Catalysis Letters, Vol. 116, Nos. 3–4, August 2007 (© 2007)
DOI: 10.1007/s10562-007-9136-3

Complete oxidation of short chain alkanes using a nanocrystalline cobalt oxide catalyst

Benjamin Solsona,[b] Isabel Vázquez,[b] Tomas Garcia,[c] Thomas E. Davies,[a] and Stuart H. Taylor[a],*
[a]*School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK*
[b]*Departament d'Enginyeria Química, Universitat de València, C/Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*
[c]*Instituto de Carboquímica (CSIC), C/Miguel Luesma, 50018 Zaragoza, Spain*

Received 1 April 2007; accepted 22 April 2007

Exceptionally high activity for the complete oxidation of propane is reported for the first time using a nanocrystalline cobalt oxide catalyst. The catalyst shows stable activity for prolonged time on stream and when the reaction temperature is cycled. Furthermore, the nanocrystalline catalyst demonstrates considerably higher activity than an alumina supported palladium catalyst, which is recognised as one of the most active reported. The high activity of the cobalt oxide catalyst is associated with the nanocrystalline nature of the material, which gives rise to new catalytically active surface sites. A broader comparison with other reported high activity catalysts emphasises the high efficacy of nanocrystalline cobalt oxide for total oxidation and demonstrates that it has significant potential for important applications, such as control of emissions from liquid petroleum gas powered vehicles and alkane volatile organic emissions from stationary sources.

KEY WORDS: alkanes; catalysis; cobalt oxide; oxidation; VOC.

1. Introduction

The release of volatile organic compounds (VOCs) to the atmosphere results in tangible environmental damage. For example, VOCs have been implicated in the formation of ground level ozone [1], ozone depletion [2] and often they act as greenhouse gases [3]. Catalytic oxidation is recognised as one of the best methods for the abatement of VOC emissions, as it provides the potential to efficiently destroy pollutants to carbon dioxide and water. Volatile organic compounds are wide ranging in chemical functionality and their emission sources, but it is clear that linear short chain alkanes are some of the most difficult to destroy [4]. Currently, the most active catalysts are based on platinum and palladium, which are dispersed on a high surface area refractory support. However, there still remains scope for improved catalysts as more active systems offer considerable economic advantages in terms of operating costs, and the level of environmental protection provided.

Propane is an abundant short chain alkane present in both oil and natural gas. A relatively high concentration of propane is present in liquefied petroleum gas (LPG), which is mainly comprised of propane and butanes. LPG is increasingly used as a substitute for gasoline and diesel in transport vehicles, since it exhibits cleaner combustion than diesel or gasoline. The combustion process of propane is slower than butane in the internal combustion engine, and therefore the major VOC pollutant in the exhaust of a LPG fuelled vehicle is propane. In order to control the emission of automobiles that use LPG, an efficient catalyst for the total combustion of propane at low concentration ($<1\%$) is essential to minimise impact on the environment [5]. Furthermore, short chain alkanes are emitted from a range of stationary sources and their treatment is also a priority.

Recently, we have shown that nanocrystalline Co_3O_4 exhibits remarkable activity for the partial oxidation of propane to propene under ambient conditions [6]. Considering the efficacy of the cobalt oxide catalyst for propane activation and the identification of cobalt oxide as an effective catalyst for propane deep oxidation [7], it is interesting to probe the activity of the nanocrystalline catalyst for propane total oxidation. In the present work we show, for the first time, that a catalyst comprising nanocrystalline cobalt oxide is highly effective for the total oxidation of propane under conditions relevant for VOC emission control. Furthermore, it demonstrates stable conversion with time on stream, and comparison with a standard precious metal catalyst shows that it is significantly more active.

