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Degradation of VOCs and NO_x over Mg(Cu)–AlFe mixed oxides derived from hydrotalcite-like compounds



Dégradation de composés organiques volatils et d'oxydes d'azote sur des oxydes mixtes Mg(Cu)–AlFe issus de la voie hydrotalcites

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ABSTRACT

A series of Mg(Cu)–AlFe mixed oxides derived from hydrotalcite-like compounds has been prepared. These solids were characterized by various physicochemical methods and their catalytic performances were tested towards the catalytic oxidation of propene and the simultaneous elimination of propene and NO_x. X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the formation of the hydrotalcite structure for all the solids, except for Cu₄AlFe HT, for which a mixture of the hydrotalcite and the malachite phases is observed. The XRD study of the calcined samples revealed the existence of metal oxides and spinels of types MgO, CuO, γ-Fe₂O₃ or/and Fe₃O₄, MgFe₂O₄ and CuFe₂O₄. During propene oxidation, it was shown that the increase in the copper content enhanced the activity of the solids. However, Cu₂Mg₂AlFe 500, with the highest amount of surface copper species, exhibited the best activity towards the simultaneous elimination of propene and NO. Indeed surface Cu species are the active sites, while bulk Cu species could provide the adsorption sites for nitrogen species.

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R É S U M É

Une série d'oxydes mixtes Mg(Cu)–AlFe dérivée de composés hydrotalcites a été préparée. Ces solides ont été caractérisés par différentes techniques physicochimiques, puis leur performance catalytique a été testée vis-à-vis de l'oxydation catalytique du propène et de l'élimination simultanée du propène et des NO_x. L'étude par diffraction de rayons X (DRX) et la microscopie électronique à balayage (MEB) ont confirmé l'obtention de la structure hydrotalcite pour tous les solides, à l'exception du solide Cu₄AlFe HT, pour lequel les phases hydrotalcite et malachite sont observées. L'étude par DRX des échantillons calcinés

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a révélé l'existence d'oxydes métalliques et de spinelles des types MgO, CuO, γ -Fe₂O₃ ou/et Fe₃O₄, MgFe₂O₄ et CuFe₂O₄. Lors de l'oxydation du propène, il est montré que l'augmentation de la quantité de cuivre améliore l'activité des solides. Cependant, le solide Cu₂Mg₂AlFe 500 ayant le plus grand nombre d'espèces de cuivre en surface a présenté la meilleure activité vis-à-vis de l'élimination simultanée du propène et du NO. En effet, les espèces cuivriques présentes en surface sont les sites actifs, alors que les espèces cuivre dans la masse du solide semblent être des sites d'adsorption pour les espèces d'azote.

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1. Introduction

Volatile organic compounds (VOCs) and nitrogen oxides (NO_x) arising from industrial gases are dangerous pollutants and have a detrimental effect on the environment and on human health. One of the most prominent results of VOCs and NO_x emission is the formation of ground-level ozone, following the reaction between NO_x and VOCs in the presence of sunlight. Excessive O₃ in the air can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases [1]. To overcome the problem, catalytic devices appear as an efficient technology for complete oxidation of VOCs or/and NO_x reduction. Copper and iron species have been reported to be active in the selective oxidation of propene and/or in the reduction of NO_x [2–4]. Moreover, their excellent low-temperature activity and cost effectiveness makes them a good substitute for noble metal catalysts. However, the most popular copper based catalyst, Cu-ZSM-5, discovered by Iwamoto et al. in 1993 [5], was believed to be the most promising catalyst for NO_x decomposition, thus it did not appear resistant to H₂O and SO₂ present in flue gases from coal combustion [4].

In the past decade, mixed oxides derived from layered double hydroxides (LDHs) known as hydrotalcite-like compounds (HTLCs) have attracted much attention due to their large surface areas, good thermal stability, high dispersion, and basic character [6]. Among many applications, they are known to be powerful for hydrocarbons oxidation [7–9] and/or NO_x reduction with hydrocarbons [2] or ammonia [10].

In this work, a series of Cu_xMg_{4-x}AlFe catalysts derived from hydrotalcite-like compounds was synthesized, then characterized by various techniques. Subsequently, their performance was investigated in propene oxidation and in the simultaneous elimination of propene and NO. Previous studies [2,11] showed that mixed oxides derived from LDHs are potential catalysts for HC-SCR, other ones [3,4] demonstrated that copper and iron are very active species in this process. However, this work is the first to show the roles of copper and iron species coexisting in a single solid via hydrotalcite route in the HC-SCR.

