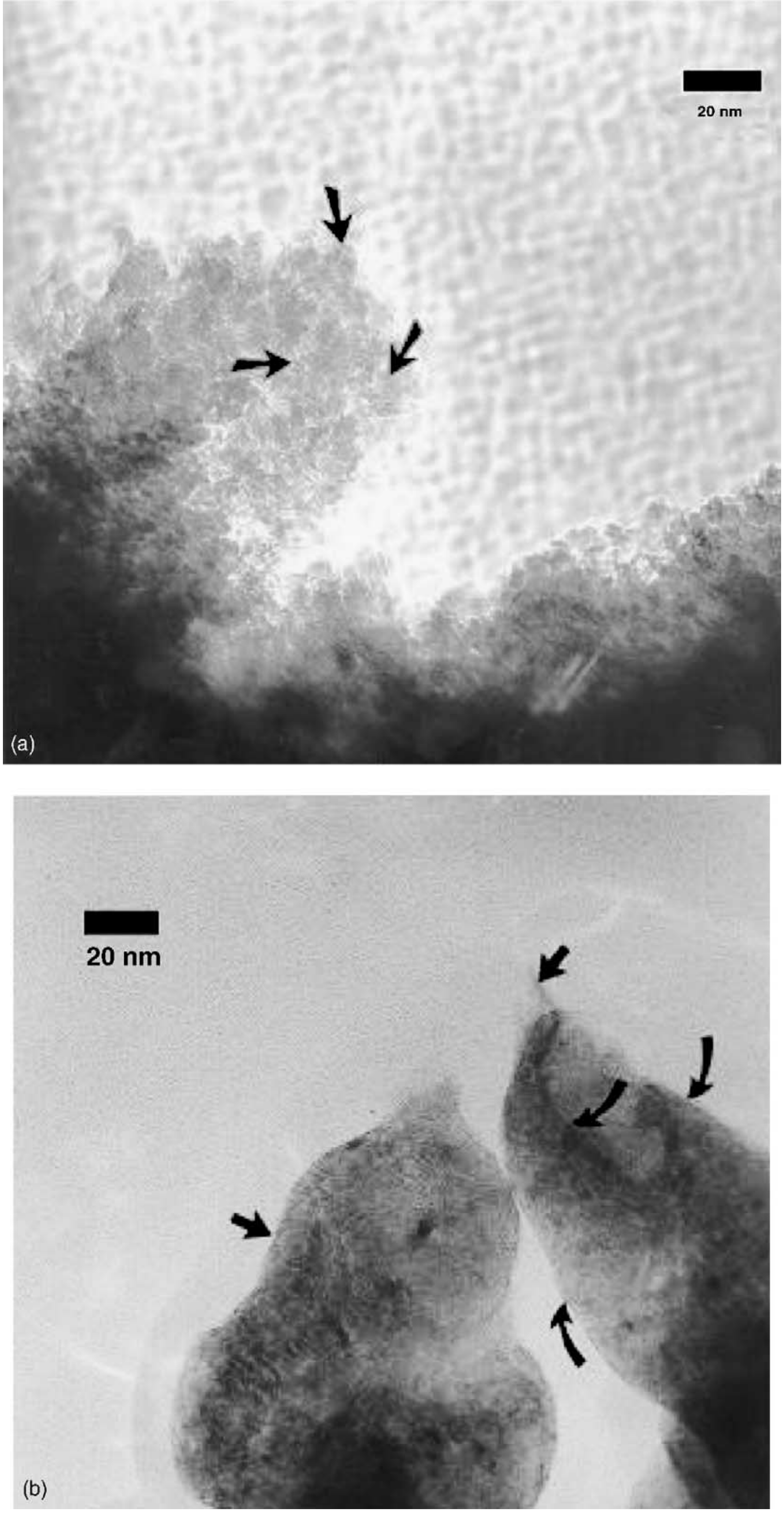

Fig. 8. HREM micrographs of NiMo/Al_2O_3–MgO (0.05) catalysts: (a) sulfided after recent preparation, (b) sulfided after 6-months exposure to ambient conditions.