2. Experimental

Nanocrystalline Co_3O_4 was prepared by solid state reaction following a method similar to that described

---

*To whom correspondence should be addressed.
E-mail: taylorsh@cardiff.ac.uk

1011-372X/07/0800–0116/0

previously [8]. $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich) and NH_4HCO_3 (2:5 molar ratio) were ground with a pestle and mortar for 0.5 h, and then thoroughly washed with distilled water and dried for 16 h at 100 °C. The precursor was calcined at 300 °C for 2 h in static air. The greatest BET surface area of the cobalt oxide catalyst, determined from the nitrogen adsorption isotherm, was 160 $m^2 g^{-1}$, hence the catalyst was denoted as 160-Co_3O_4. A further cobalt oxide catalyst with lower surface area was also prepared using a similar solid-state method to that described above, but the grinding time was reduced to less than 0.5 h. The resulting Co_3O_4 catalyst presented a surface area of 120 $m^2 g^{-1}$, and was denoted as 120-Co_3O_4.

For comparative purposes a range of cobalt containing catalysts were also tested. A commercial sample of Co_3O_4 (ex Avocado) with a surface area of 4 $m^2 g^{-1}$ (named as 4-Co_3O_4) was used as supplied. Co_3O_4 supported on γ-Al_2O_3 (6.7 wt.% Co_3O_4) and TiO_2 (9.0 wt.% Co_3O_4 on Degussa P25) were prepared by a standard wet impregnation of the supports using an aqueous solution of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich) followed by drying and calcination. In addition to surface area measurement catalysts were characterised using powder X-ray diffraction and temperature programmed reduction.

Catalyst activity was determined using a fixed bed laboratory micro reactor. Catalysts were tested in powdered form using a 1/4″o.d. stainless steel reactor tube. The reaction feed consisted of 5000 vppm hydrocarbon in air. A total flow rate of 50 mL min^{-1} was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 45,000 h^{-1} (13 s^{-1}) for all studies. Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame ionisation detectors. Catalytic activity was measured over the range 100–450 °C and temperatures were measured by a thermocouple placed in the catalyst bed. Conversion data were calculated by the difference between inlet and outlet concentrations. Activity measurements were obtained once steady state was attained and data are an average of at least 3 consistent analyses. In all cases the carbon balances were 100 ± 3%.

3. Results and discussion

Characterisation by powder X-ray diffraction showed that the catalysts prepared by the solid-state procedure were comprised of Co_3O_4, however, diffraction peaks were very broad. Analysis of the X-ray line widths using the Scherrer method gave an average crystallite size of 12 nm for 160-Co_3O_4 and hence the catalyst is denoted as nanocrystalline. Further analysis using temperature programmed reduction confirmed that the catalyst was Co_3O_4 [6].

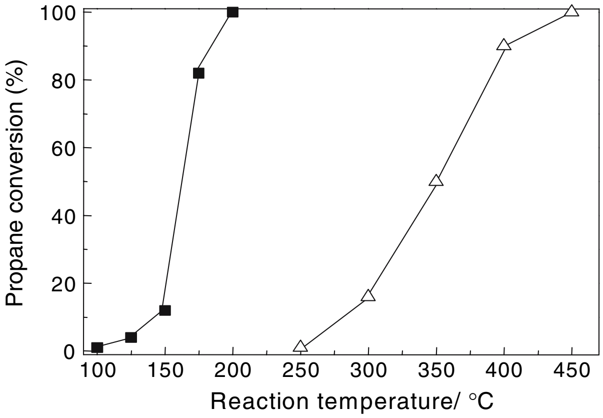

Figure 1. Comparison of propane oxidation over nanocrystalline CO_3O_4 with 5% Pd/alumina catalyst. Symbols: Nanocrystalline 160-Co_3O_4 (■), 5% Pd/Al_2O_3 (△).