2. Experimental

Mg(Cu)–AlFe hydrotalcite-like samples with a molar ratio equal to 2 were synthesized by a co-precipitation method. An aqueous solution containing appropriate amounts of Mg(NO₃)₂·6 H₂O (FLUKA, 99%), Cu(NO₃)₂·

6 H₂O (PANREAC, 98%), Al(NO₃)₃·9 H₂O (ACROS, 99%) and Fe(NO₃)₃·9 H₂O (ACROS, 99%), was added dropwise into a vigorously stirred deionized water solution. During synthesis, temperature and pH were maintained constant at respectively 60 °C and 8 by dropwise addition of a solution of Na₂CO₃ 1 M and NaOH 2 M. The obtained solution was stirred at 60 °C for a further hour, and then placed in the oven for 18 h. The precipitate was then filtered, washed several times with hot deionized water (55 °C) and dried at 60 °C for 48 h. The samples were denoted Cu_xMg_{4-x}AlFeHT (0 < x < 4). The solids were then calcined at 500 °C under a flow of air (2 L·h⁻¹).

X-ray diffraction experiments were performed at room temperature using a Bruker D8 Advance diffractometer equipped with a copper anode emitting a K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a LynxEye detector. A step size of 0.02° and a count time of 4 s per step were used for data collection. The crystalline phases were identified by comparing the diffractograms with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) established by the International Center for Diffraction Data (ICDD).

The specific surface area of the dried and the calcined samples was determined by low-temperature nitrogen adsorption (–196 °C) using the Brunauer–Emmett–Teller (BET) method, with a thermo-Electron QSurf M1 sorptometer, while the Barrett–Joyner–Halenda (BJH) pore diameters were determined by Sorptomatic 1990 sorption analyzer. Prior to the measurements, each sample was degassed at 400 °C for 3 h.

Scanning electron microscopy analysis was performed on a Mira4 Tescan instrument equipped with an energy dispersive X-ray spectrometer (SEM-EDX). Samples were adhered on aluminum stubs covered with 12-mm carbon adhesive tabs and then coated by a thin film of gold. Typical working parameters were an accelerating voltage of 20 kV, and a beam current of 60 μ A.

The reducibility of the calcined samples was studied by H₂ temperature-programmed reduction (TPR). H₂-TPR experiments were carried out in an Altamira AMI 200 apparatus. Prior to the experiments, samples (10 mg) were activated under argon at 150 °C for 1 h. The samples were then heated from ambient temperature to 900 °C under a H₂ flow (5 vol.% in argon–30 mL min⁻¹) at a heating rate of 5 °C min⁻¹.

In each test, a flow of the reaction mixture (6000 ppm propene + air for propene test and 6000 ppm propene + 1000 ppm NO + air for propene–NO test) passes through 100 mg of a catalyst placed in a fixed-bed reactor. The reaction products (NO, CO and CO₂) were analyzed