Table 2
Catalytic activity of freshly prepared and 6-month exposed to ambient conditions NiMo/Al_2O_3–MgO (x) catalysts, in thiophene HDS at different reaction temperatures

Catalyst	Sample	Reaction temperature* (K)			
		533	563	593	623
NiMo/Al_2O_3–MgO (0.0)	Freshly prepared	4.52	8.86	14.60	20.90
	6-month exposed	4.50	8.80	14.59	20.91
NiMo/Al_2O_3–MgO (0.05)	Freshly prepared	2.73	5.19	9.03	13.6
	6-month exposed	3.15	6.25	10.50	16.30
NiMo/Al_2O_3–MgO (0.25)	Freshly prepared	2.20	4.20	7.70	11.70
	6-month exposed	2.50	5.20	9.20	14.40
NiMo/Al_2O_3–MgO (1.0)	Freshly prepared	1.19	1.62	2.41	3.83
	6-month exposed	1.50	2.10	3.90	6.00

* Reaction rate × 10^4 mmol thiophene g^{-1} s^{-1}.

Table 3
Percent conversion of thiophene (CT) and to Butane (CB) in freshly prepared and exposed to ambient conditions NiMo/Al_2O_3–MgO (x) catalysts

	533 K		563 K		593 K		623 K	
	CT	CB	CT	CB	CT	CB	CT	CB
Fresh NiMo/Al_2O_3	5.3	0.22	10.4	0.60	17.1	1.21	24.5	1.90
Ambient conditions exposure	5.4	0.23	10.5	0.62	17.3	1.11	23.4	1.70
Fresh NiMo/Al_2O_3–MgO (0.05)	3.2	0.25	6.2	0.35	10.6	1.11	16.0	1.20
Ambient conditions exposure	3.3	0.25	7.1	0.28	12.1	1.11	18.3	1.50
Fresh NiMo/Al_2O_3–MgO (0.25)	2.2	0.12	4.2	0.40	7.7	0.69	11.7	0.99
Ambient conditions exposure	2.5	0.11	5.2	0.42	9.2	0.69	14.4	1.23
Fresh NiMo/Al_2O_3–MgO (1.0)	1.4	0.01	2.0	0.15	2.8	0.20	4.5	0.31
Ambient conditions exposure	1.5	0.07	2.2	0.16	3.9	0.30	6.0	0.40

4. Conclusions

Prolonged exposure to ambient conditions affect textural and structural properties only at magnesia contents beyond $x = 0.25$, at lower magnesia contents ($x = 0.05$) the textural and also the structural properties did not show any change.

Al_2O_3–MgO (x) mixed oxide supports are stable in contact with ambient air when MgO content is low ($x < 0.25$). However, supports with $x \geq 0.25$ react with CO_2 and H_2O from ambient air giving rise to the formation of magnesium carbonates and brucite ($Mg(OH)_2$) phase. This changes lead to structural and chemical deterioration of the magnesia containing supports and catalysts. However, catalytic activity of 6-month-aged NiMo catalysts in thiophene HDS was higher than of the freshly prepared analogs (counterparts) and even in cases when the catalysts is supported on pure magnesia, the performance was better than freshly prepared ones.

Catalysts (x = 0.05 and 0.25) exposed for six months have a slight increase on catalytic activity (1.1–1.2 times) than those freshly evaluated. Unexpectedly, catalytic activity of the 6-month exposed magnesia supported catalyst was 1.3–1.6 times higher than the obtained on the freshly prepared sample, as it has already been discussed. The change in catalytic activity and selectivity when samples were exposed to ambient conditions was associated to changes in the MoS_2 morphology and to those observed on textural properties. When the magnesia structure collapses, the metal phase agglomerates on the surface material and then, during the sulfidation, a metal re-dispersion occurs, leading possibly to higher activity.

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