Catalytic activity results of propane oxidation over the nanocrystalline 160-Co_3O_4 and Pd/alumina catalyst is shown in figure 1. The Co_3O_4 catalyst showed initial steady state activity at 100 °C and conversion increased rapidly as the reaction temperature increased. Complete propane conversion was observed at 200 °C. At 120 °C and below a trace quantity of propene was observed. However, above 120 °C the sole reaction product from propane oxidation was CO_2. Alumina supported Pd catalysts are known to be one of the most active catalysts for deep oxidation of hydrocarbons. Thus, comparison with a commercial 5 wt.% Pd/alumina catalyst (S_{BET} = 130 $m^2 g^{-1}$) has been carried out. Using the same relevant conditions the Pd/alumina catalyst was considerably less active than the nanocrystalline cobalt oxide catalyst. Pd/alumina was initially active at 250 °C and propane conversion increased with temperature, giving 100% at 450 °C. The only reaction product for the Pd/alumina catalyst was CO_2. It is noteworthy that at 250 °C only traces of propane have been converted to CO_2 employing Pd/Al_2O_3, whereas total propane conversion has been obtained with the nanocrystalline cobalt oxide at 50 °C lower temperature.

Comparison of the activity of the nanocrystalline Co_3O_4 catalyst for propane oxidation has also been made with a range of cobalt oxide catalysts. A commercial sample of Co_3O_4 (ex Avocado) was considerably less active than the nanocrystalline catalyst. The comparison in figure 2 also includes data for supported cobalt oxide catalysts on γ-Al_2O_3 and TiO_2. Both of the supported catalysts were inactive below 250 °C, whilst the nanocrystalline catalyst demonstrated 100% conversion below this temperature. The propane conversion increased to *ca.* 70% at 400 °C for the CoO/TiO_2 catalyst, whilst it was only *ca.* 15% for the CoO/Al_2O_3 catalyst at the same temperature. The product selectivity over both supported catalysts was 100% towards CO_2.

Table 1 shows a summary of some of the physical and catalytic properties of the range of cobalt containing

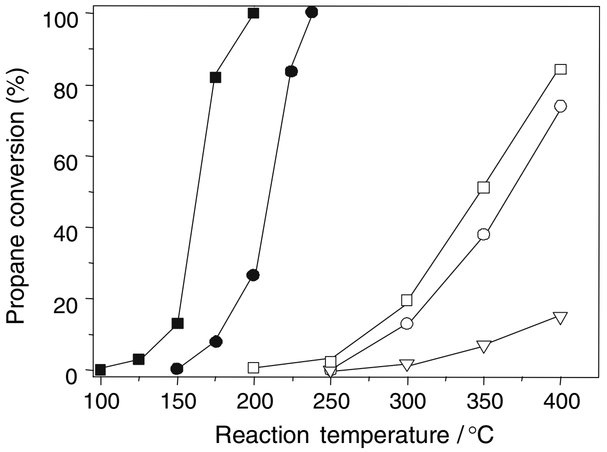

Figure 2. Propane conversion over a range of cobalt oxide catalysts. Symbols: Nanocrystalline 160-Co_3O_4 (■), 120-Co_3O_4 (●), Commercial 4-Co_3O_4 (□), Co/TiO_2 (○), Co/Al_2O_3 (▽).

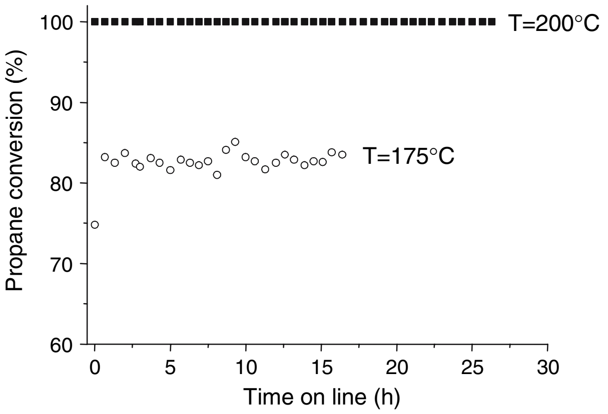

Figure 3. Propane oxidation over nanocrystalline cobalt oxide as a function of time on stream. Symbols: Reaction Temperature = 200 °C (■), Reaction Temperature = 175 °C (○).