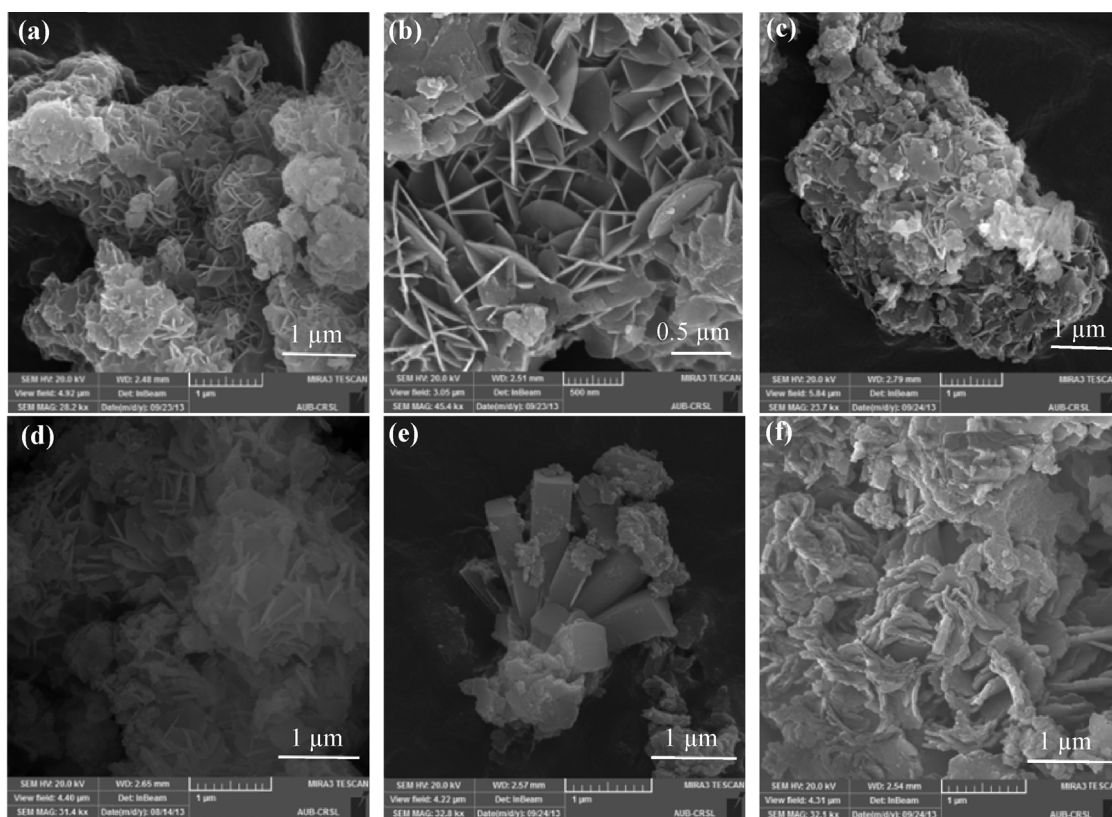


Fig. 2. Scanning electron microscopy (SEM) micrographs of the $\text{Cu}_x\text{Mg}_{4-x}\text{AlFe}$ HT samples: a: Mg_4AlFe HT; b: CuMg_3AlFe HT; c: $\text{Cu}_2\text{Mg}_2\text{AlFe}$ HT; d: Cu_3MgAlFe HT; e and f: Cu_4AlFe HT.

The sharp decrease in the pore volume is related to the sintering and the formation of spinel phases when copper is substituted for magnesium. According to Valente et al. [14], the porosity of the calcined samples is due to two different processes: small intraparticle porosity is generated by a “cratering” process, and the interparticle pores are created by the irregular stacking of the plate-like particles.

The morphology of the hydrotalcite-like compounds is revealed by SEM and is shown in Fig. 2. SEM images show highly crystalline particles. All the samples, with the exception of Cu_4AlFe HT, showed a flower-like hierarchical morphology typical of LDHs. Similar shapes were obtained by Gennequin et al. [6] for Mg-Al hydrotalcite. However, Cu_4AlFe HT showed a mixture of crystalline and irregular nanoflake structures, in accordance with the XRD results, which revealed the presence of both hydrotalcite and malachite phases.

The redox properties of the samples were investigated by temperature-programmed reduction, with the H_2 -TPR profiles shown in Fig. 3. The curves of the catalysts display two reduction regions: the reduction of the copper oxide species present in the forms of CuO and CuFe_2O_4 occurs in the low-temperature range ($T < 350^\circ\text{C}$), while the reduction of iron oxide phases present in the forms of $\gamma\text{-Fe}_2\text{O}_3$ or/and Fe_3O_4 appears at higher temperatures ($T > 350^\circ\text{C}$) [10]. The reduction peaks due to copper and iron species were deconvoluted, and the curve-fitting results are

summarized in Table 2. The peaks below 200°C (peak α and peak β) correspond to the stepwise reduction of highly dispersed CuO species (isolated copper ions and small clusters) i.e., $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ and $\text{Cu}^+ \rightarrow \text{Cu}^0$ [2]. Moreover, the peaks at 217°C , 222°C and 263°C are attributed to more aggregated copper oxide phases such as bulky CuO [3] and the reduction of CuFe_2O_4 into metallic copper and Fe_2O_3 (peaks δ and χ). On the other hand, the peaks at higher temperatures are ascribed to the reduction of Fe_2O_3 into Fe_3O_4 and of Fe_3O_4 into 3FeO (peak φ) [15]. It can be noted that H_2 consumption increases with enhancing the copper content.

