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Noble-free potassium-bimetallic catalysts supported on beta-zeolite for the simultaneous removal of NO_x and soot from simulated diesel exhaust

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Abstract

This paper deals with the activity of the KCu and KCo catalysts supported on beta-zeolite for the simultaneous NO_x/soot removal from a simulated diesel exhaust, containing C_3H_6 as model hydrocarbon. In order to reveal the effect of potassium, the corresponding monometallic catalysts (Co/beta and Cu/beta) were analyzed and different potassium loadings were used. In addition, for comparative purpose, the performance of a platinum based catalyst (Pt/beta) was studied. All noble-free catalysts show, at 450 °C, a high activity for the simultaneous NO_x/soot removal. Among them, K1Cu/beta presents the best global performance at 350 and 450 °C achieving a high soot consumption rate (comparable to platinum catalysts) and the highest NO_x reduction. In contrast to platinum catalysts, K1Cu/beta has the advantage that the main reaction products are N_2 and CO_2.

Keywords: Diesel; Soot; NO_x; C_3H_6; Bimetallic; Pt; K; Cu; Co; Beta

1. Introduction

Because of the shortages of petroleum resources, diesel engines have become the main option for vehicles. Compared to gasoline engines, diesel engines present the advantage of lower consumption of fuel and lower emission of CO_2, CO and hydrocarbons (HC). However, the diesel engine generates more nitrogen oxides (NO_x) than gasoline engine equipped with three-way catalyst (TWC) and, in addition, carcinogenic particulate matter (soot) [1]. Legal limitations to toxic emissions from diesel engines are being severely tightened and become, essentially, the same as for gasoline engines in a near future [2,3].

At present, the most interesting option for NO_x and soot removal is the use of combined systems composed by filters to soot oxidation with SCR catalysts for NO_x reduction [2,3]. An interesting alternative to these complex systems is the use of a single catalyst for the simultaneous abatement of the two pollutants. This solution is clearly much more difficult and has been considered only recently [4–10].

Thus, considering the promising performance of potassium-bimetallic catalysts supported on alumina [10] and the benefits of using beta-zeolite as support for C_3H_6–SCR–deNO_x [11,12], this paper deals with the activity of the KCu and KCo catalysts supported on beta-zeolite for the simultaneous NO_x/soot removal from a simulated diesel exhaust, containing C_3H_6 as model hydrocarbon. In order to reveal the effect of potassium, the corresponding monometallic catalysts (Co/beta and Cu/beta) were analyzed and different potassium loadings were used. In addition, for comparative purpose, the performance of a platinum based catalyst (Pt/beta) was studied.

2. Experimental

A charcoal (C), prepared from a Spanish high-volatile A bituminous coal by pyrolysis (N_2, 500 °C, 2 h), was used as model soot. The physical characteristics of the charcoal (C), elemental analysis, ash content in dry bases, average particle size and BET surface area, are given in Table 1

To obtain the catalysts, the metals (K and Co or Cu) were added to beta support by excess solution impregnation, using aqueous metal nitrate solutions (10 ml/g of support). (The beta-zeolite, supplied by Zeolyst (CP814E), has a SiO_2/Al_2O_3 molar ratio of 25, an average particle size of 0.02 μm (forming

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Table 1
Characteristics of the model soot

	Charcoal
BET surface area (m^2/g)	<4
Particle size (mm)	<1
C (%, w/w)	71.8
H (%, w/w)	2.5
N (%, w/w)	2.2
S (%, w/w)	0.9
Ash (%, w/w)	11.7

aggregates of different sizes) and a BET surface area of 680 m^2/g.) The solution mixture was exposed to an air flow to evaporate the water and, then, dried at 110 °C for 12 h. Subsequently, the catalysts were calcined in air at 400 °C for 2 h. The Pt/beta catalyst was obtained by the ionic exchange method, using a 3×10^{-4} M aqueous solution of the metal precursor ($[Pt(NH_3)_4](NO_3)_2$). The exchanged zeolite was filtered, washed with de-ionized water, dried at 110 °C for 12 h, calcined at 550 °C during 5 h and finally reduced at 350 °C in pure H_2 atmosphere for 8 h. The metal contents of catalysts were determined by ICP (Pelkin-Elmer, Optimal 3000) and Table 2 shows the results obtained.