catalysts. It can be seen that the specific catalytic activity (per m^2 of surface area) is greatest for the nanocrystalline cobalt oxide. It is apparent that the high activity of the nanocrystalline Co_3O_4 is not a simple function of the increased surface area, otherwise surface area normalised reaction rates would be expected to have similar values for the different unsupported cobalt oxide catalysts. As all the cobalt oxide catalysts are comprised of the same phase, Co_3O_4, the differences of activity are influenced strongly by the crystallite size, and in particular nanocrystalline material is critical for exceptionally high activity. Table 1 also shows turnover per atom of cobalt, for the different catalysts. Comparison of the unsupported cobalt oxides reveals that decreasing the crystallite size increased the turnover. These data are not surprising as the values are calculated on total cobalt atoms and the ratio of surface atoms to total atoms increases as crystallite size decreases. Higher turnover values per cobalt atom can be obtained for the supported catalyst; however, these were observed at much higher temperatures and were largely due to the lower amount of cobalt present.

One of the limitations reported for Co_3O_4 based catalysts is that they decompose at temperatures above 700 °C giving CoO, which is significantly less active, and sinters at lower temperatures [9]. However, with the nanocrystalline catalyst total conversion is achieved at much lower temperatures and the potential for deactivation *via* this mechanism is reduced. The activity of the nanocrystalline Co_3O_4 with time on line has also been investigated (figure 3).

The conversion was stable with time on stream and no deactivation was evident. Furthermore, CO_2 was the only reaction product and the yield was unchanged over the test period. Catalyst stability tests were carried out at two different temperatures, *i.e.* 200 °C, to determine whether total propane conversion was maintained, and at 175 °C. The lower temperature was investigated as it resulted in conversion less than 100%, providing a more sensitive indication of changes of the catalyst performance with time on stream. Considering the nanocrystalline nature of the cobalt oxide catalyst stability for combustion was probed in a series of temperature cycles. The temperature of the catalyst was increased in steps as indicated in figure 1, and once complete conversion was attained the temperature was maintained for a short time and the catalyst was then cooled to room temperature. This cycle was repeated 8 times using the same catalyst sample and the conversion data for each cycle was super-imposable. Moreover, there was no change in

Table 1

Surface area and catalytic properties of cobalt containing catalysts

Catalyst	S_{BET} [m^2 g^{-1}]	Catalytic activity×10^3 [g_{C_3} g_{cat}^{-1} h^{-1}]		Specific activity×10^5 [g_{C_3} m^{-2} h^{-1}]		Turnover frequency×10^3 [g_{C3} $g_{Co_3O_4}^{-1}$ h^{-1}]	
		200 °C	300 °C	200 °C	300 °C	200 °C	300 °C
160-Co_3O_4	159	> 27.0	n/a	> 17.0	n/a	> 27.0	n/a
120-Co_3O_4	120	7.6	n/a	6.4	n/a	7.6	n/a
4-Co_3O_4	4	0.05	4.8	1.5	120	0.05	4.8
Co/TiO_2	45	0	3.2	0	7.5	0	35.6
Co/Al_2O_3	111	0	0.4	0	0.5	0	6.0