The catalytic activity of $\text{Cu}_x\text{Mg}_{4-x}\text{AlFe}$ 500 was studied in the oxidation of propene.

Fig. 4a represents the conversion of propene versus temperature for the different supports in the absence of NO . The light-off curves (temperatures in which 50% of the propene is converted) and the intrinsic activity are shown in Table 3. The temperature used for the calculation of the intrinsic activity corresponds to a propene conversion of 20% of the catalyst that exhibited the best activity. It was observed that the introduction of copper enhanced the catalytic performance, which attests to the fact that copper and iron oxide species as well as the spinel phase CuFe_2O_4 play an important role in this process. Compared to the other supports, Mg_4AlFe showed the lowest catalytic activity. However, the better activity of the samples with high copper content is due to their higher

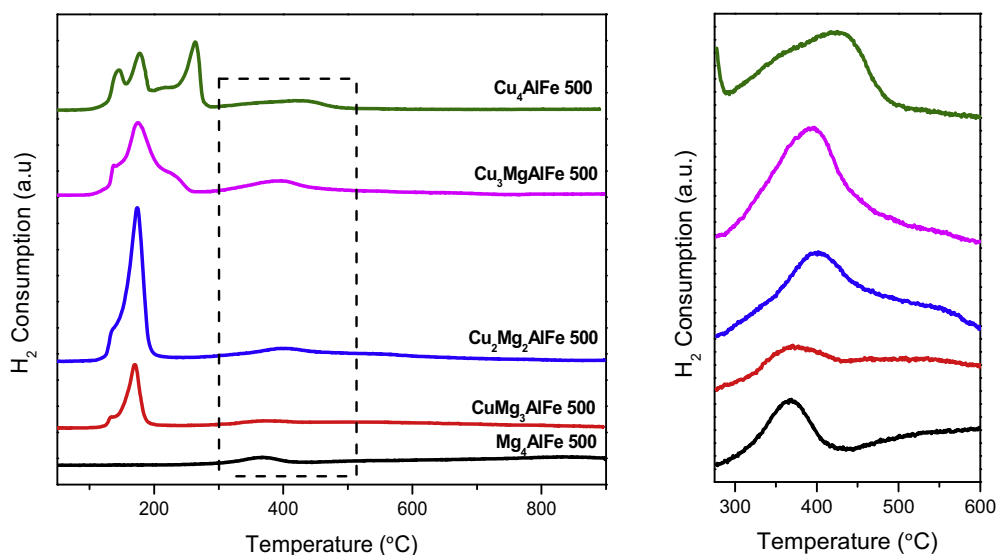


Fig. 3. (Color online.) H₂-temperature-programmed reduction (TPR) profiles of the calcined samples.

Table 2

The temperature and the H₂ consumption corresponding to the peaks in H₂-TPR.

Samples	Temperature (°C) [H ₂ consumption (μmol·g ⁻¹)]					Total H ₂ consumption (μmol·g ⁻¹)
	α	β	δ	Σ	φ	
Mg ₄ AlFe 500						368 (729.9)
CuMg ₃ AlFe 500	134 (538.3)	170 (2453.6)				371 (1970.6)
Cu ₂ Mg ₂ AlFe 500	133 (757.8)	174 (8326.6)				401 (1290.6)
Cu ₃ MgAlFe 500	138 (698.4)	175 (6892.7)	222 (899.1)			397 (2449.5)
Cu ₄ AlFe 500	145 (1901.6)	177 (3043.2)	217 (2128.8)	263 (3576.9)	426 (1753.1)	12403.6

TPR: temperature-programmed reduction.

