Catalysis Today 176 (2011) 361–364

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Soot oxidation in the presence of NO over alumina-supported bimetallic catalysts K–Me (Me = Cu, Co, V)

M.E. Gálvez[a], S. Ascaso[a], I. Suelves[a], R. Moliner[a], R. Jiménez[b], X. García[b], A. Gordon[b], M.J. Lázaro[a,*]

[a] *Instituto de Carboquímica, CSIC, Miguel Luesma Castán, 4, 50018 Zaragoza, Spain*
[b] *Dpto. Ingeniería Química, Universidad de Concepción, Edmundo Larenas, s/n, Concepción, Chile*

ARTICLE INFO

Article history:
Received 29 September 2010
Received in revised form
15 November 2010
Accepted 16 November 2010
Available online 18 December 2010

Keywords:
Soot oxidation
NO_x removal
Diesel exhaust gas cleaning
Alumina supported catalysts

ABSTRACT

Alumina supported catalytic systems K–Me (Me = Cu, Co and V) for the simultaneous removal of soot and NO_x, were prepared by impregnation of a powder particle size alumina, using nitrate solutions of the corresponding metals. Physico-chemical characterization of the prepared catalysts was performed by means of XRD, SEM-EDX, ICP, N_2-adsorption and TPR. The activity of the catalysts was assayed both, by thermogravimetric analysis and in a laboratory-scale fixed bed reactor. The effect of catalyst composition was examined. The catalysts showed high activity on the simultaneous removal of soot and nitrogen oxides at temperatures between 350 and 550 °C. Full selective conversion of NO_x and total oxidation of the soot was attained; observing higher reaction rates in the case of the catalysts prepared using Cu as the active metal.

1. Introduction

Environmental concern and increasingly stricter regulations for diesel engine exhausts [1] have forced the development of novel and each time more efficient after-treatment technologies, which mostly focus on the elimination of nitrogen oxides (NO_x) and particulate matter, i.e. soot. Procedures such as selective catalytic reduction (SCR) [2,3] and NO_x storage-reduction (NSR) [4] allow the removal of nitrogen oxides from automobile exhausts under excess oxygen, and have been extensively studied in the last years. However, SCR systems need the presence of a reducing agent, normally urea, and its corresponding storage and feed units, whereas NSR catalytic systems still suffer from serious problems such as low catalytic activity, narrow temperature window of operation and deactivation in the presence of other components in the exhaust [5]. Diesel particulate filters (DPF) have been successfully applied for soot removal [6]. These filters have to be continuously regenerated, generally by a temperature increase which leads to the oxidation of the soot particles retained. The presence of a catalyst on the filter surface favours soot oxidation. Transition metal oxides, i.e. Co_3O_4, V_2O_5, CuO, Fe_2O_3, have been previously employed [7,8] together with alkali compounds, such as K, which act as promoters, favouring soot–catalyst contact [8] and formation of active oxygen species [9]. One of these efforts focuses on the simultaneous removal of particulates and NO_x. Still, effective catalytic systems need to be developed to oxidize trapped soot particles and simultaneously reduce nitrogen oxides at 150–500 °C. In the present work, several alumina-supported K–Me (Me = Cu, Co, V) catalysts were prepared and tested for soot oxidation and the simultaneous removal of soot and NO, aiming to maximise conversion of both pollutants.

2. Materials and methods

Catalysts were prepared by excess impregnation of a powder γ-Al_2O_3, using solutions of the metal precursors ($Cu(NO_3)_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ or NH_4VO_3) and promoter (KNO_3). Three catalyst compositions K/Me were considered, 5:10, 10:5 and 10:10, % weight. Excess water was removed by evaporation (stirring 24 h). Catalysts were dried at 110 °C for 24 h, calcined in air at 450 °C for 3 h and characterized by N_2 adsorption, XRD, SEM-EDX and temperature programmed reduction (TPR). The relatively low calcination temperature may result in the presence of residual nitrates in the catalysts. Temperature programmed decomposition under Ar flow, heating up 300 mg of catalyst from 250 to 650 °C at 5 K/min, and following NO, N_2O and NO_2 evolution by mass spectrometry (Balzers 422) evidenced that, in the worst case, only 2.2% of the total K content in the catalyst remains in the form of KNO_3 after calcination. Catalytic activity for soot combustion was assayed in a thermogravimetric apparatus (Netzsch), using carbon black as model compound for soot (Cabot, Elftex 430). Mixtures of carbon black and catalyst (1:4, weight basis) were carefully hand-milled for 10 min in ceramic mortar. These loose-contact mixtures of car-