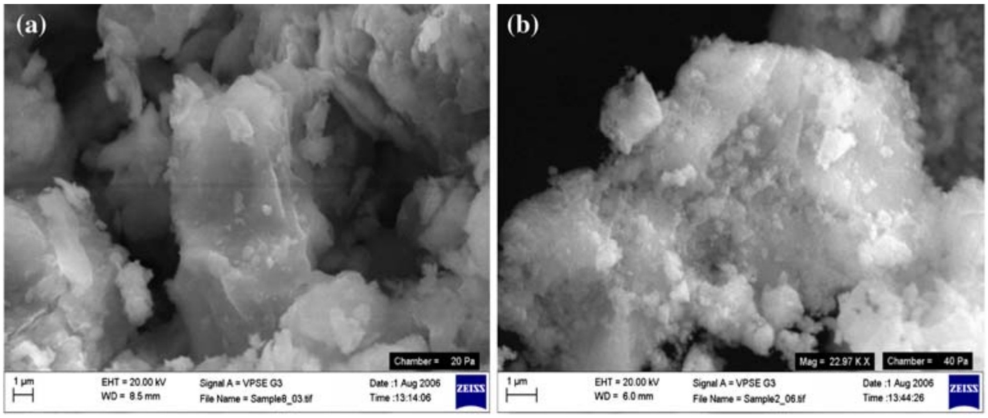

Figure 4. Scanning electron microscopy secondary electron images of (a) fresh nanocrystalline 160-Co_3O_4 and (b) used nanocrystalline 160-Co_3O_4.

the light-off temperature for the various cycles and these data indicate further that the catalyst exhibits stable activity.

Scanning electron microscopy characterisation of the nanocrystalline Co_3O_4 showed that particle sizes were of micron dimensions (figure 4). The particles appeared relatively smooth and there was evidence for smaller particles also present. In combination with evidence from powder XRD the morphology of the catalyst is likely to be comprised from an agglomeration of the nanocrystalline particles. After prolonged use and temperature cycling there was no deactivation of the catalyst. However, the morphology of the used catalyst was different from the fresh catalyst. The used catalyst presented a rougher surface structure. Although morphological differences were apparent, these differences did not strongly influence the catalytic activity.

Previous studies have identified Co_3O_4 as an active metal oxide catalyst for complete oxidation of hydrocarbons [7, 10, 11]. However, there is no data on the total oxidation activity of nanocrystalline Co_3O_4. The activity of the nanocrystalline Co_3O_4 catalyst has also been probed for the oxidation of *n*-butane. The activity for *n*-butane oxidation was higher than that reported for propane (figure 1). Initial conversion was observed at the same temperature as propane; however, the same level of conversion was attained at *ca*. 25 °C lower for *n*-butane when compared with propane. These data are significant as LPG contains a considerable concentration of butane and the nanocrystalline Co_3O_4 is also very efficient for its total oxidation.

It is clear from the present study that the synthesis of nanocrystalline cobalt oxide significantly increases the total oxidation activity. It could be suggested that the increase of the catalytic activity is simply the consequence of an increased surface area. However as observed in table 1 the specific catalytic activity (per m^2 of catalyst) is still considerably higher over nanocrystalline Co_3O_4 compared with the commercial catalyst. Therefore, the small size of the crystallites seems to give rise to new and more easily accessible active sites, which are not apparent on more highly crystalline Co_3O_4 catalysts. The specific nature of the active sites responsible for total oxidation is still unclear, however, the catalytic activity of alkane combustion has been reported to be related to the catalyst reducibility [12]. Busca and coworkers demonstrated that for a Co_3O_4 catalyst lattice O^{2-} anions (nucleophilic oxygen species) were those involved in propane catalytic combustion [12]. Therefore, the reaction occurred through a Mars Van-Krevelen mechanism involving lattice oxygen via a redox cycle. Consequently the reducibility of the catalyst is an important factor for the reactivity of the catalysts. The major reduction bands in the TPR profiles of nanocrystalline cobalt oxide (254 and 339 °C) are present at temperatures lower than those of the commercial Co_3O_4 (300 and 384 °C) [6]. Furthermore, we have identified a low temperature feature on the nanocrystalline Co_3O_4 at 80–90 °C, which is not present on other Co_3O_4 samples [6]. Hence, the nanocrystalline 160-Co_3O_4 catalyst has facile oxygen species that are very reactive and readily oxidise propane to CO_2 at temperatures above 120 °C. The crystallite size of the nanocrystalline Co_3O_4 will give rise to a greater number of low coordination defect lattice oxygen sites when compared with more highly crystalline catalysts, and these may significantly contribute to the high activity.