The reducibility of the catalysts was determined by temperature-programmed reduction (TPR-H_2). The TPR-H_2 was performed in an automatic apparatus (Pulse Chemisorb 2705; Micromeritics) equipped with a thermal conductivity detector. The catalyst (0.1 g) was submitted to a heat treatment (10 °C/min up to 900 °C) in a flow (60 ml/min) of a gas mixture containing 5% H_2 in N_2. In addition, XRD (using a 2002 Seifert powder diffractometer, a scanning rate of 2 °C/min and Cu Kα radiation source), XPS (using a VG-Microtech Multilab electron spectrometer, a Mg Kα radiation source and a chamber pressure lower than 5×10^{-10} mbar) and TEM (using a JEOL, model JEM-2010, microscope) were used to characterize the catalysts.

The NO_x/soot reaction was carried out, at atmospheric pressure, in a quartz-tube fixed-bed reactor. The feed consisted of a gas mixture containing 600 ppm NO, 1500 ppm C_3H_6 and 5% O_2, balanced with He. The amount of sample (soot + catalyst) and the total flow rate were 500 mg and 100 ml/min, respectively. A soot/catalyst weight ratio of 1/3 was used [10]. The soot was physically mixed with the catalyst by using a spatula (loose contact). The outlet gases were continuously analyzed with a chemiluminiscence NO–NO_2 analyzer (Signal 4000VM) and discontinuously analyzed by a gas chromatograph (HP 6890 Plus Series), equipped with a thermal conductivity detector, using two serial columns Porapak Q 80/100 (for the separation of CO_2 and N_2O) and Molecular Sieve 13X (for O_2, N_2 and CO separation) joined by a six-way valve. Two types of experiment were carried out: (i) temperature-programmed reaction (TPR), consisting in a heating at 2 °C/min up to 500 °C and (ii) isothermal reaction at selected temperatures.

Table 2
Nomenclature and metal content of catalysts

Catalysts	wt.% M (M = Co, CuO and Pt)	wt.% K
Co/beta	2.7	0.0
K1Co/beta	2.5	0.8
K5Co/beta	2.4	3.8
Cu/beta	2.9	0.0
K1Cu/beta	4.0	0.8
K5Cu/beta	3.9	3.8
Pt/beta	1.0	0.0

3. Result and discussion

3.1. Noble-free catalysts

Fig. 1 shows the evolution during TPR experiments of the NO_x reduction, the propene conversion, and the CO_2 emission curves (produced by soot consumption and C_3H_6 conversion) versus temperature (from 200 to 500 °C) for the lowest potassium content (1%) catalysts (K1Co/beta and K1Cu/beta) and for the corresponding monometallic catalysts (Co/beta and Cu/beta). The dashed line included in Fig. 1 indicates the stoichiometric CO_2 content corresponding to 100% C_3H_6 conversion. In agreement with previous results obtained in similar experimental conditions [10], the copper catalysts are