---

[*] Corresponding author. Tel.: +34 976 733 977; fax: +34 976 733 318.
E-mail address: mlazaro@icb.csic.es (M.J. Lázaro).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.11.045

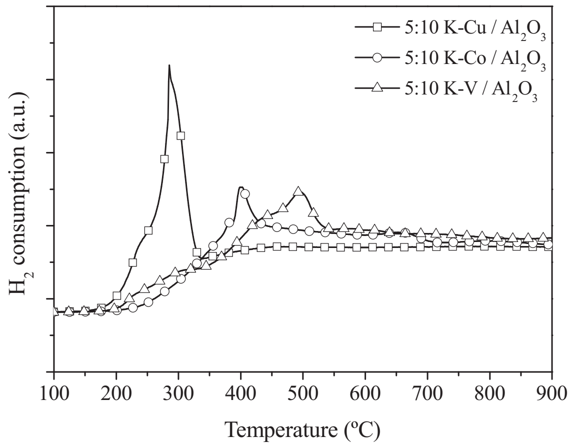

Fig. 1. Hydrogen consumption curves obtained during TPR experiments in the presence of the 5:10 K–Me catalysts.

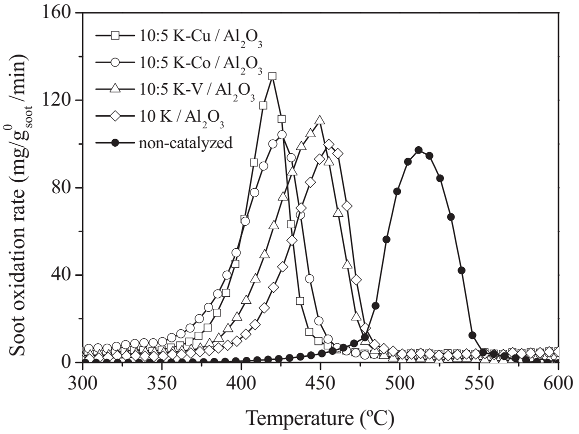

Fig. 2. Thermogravimetric curves for carbon black oxidation in the presence of the 10:5 K–Me catalysts.

bon black and catalyst were heated up in 15% O_2–Ar atmosphere from ambient temperature to 650 °C at 5 K/min. Reproducibility of the thermogravimetric runs was checked by means of repeating at least 2 times each soot oxidation experiment.

Simultaneous removal of carbon black and NO was tested in a bench-scale fixed-bed setup, flowing 50 mL/min of a reactant gas containing 600 ppm NO and 5% O_2 in Ar through 300 mg of carbon black–catalyst mixture, corresponding to a residence time of approximately 0.7 s. Temperature was increased from 250 °C to 650 °C, 5 K/min heating rate. Concentrations in the exiting gas flow were continuously measured by mass spectrometry (Balzers 422) and gas chromatography (HP 5890).

3. Results and discussion

Textural characterization by means of N_2 adsorption yielded surface areas for the catalysts in the range from 41 to 112 m^2/g. Both γ-Al_2O_3 used as support and the synthesized catalysts can be considered mainly as mesoporous materials. XRD patterns obtained for the prepared catalysts evidenced the diffraction peaks for both the γ-Al_2O_3 used as support and the corresponding metal oxides, CuO and Co_3O_4, except in the case of the V-loaded catalysts, which showed only the typical reflectances of γ-Al_2O_3. This fact was attributed to the lack of crystalline V species in these series of catalysts, most probably due to the formation of K–V mixed compounds. SEM-EDX confirmed the presence of V and the other metals used in the preparation of the catalysts. Metal and K dispersion on the support's surface was found to be adequate, with some agglomerates appearing for the catalysts with higher K load. TPR analysis was useful for qualifying catalyst reducibility. Fig. 1 shows the TPR profiles determined for the 5:10 K/Me catalysts. Catalyst reducibility was found to be higher for the Cu-loaded catalysts, independently of the K content. Main peak of H_2 consumption appeared at lower temperatures for these catalysts, followed by Co-loaded and V-catalysts, which showed the lowest affinity towards H_2 in this series. Increased K content resulted in a noticeable increase in the H_2 uptake, in all cases, pointing to the formation of K–Me mixed phases which are easily reduced in the presence of H_2 [10]. TPR profiles for K–Cu catalysts showed a characteristic peak at 230–250 °C, previously attributed to the reduction of Cu oxides and mixed Al–Cu oxides [11]. The shoulder observed at about 550 °C indicates the reduction of residual nitrates left after the catalyst preparation process [12]. K–Co catalysts present an H_2 uptake peak at 250–450 °C typical of the presence of Co_3O_4, and its 2-step reduction. $Co_3O_4 \rightarrow CoO \rightarrow Co$ [13]. Dispersed Co-species are reduced at temperatures between 500 and 700 °C [10]. TPR profile for 5:10 K–V catalyst shows several H_2 uptake peaks at 200–700 °C, pointing to the presence of V-species of different stoichiometry [14]. Main reduction peak appears at about 425–500 °C. Most of the shoulders that can be observed for the 5:10 K–V catalysts were no longer present in the TPR profiles obtained for the catalysts prepared increasing K content, at the same time reduction was enhanced and H_2 uptake shifted to lower temperatures.