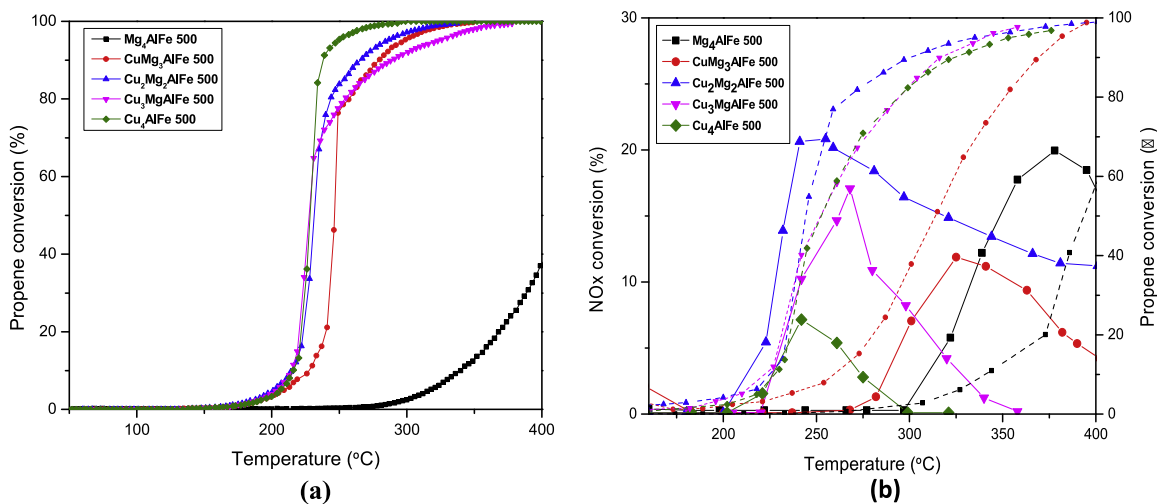


Fig. 4. (Color online.) Catalytic performance of the catalysts Cu_xMg_{4-x}AlFe 500 as a function of temperature: a: propene conversion (%) in the absence of NO; b: NO_x conversion (—) and propene conversion (---).

Table 3

Light-off temperatures and intrinsic activities of propene conversion in the absence and in the presence of NO over the Mg(Cu)–AlFe mixed oxide catalysts.

Catalysts	Mg ₄ AlFe 500	CuMg ₃ AlFe 500	Cu ₂ Mg ₂ AlFe 500	Cu ₃ MgAlFe 500	Cu ₄ AlFe 500
<i>T</i> ₅₀ (°C) without NO	419	247	231	227	228
Intrinsic activity (mol·s ⁻¹ ·m ⁻²)	4.9 10 ⁻⁹	2.37 10 ⁻⁷	6.41 10 ⁻⁷	1.49 10 ⁻⁶	1.13 10 ⁻⁶
<i>T</i> ₅₀ (°C) with NO	395	315	245	250	253
Intrinsic activity (mol·s ⁻¹ ·m ⁻²)	1.2 10 ⁻⁸	2.57 10 ⁻⁷	8.98 10 ⁻⁷	1.96 10 ⁻⁶	1.16 10 ⁻⁶

NO: nitrogen oxide.

reducibility, which promotes a redox cycle favorable to the oxidation of propene in the presence of air, as shown in the TPR profiles.

Concerning propene oxidation, it is to be noted that when the conversion is complete, H₂O and CO₂ are the only products observed.

Calcined hydrotalcites were then tested as catalysts in the simultaneous elimination of propene and NO. Fig. 4b shows the conversion of NO_x (–) and propene conversion (– –) as a function of the reaction temperature. With increasing temperature, NO conversion enhanced until a maximum was reached. After that, it declined, because propene is nearly completely oxidized. When Cu loading was increased (from *x* = 1 to *x* = 2), the maximum of NO conversion increased and *T*₅₀ decreased. After reaching an optimum value for copper content (*x* = 2), the maximum NO conversion started to decrease and *T*₅₀ increased (Table 3). This can be explained by the fact that, when the copper quantity in the sample increase, this leads to the aggregation of the surface CuO, thus blocking the active sites for propene oxidation and NO reduction. Furthermore, during the simultaneous elimination of C₃H₆ and NO, the competition on the metallic sites makes NO reduction more difficult. Hence, the best activity is obtained for Cu₂Mg₂AlFe 500, where the maximum of NO conversion is 21% at 255 °C and *T*₅₀ is 245 °C. This catalyst exhibited the best activity because it contains the highest amount of surface copper species. A study by Yuan et al. [2] showed similar results in the catalytic reduction of NO by C₃H₆ over Cu_xTi₁ mixed oxides derived from hydrotalcite-like compounds catalysts. They showed that surface Cu species are the active sites, while bulk Cu species could provide the adsorption sites for nitrogen species. Moreover, Worch et al. [16] studied the SCR of NO with propene over transition metal oxides (Fe-, Cu-, V-, and Ce-) supported on Al₂O₃, phosphated Al₂O₃, or SAPO-11. The results shown in Fig. 4b presented a relatively better NO conversion and propene oxidation rates at lower temperatures compared to the study of Worch et al. Therefore, it is to be pointed out that the presence of both copper and iron species in a single solid has resulted in lower temperatures of complete propene conversion and in a better NO conversion. Other studies [10,15] showed that mixed metal oxides of Cu, Mg, Al and Fe derived from hydrotalcite-like compounds, tested in the selective catalytic oxidation of ammonia to dinitrogen, are active in the process of NO reduction with ammonia to N₂ and N₂O. The activity of the

catalysts depended on their chemical composition, mainly on the presence of copper oxide phases, and on their redox properties.