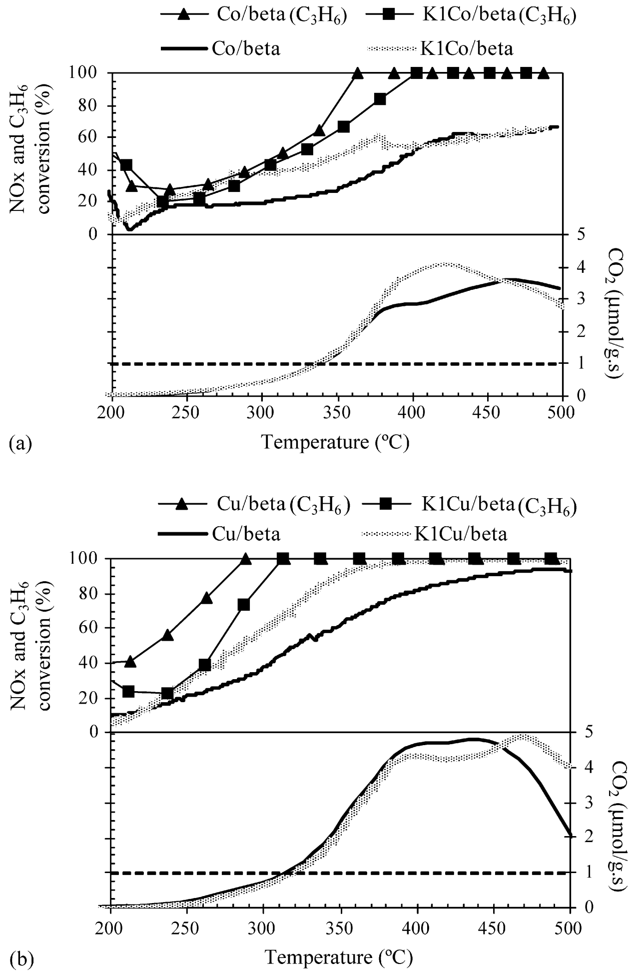

Fig. 1. TPR curves: (a) Co/beta and K1Co/beta and (b) Cu/beta and K1Cu/beta. The dashed line indicates the stoichiometric CO_2 corresponding to 100% C_3H_6 conversion.

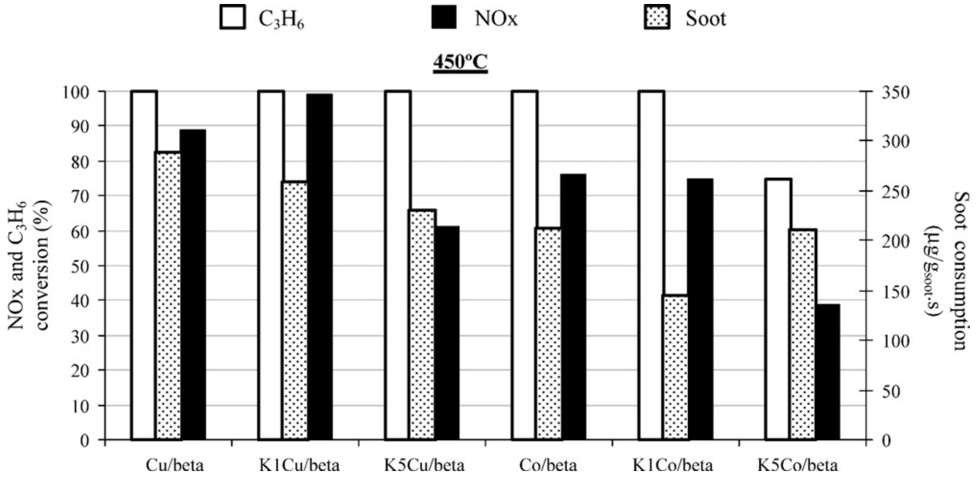

Fig. 2. Isothermal reaction activity data at 450 °C.

more active than the cobalt one for both NO_x conversion (mainly to N_2 and CO_2) and for soot consumption (to CO_2). This activity sequence, also observed when the soot was not present [13], was justified considering that the copper species were easier reduced, in reaction conditions, than the cobalt one [10].

In relation with potassium, it is observed that, for the copper catalysts, the addition of a low amount (less than 1%, see Table 1) of potassium increases the NO_x conversion from 200 to 500 °C. However, for the cobalt catalysts, the positive effect of potassium is only observed at temperature lower than 400 °C approximately. In terms of the CO_2 evolution (related with soot consumption), a different effect is observed for each catalyst: for the copper catalysts, an increase is observed at temperatures higher than 450 °C approximately and, for the cobalt catalyst, the highest CO_2 evolution is detected between 370 and 450 °C. The positive effect of potassium, added to transition metal catalysts supported on activated carbon, was previously observed for the NO_x reduction by carbon in the presence of oxygen [14]. It was also reported in the literature [15,16] that potassium enhances the surface mobility improving the soot–catalyst contact, and also, increases the surface basicity. Kureti et al. [6,7] reported that the addition of a low potassium amount to an iron based mixed oxide increases the catalyst activity for NO_x reduction by soot. However, the deactivation of the potassium-containing catalyst, due to potassium agglomeration, is a problem to solve in view to practical application. In this work no agglomeration and no lost of potassium were detected for K1Cu/beta which showed the same catalytic activity after several runs at 450 °C. In relation to C_3H_6 conversion, a clear delay in the temperature for 100% conversion is observed in the presence of potassium. These facts can be related with the decrease of the support surface acidity after potassium addition [6,7].