Fig. 2 shows the thermogravimetric curves for soot oxidation in the presence of the 10:5 K–Me catalysts, as well as non-catalyzed carbon black oxidation. Cu-containing catalyst showed the highest activity in soot oxidation, whereas V was found to be the less active among the metals employed. Maximal soot oxidation rate for the latter appears at slightly lower temperatures than in the case of using the catalyst prepared in absence of metal, 10 K. In general, any of the catalysts tested is able to bring down the temperature window for soot oxidation. Soot oxidation in the absence of a catalyst occurs at considerably higher temperatures, its TG curve presenting maximal soot oxidation rate at about 512 °C, 40 to 100 °C higher than in the presence of the several catalysts presented in this work. Table 1 shows the initial, T_i, peak, T_m, and final, T_f, temperatures, as well as the temperature interval $\Delta T = T_f - T_i$, deduced from the TG curves for all the catalysts tested. As can be observed, presence of K is fundamental in soot oxidation. Increased K content results in lower initial and final temperatures for soot oxidation, with maximal rate occurring at lower temperatures. Metal load slightly influences these series of parameters, although it is clear that the presence either of Cu, Co or V in the catalyst composition further enhances soot oxidation, i.e. maximal soot oxidation rate temperature, T_m, for 10:5 K–Cu is 417.6 °C, in comparison to 455.1 °C, calculated for the catalyst prepared in absence of Cu, 10 K.

Table 1
ΔT, initial, T_i, peak, T_m, and final, T_f, temperatures for carbon black oxidation over the K–Me catalysts.

Catalyst	T_i (°C)	T_m (°C)	T_f (°C)	ΔT
5:10 K–Cu	339.6	449.2	525.4	185.8
5:10 K–Co	339.7	466.4	533.1	193.4
5:10 K–V	367.1	466.7	540.4	173.3
10:5 K–Cu	338.2	417.6	477.8	139.6
10:5 K–Co	338.7	425.8	478.1	139.4
10:5 K–V	345.3	449.5	507.4	162.1
10:10 K–Cu	340.8	414.8	462.8	122.0
10:10 K–Co	340.9	431.8	480.9	140.0
10:10 K–V	342.8	455.1	534.4	191.6
5 K	369.2	472.2	532.5	163.3
10 K	344.9	455.1	507.3	162.4
Non-catalyzed	448.7	511.9	579.7	131.0