It should be noted that N₂, CO₂, and H₂O were the main products of the reactions; however, traces of CO and N₂O in the reaction products were also found.

4. Conclusion

Mg(Cu)–AlFe hydrotalcite-like compounds with different copper contents were successfully synthesized. Their thermal decomposition at 500 °C leads to the formation of metal oxides and spinels that play a major role in propene oxidation and NO_x reduction. In propene oxidation, the increase in copper loading enhanced the catalytic performance of the supports. This was explained by a higher reducibility of those solids and to the presence of oxide phases such as CuO and CuFe₂O₄. As for the simultaneous elimination of C₃H₆ and NO, the Cu₂Mg₂AlFe 500 presented the highest activity; this is mainly due to the presence of well-dispersed surface copper and iron species. Hence, increasing copper concentrations leads to agglomerated copper species, thus reducing the activity of the catalysts. The coexistence of copper and iron in a single material leads to an interesting activity for NO_x reduction by propene, but the Cu/Fe ratio should still be adjusted to increase the catalytic properties.

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References

- [1] European Environment Agency, Air Quality in Europe - Report 2012, European Environment Agency (EEA web site), 2012.
- [2] D. Yuan, X. Li, Q. Zhao, J. Zhao, M. Tade, S. Liu, J. Catal. 309 (2014) 268.
- [3] J. Liu, X. Li, Q. Zhao, D. Zhang, P. Ndokoye, J. Mol. Catal. A: Chem. 378 (2013) 115.
- [4] A. Łamacz, A. Krztoń, G. Djéga-Mariadassou, Appl. Catal., B 142 (2013) 268.
- [5] M. Iwamoto, N. Mizuno, H. Yahiro, Stud. Surf. Sci. Catal. 75 (1993) 1285.
- [6] C. Gennequin, T. Barakat, H.L. Tidahya, R. Cousin, J.-F. Lamonier, A. Aboukaïs, S. Siffert, Catal. Today 157 (2010) 191.
- [7] E. Genty, R. Cousin, S. Capelle, C. Gennequin, S. Siffert, Eur. J. Inorg. Chem. 2012 (2012) 2802.

- [8] C. Gennequin, S. Kouassi, L. Tidahy, R. Cousin, J.F. Lamonier, G. Garcon, P. Shirali, F. Cazier, A. Aboukaïs, S. Siffert, C.R. Chimie 13 (2010) 494.
- [9] J. Carpentier, J.-F. Lamonier, S. Siffert, H. Laversin, A. Aboukaïs, Stud. Surf. Sci. Catal. 142 (2002) 1197.
- [10] M. Jabłonska, L. Chmielarz, A. Wegrzyn, K. Guzik, Z. Piwowarska, S. Witkowski, R.I. Walton, P.W. Dunne, F. Kovanda, J. Therm. Anal. Calorim. 114 (2013) 731.
- [11] D. Yuan, X. Li, Q. Zhao, J. Zhao, S. Liu, M. Tade, Appl. Catal., A 451 (2013) 176.
- [12] J. Carpentier, S. Siffert, J.F. Lamonier, H. Laversin, A. Aboukaïs, J. Porous Mater. 14 (2007) 103.
- [13] W. Gao, Y. Zhao, J. Liu, Q. Huang, S. He, C. Li, J. Zhao, M. Wei, Catal. Sci. Technol. 3 (2013) 1324.
- [14] J.S. Valente, J. Hernandez-Cortez, M.S. Cantu, G. Ferrat, E. Lopez-Salinas, Catal. Today 150 (2010) 340.
- [15] L. Chmielarz, M. Jabłonska, A. Struminski, Z. Piwowarska, A. Wegrzyn, S. Witkowski, M. Michalik, Appl. Catal., B 130 (2013) 152.
- [16] D. Worch, W. Suprun, R. Glaser, Catal. Today 176 (2011) 309.