Considering the TPR performance of the noble-free catalysts, isothermal reactions at 450 °C were carried out. Fig. 2 shows the NO_x reduction, the C_3H_6 conversion, and the soot consumption rate in $\mu g/g_{\mathrm{initial\ soot}}$ s (calculated from CO_2 evolution data). Note that at 450 °C, in agreement with TPR results, all noble-free catalysts show a high activity for the simultaneous conversion of NO_x/soot to N_2 and CO_2 as main reaction products. It is remarkable that these catalysts are able to carry out the simultaneous NO_x/soot removal in the absence of any external reductant. This is a great advantage versus other proposed schemes where the presence of an external redundant, as hydrogen, is required [8,17].

On the other hand, it is confirmed that the presence of potassium affects the catalytic performance. The effect depends on both the catalysts and the potassium content. Thus, for the copper-based catalysts, only the addition of a low amount of potassium seems to be effective increasing the NO_x conversion percentage from 90% to a ca. 100%). Considering the soot consumption rate, the addition of potassium generates a slight decrease which is proportional to the potassium amount. Respect to C_3H_6 conversion, the addition of potassium to the copper catalysts does not modify the corresponding values. Focus the attention to the cobalt based catalysts, and in agreement with TPR results (see Fig. 1a), the presence of a low amount of potassium seems not affect the NO_x conversion, however, for the highest potassium content catalyst (K5Co/beta), a notable decrease is observed. In terms of soot consumption, a reduction is shown by the lowest potassium content catalyst (K1Co/beta). Finally, in relation with the C_3H_6 conversion, only the highest potassium-content cobalt catalyst (K5Co/beta) shows a considerable decrease (from 100 to 75% approximately).

In order to understand the relation between catalysts activity and potassium-content, the catalysts were characterized by using TPR-H_2, XRD, XPS and TEM techniques (see Section 2). Fig. 3 shows, as an example, the TPR-H_2 curves (Fig. 3a) and the XPS profiles (Fig. 3b) obtained for the catalysts based on copper. For the potassium free catalyst, a broad hydrogen consumption peak is observed with a maximum at around 270 °C which can be assigned to the reduction of CuO. The XRD (not shown), and the XPS data reveal the absence of Co and Cu nitrates. The higher intensity of the reduction peak for the potassium catalysts indicates that this alkaline metal enhances the reducibility of copper oxide, as was previously observed for transition metal catalysts supported on activated