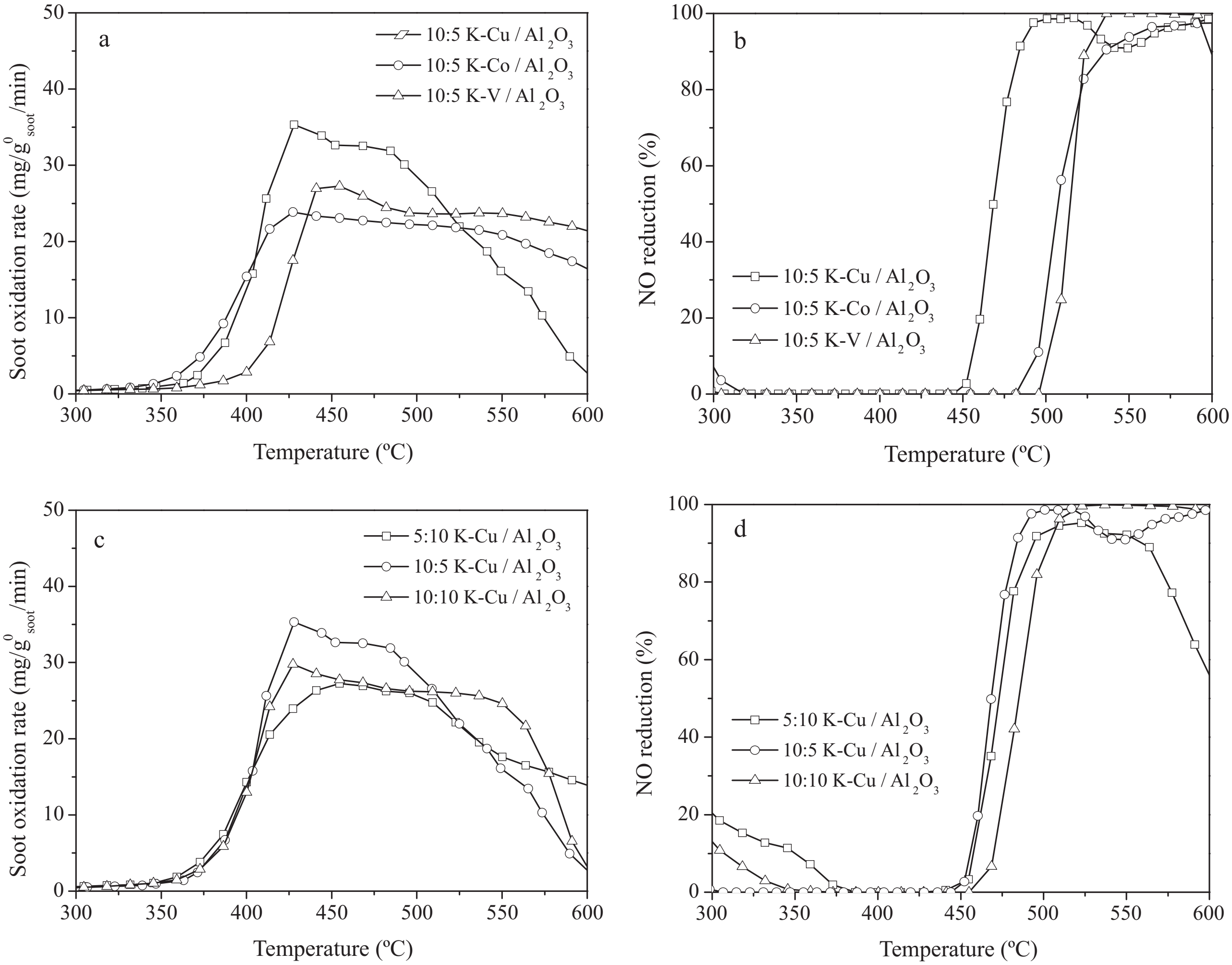

Fig. 3. Carbon black oxidation rate (a and c) and NO reduction (b and d) as a function of temperature, measured during simultaneous removal experiments in the presence of K–Me catalysts.

Catalysts showing higher reducibility during H_2-TPR characterization exhibited also higher activity in soot oxidation. Querini et al. [15] observed that the activity of their catalyst was directly related to Co reducibility, indicating that the reaction was carried out by a redox mechanism. In this mechanism oxygen is probably transferred from the metal oxides in the catalyst to the carbon material surface, the reduced metal species being regenerated by the oxygen contained in the reactant gas. Lower activity in the case of the V-containing catalysts might be ascribed to the presence of V-species of different stoichiometry evidenced by H_2-TPR profiles, as well as to the formation of V–K mixed compounds during catalyst preparation.

Fig. 3 shows the soot oxidation rate, a and c, and NO conversion, b and d, for some of the catalysts prepared. In the 10:5 K–Me series, Cu-containing catalysts showed the highest activity both in soot oxidation and NO reduction. Activity in the simultaneous removal of soot and NO also corresponds to catalysts reducibility assayed by means of H_2-TPR. Almost total oxidation of the amount of carbon black initially loaded on the 10:5 K–Cu catalyst was achieved. Full NO conversion was attained at about 475 °C in this case, whereas NO reduction started at higher temperatures for the Co and V-loaded catalysts. Selectivity towards CO_2 formation was considerably high for all the catalysts tested, ranging from 82.6 to 99.6% CO_2 formation as a result of carbon black oxidation. NO reduction was found to be completely selective to N_2. NO_2 formation takes place, corresponding to maximal soot oxidation rate, but it was reduced together with NO through the experiments, i.e. 124 ppm of NO_2 were measured at 475 °C in the presence of the 10:5 K–Cu catalysts, which were further reduced to 22 ppm once a temperature of 525 °C was reached. In fact, NO_2 formation seems to be of key importance in the simultaneous elimination reaction mechanism, as this maximal evolution of NO_2 and soot oxidation rate always preceded NO reduction in this range of temperatures. NO_2 is thus involved in the catalytic cycle most probably through enhancing oxygen transfer between metallic sites and the carbon surface. Fig. 3c and d shows the influence of the K and Me contents in the K–Cu series. As in TG analyses, K content enhances catalytic activity towards soot oxidation. Final soot oxidation reaction extent is much higher for the catalysts prepared using 10% K. NO reduction ability is also slightly favoured at higher K contents, starting at lower temperatures for the 10:5 K–Cu catalysts. On the other hand, increasing metal content to 10%, 10:10 K–Cu, resulted in slightly higher set off temperatures for NO reduction, pointing to 5% metal content as optimal for achieving maximal catalytic activity.

4. Conclusions

The prepared K–Me (Me = Cu, Co, V)/Al_2O_3 catalysts showed considerable activity in the simultaneous removal of soot and NO, at 250–650 °C. XRD characterization showed typical diffraction peaks of Cu and Co oxides, except for V-containing catalysts, due to the formation of amorphous K–V mixed compounds. TPR showed higher reducibility for the Cu and Co prepared catalysts in comparison to V-loaded ones. TG soot oxidation experiments showed higher activity for Cu-containing catalysts, followed by Co and V. The presence of a catalyst substantially reduced the temperature for maximal soot oxidation rate. Increased K content resulted in an increased ability of the catalysts to oxidize soot, whereas metal loading slightly influenced initial, maximal and final soot oxidation temperatures. Catalytic activity in soot oxidation was found to be directly related to catalyst reducibility, indicating that the reaction is carried out by a redox mechanism in which oxygen is transferred from among metal sites, carbon surface and reactant gas phase. Simultaneous removal experiments showed 100% NO reduction at 475 °C and almost full soot conversion in most cases. NO_2 formation took place corresponding to maximal soot oxidation rate during the experiments. NO_2 evolution and maximal soot oxidation preceded NO reduction, pointing to NO_2 formation as a key step in the simultaneous removal reaction mechanism. Increasing K content in the catalysts composition resulted in higher soot oxidation extents and slightly favoured NO conversion. Increasing metal content, however, resulted in higher set off temperatures for NO reduction.

Acknowledgements

Authors acknowledge AECI (A/18200/08, A/9858/07), Gobierno de Aragón-La Caixa (GA-LC-030/2008), Fondecyt (Chile) 11060301, 1101005 and Conicyt (Chile) PFB-27. M.E. Gálvez is indebted to the Spanish Ministry of Science and Innovation for her “Juan de la Cierva” post-doctoral grant.

References

[1] Regulation (EC) No. 715/2007.
[2] A. Boyano, M.J. Lázaro, C. Cristiani, F.J. Maldonado-Hodar, P. Forzatti, R. Moliner, Chem. Eng. J. 149 (2009) 173–182.
[3] A. Boyano, N. Lombardo, M.E. Gálvez, M.J. Lázaro, R. Moliner, Chem. Eng. J. 144 (2008) 343–351.
[4] P. Forzatti, L. Castoldi, I. Nova, L. Lietti, E. Tronconi, Catal. Today 117 (2006) 316.
[5] S. Matsumoto, Catal. Today 90 (2004) 183–190.
[6] L. Castoldi, R. Matarrese, L. Lietti, P. Forzatti, Appl. Catal. B: Environ. 90 (2009) 278–285.
[7] G. Neri, G. Rizzo, S. Galvano, A. Donato, M.G. Musolino, R. Pietropaolo, Appl. Catal. B: Environ. 42 (2003) 381–391.
[8] D. Fino, N. Russo, C. Baldini, G. Saracco, V. Specchia, AIChE J. 8 (2003) 2173–2180.
[9] R. Jiménez, X. García, C. Cellier, P. Ruiz, A.L. Gordon, Appl. Catal. A: Gen. 314 (2006) 81–88.
[10] G. Bagnasco, C. Cammarano, M. Turco, S. Esposito, A. Aronne, P. Pernice, Thermochim. Acta 471 (2008) 51–54.
[11] P. Larsson, A. Andersson, Appl. Catal. B: Environ. 24 (2000) 175–192.
[12] N. Nejar, M.J. Illán-Gómez, Appl. Catal. B: Environ. 70 (2007) 261–268.
[13] Z. Wang, Z. Jing, W. Shangguan, Catal. Commun. 8 (2007) 1659–1664.
[14] J. Liu, Z. Zhao, C. Xiu, A. Duan, L. Zhu, X. Wang, Appl. Catal. B: Environ. 61 (2005) 36–46.
[15] C.A. Querini, L.M. Cornaglia, M.A. Ulla, E.E. Miro, Appl. Catal. B: Environ. 20 (1999) 165–177.