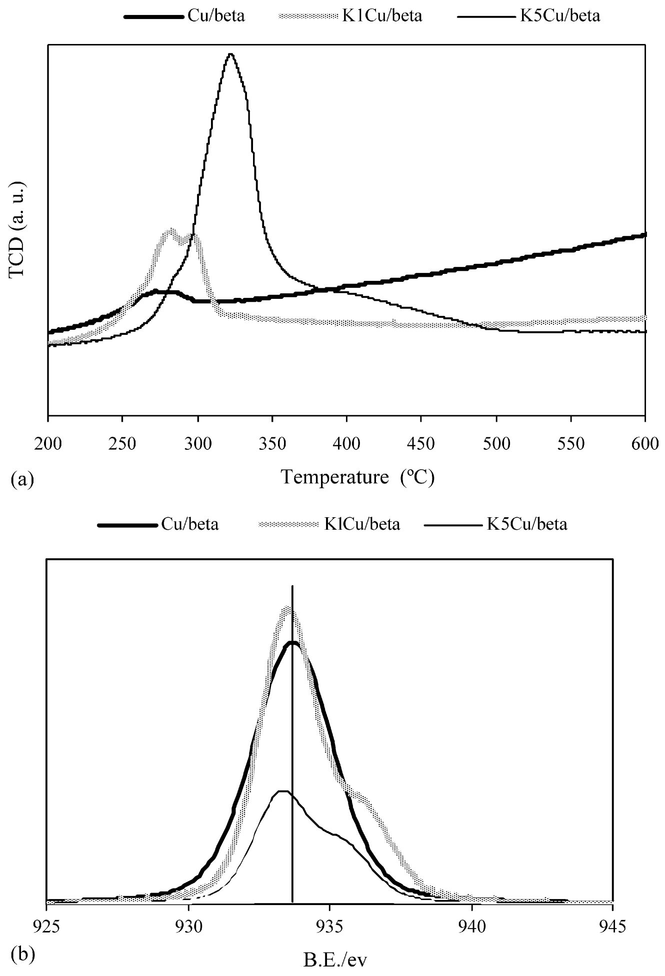

Fig. 3. Copper-based catalysts characterization: (a) TPR-H_2 curves and (b) XPS profiles.

carbon [14]. However, even the intensity of the reduction peaks is higher for the catalysts with potassium, the maximum for the hydrogen consumption peak is shifted to higher temperatures. In addition, note that K5Cu/beta shows a more intense hydrogen consumption peak than K1Cu/beta, but a lower activity for NO_x reduction. For these catalysts, the XRD data indicates that the size of metal particles (CuO) increases with the potassium amount. Also, the TEM analysis of the copper catalysts (not shown), reveals an increase of the particle size after potassium addition, being this more important for K5Cu/beta. On the other hand, the XPS profiles in Fig. 3b, after peak deconvolution, shows that for the potassium catalysts two copper species can be assigned [13]: the main peak at 933.6 eV corresponding to CuO, this peak shifts to lower BE energy due to the interaction of Cu with an electropositive element as potassium; and a shoulder at around 936.0 eV which can be assigned to Cu^{2+} ionic-exchanged on beta-zeolite or, at least, to a CuO with a more intense interaction with the beta-zeolite support. It is also featured that the increase of the potassium content shifts the two XPS signals to lower BE energy, and also enhances the ratio Cu^{2+}/CuO even though a less intense XPS signal is detected, probably due to the presence of a larger amount of potassium which can cover the copper species (CuO and Cu^{2+}). The XPS results seem to explain the shift of the TPR-H_2 peak maximum at higher temperatures observed in Fig. 3a. Thus, the decrease of activity for NO_x reduction at high potassium content seems to be due to an increase in the amount of the less reducible copper species but also to a higher metal particle size and, perhaps, to a lower accessibility to the metal particles. For the cobalt-based catalysts, a similar relation between the potassium-content and the catalysts activity is observed, but the effect of potassium is less pronounced than for the copper catalysts.

To be used in real conditions, it is important to explore the catalysts isothermal performance at other temperatures. For that, the best catalyst K1Cu/beta was selected. The reaction data obtained at 350 °C reveals that, in agreement with TPR curve, the NO_x reduction decreases from 98 to 88%, the C_3H_6 conversion is not affected and, finally, the soot consumption rate suffers a more significant decrease from around 260 $\mu g/g_{initial\ soot}\ s$ till approximately 60 $\mu g/g_{initial\ soot}\ s$. This notable decrease was previously observed using potassium-bimetallic catalysts supported on alumina [10] and it seems to be consequence of the larger temperature dependence of soot

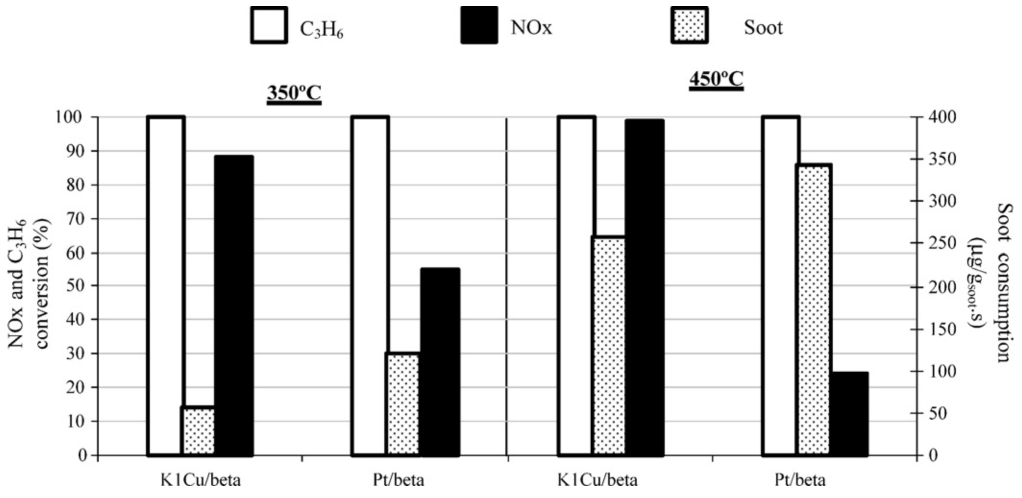

Fig. 4. Isothermal reaction data at 350 and 450 °C for K1Cu/beta and Pt/beta catalysts.

consumption due to the contribution of O_2-soot reaction which is favored at high temperatures [11,18].

Thus, it can be concluded that K1Cu/beta is a promising catalyst for the simultaneous NO_x/soot removal from diesel exhaust because it presents, in a C_3H_6 containing simulated diesel exhaust, the highest NO_x and C_3H_6 conversion and a high soot consumption rate, close to the soot emission rate of diesel engine [19]. It is noticeable that with this catalyst, NO_x is reduced to N_2 and CO_2 and "NO slip" is not observed as happens for others soot oxidation catalysts [20,21]. Related with the use of copper as catalyst for diesel exhaust, it was reported in the literature that metals such copper and iron can increase the rate of dioxins formation in the presence of chlorine [22,23]. Nevertheless, it has to be underline that the catalysts used in this work are chlorine free (see Section 2).

3.2. K1Cu/beta versus Pt/beta

The K1Cu/beta catalyst seems to be effective for simultaneous NO_x and soot removal in the presence of C_3H_6. At this point it is interesting to compare the activity of this catalyst with that of a highly-active deNO_x HC-SCR platinum based catalyst (Pt/beta) [11]. In a previous study, using identical experimental conditions [10], two regions of activity were clearly observed for the Pt/beta catalyst. At low temperatures ($T < 300$ °C), the maximum of NO_x reduction (to N_2, N_2O and CO_2) is observed with a low soot consumption. At high temperatures ($T > 300$ °C) the maximum of soot consumption is reached however, the NO_x reduction is low. In conclusion, for the Pt/beta catalyst it is not possible to select a temperature at which both a high level of NO_x reduction and a high level of soot consumption rate are achieved.

Thus, considering the above commented results, 350 and 450 °C were selected as temperatures for the comparison of K1Cu/beta and Pt/beta performance. The isothermal reaction data (%NO_x, % C_3H_6 conversion and soot consumption rate) are shown in Fig. 4. Note that, at both temperatures, the copper catalyst shows the highest NO_x reduction meanwhile the soot consumption rate is higher for the platinum catalyst. The C_3H_6 conversion is identical (100 %) for both catalysts due to the influence of the beta support [10,11]. Thus, it can be concluded that K1Cu/beta catalyst presents the best global performance at 350 and 450 °C, achieving a high soot consumption rate (comparable to platinum catalyst), and the highest NO_x reduction with the advantage respect to the platinum catalyst, that the main reaction products are N_2 and CO_2.

4. Conclusions

At temperatures higher than 300 °C, all noble-free beta-supported catalysts (Co/beta, K1Co/beta, K5Co/beta, Cu/beta, K1Cu/beta, K5Cu/beta) are active for the simultaneous NO_x/soot removal from a simulated diesel exhaust in the absence of an external reductant.

For the copper based catalyst, the most active one, the addition of a low amount of potassium (less than 1%) increases the NO_x reduction without any significant effect in soot consumption rate. As consequence, K1Cu/beta is the most promising catalyst.

Respect to Pt/beta catalyst, K1Cu/beta shows, at 350 and 450 °C, the highest NO_x reduction (to N_2 and CO_2) and a comparable high soot consumption rate.

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References

[1] L. Shirnamé-Moré, Diesel Exhaust: A Critical Analysis of Emissions, Exposure and Health Effects, A Special Report of the Institute's Diesel Working Group, Health Effects Institute, Cambridge, MA, 1995, p. 221.

[2] www.dieselnet.com.

[3] Diesel Exhaust Emissions Control, Developments in Regulation and Catalytic Systems, SP-1581, SAE International, Society of Automotive Engineers, USA, 2001.

[4] Y. Teraoka, K. Kanada, Appl. Catal. B: Environ. 34 (2001) 73.

[5] D. Fino, P. Fino, G. Saracco, V. Specchia, Appl. Catal. B: Environ. 43 (2003) 243.

[6] S. Kureti, W. Weisweiler, K. Hizbullah, Appl. Catal. B 43 (2003) 281.

[7] K. Hizbullah, S. Kureti, W. Weisweiler, Catal. Today 95 (2004) 839.

[8] V.G. Milt, M.A. Ulla, E.E. Miró, Appl. Catal. B: Environ. 57 (2005) 13.

[9] N. Nejar, J.M. García-Cortés, C. Salinas-Martínez de Lecea, M.J. Illán-Gómez, Catal. Commun. 6 (2005) 79.

[10] N. Nejar, M.J. Illán-Gómez, in: Proceedings of the Fourth International Conference on Environmental Catalysis, Heidelberg, Germany, June 5–8, (2005), p. 96.

[11] J.M. García-Cortés, J. Pérez-Ramírez, J.N. Rouzaud, A.R. Vaccaro, M.J. Illán-Gómez, C. Salinas Martínez de Lecea, J. Catal. 218 (2003) 111.

[12] A. Bueno-López, D. Lozano-Castelló, I. Such-Basáñez, J.M. García–Cortés, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea, Appl. Catal. B: Environ. 58 (2005) 1.

[13] M.N. Debbagh-Boutarcouch, I. Such-Basáñez, J.M. García-Cortés, M. Soussi, C. Salinas-Martínez de Lecéa, SECAT'03, Torremolinos, Spain, p. 259.

[14] M.J. Illán-Gómez, S. Brandán, A. Linares-Solano, C. Salinas-Martínez de Lecea, Appl. Catal. B 25 (2000) 11.

[15] V.G. Milt, C.A. Querini, E.E. Miró, M.A. Ulla, J. Catal. 220 (2003) 424.

[16] M.L. Pissarello, V.G. Miltt, M.A. Peralta, C.A. Querini, E.E. Miró, Catal. Today 75 (2002) 465.

[17] V.G. Milt, M.L. Pissarello, E.E. Miró, C.A. Querini, Appl. Catal. B 41 (2003) 397.

[18] A. Bueno-López, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea, in: Proceedings of the Fourth International Conference on Environmental Catalysis, Heidelberg, Germany, June 5–8, 2005.

[19] P.G. Harrison, I.K. Ball, W. Daniell, P. Lukinskas, M. Céspedes, E.E. Miró, M.A. Ulla, Chem. Eng. J. 95 (2003) 47.

[20] A. Setiabudi, B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Appl. Catal. B 35 (2002) 159.

[21] M. Seipenbusch, J. van Erven, T. Schalow, A.P. Weber, A.D. Van Langeveld, J.C. Marijnissen, S.K. Friedlander, Appl. Catal. B 55 (2005) 31.

[22] P.H. Taylor, D. Lenoir, Sci. Total Environ. 269 (2001) 1.

[23] E. Finocchio, G. Busca, M. Notaro, Appl. Catal. B 62 (2005) 12.