In this study, we have shown that the nanocrystalline Co_3O_4 is considerably more active than a highly active supported palladium catalyst. It is also interesting to compare the performance of the nanocrystalline catalyst with other catalysts reported in the literature for propane deep oxidation (table 2). The comparison is not exhaustive. A wide range of catalysts have been investigated and test conditions do vary, however, it is evident that the nanocrystalline Co_3O_4 catalyst is the most active. Only sulphated Pt/Al_2O_3 seems to present lower but comparable catalytic activity. It is particularly

Table 2
Comparison of propane total oxidation over nanocrystalline cobalt oxide with catalysts reported in the literature

Catalyst	GHSV/s^{-1}	Reaction conditions	T_{10} /°C	T_{50}/°C	T_{100}/°C	Ref.
Nanocrystalline Co_3O_4	13	0.5% C_3 20% O_2	145	165	200	This work
Co_3O_4–Avocado 4 m^2 g^{-1}	13	0.5% C_3 20% O_2	275	340	>400	This work
Co_3O_4 (15 m^2 g^{-1})	26	2% C_3, 10% O_2	250	290		[10]
Co_3O_4/CuO/Ni	6	0.5% C_3, 10% O_2	315	380	450	[13]
Perovskite LaCaCoO	5	2% C_3, 10% O_2	205	267	400	[14]
Au/Co_3O_4–Al_2O_3	2	1% C_3, 16% O_2	275	325	>400	[15]
Co_3O_4–Al_2O_3	2	1% C_3, 16% O_2	305	355	>450	[15]
Pt/Al_2O_3	2	1% C_3, 16% O_2	215	265	350	[15]
5% Pd/SiO_2–ZrO_2	260	0.25% C_3, 3% O_2	300	350		[16]
0.02% Pd/ZrO_2	19		340	510		[17]
0.33% Pt/Beta	17	0.8% C_3, 10% O_2	200	212	270	[18]
0.36% Pt/ZSM-5	17	0.8% C_3, 10% O_2	210	227	280	[18]
Perovskite LaSrMnNiO	10	1% C_3, 20% O_2	277	336		[19]
Perovskite LaSrCuFeO	10	1% C_3, 20% O_2	300	370		[19]
Rh/Al_2O_3	7	5% C_3, 25% O_2	360	380	400	[20]
Rh/Al_2O_3–SO_4	7	5% C_3, 25% O_2	320	330	340	[20]
1% Pt/Al_2O_3	45	0.4% C_3, 4% O_2	270	310	450	[21]
SO_2–1% Pt/Al_2O_3	45	0.4% C_3, 4% O_2	175	185	275	[21]
Sulphated 1% Pt/Al_2O_3	7	2.5% C_3, 15% O_2	150–200	210	240	[22]
1% Pt/TiO_2	4	0.4% C_3, 12% O_2	180–190	260	375	[23]
SO_2–1% Pt/TiO_2	4	0.4%C_3, 12% O_2			300	[23]

T_X is the temperature required to achieve the specified conversion.

noteworthy that the nanocrystalline Co_3O_4 is significantly more active than a range of conventional precious metal catalysts.

The catalyst prepared in the present work shows very promising performance in the deep oxidation of propane due to the very high activity and stability. The nanocrystalline Co_3O_4 provides a viable alternative catalyst to precious metal based catalysts. In general terms metal oxide catalysts offer some advantages over precious metal catalysts. Often they are cheaper, offer lower toxicity and often they are more tolerant to poisons, such as sulphur, that may be present in VOC laden waste streams. On the other hand, they usually exhibit lower intrinsic catalytic deep oxidation activity when compared with precious metals. In the current work we have successfully addressed the lower activity of a metal oxide catalyst for the deep oxidation of short chain alkanes and the data presented are significant for the formulation of improved catalysts.

4. Conclusions

Nanocrystalline Co_3O_4 is extremely active for the total oxidation of propane and butane. Under our reaction conditions total conversion is achieved at a temperature as low as 200 °C. The high reactivity can be related to the generation of readily accessible active surface sites due to the nanocrystalline nature of the catalyst. Furthermore, new oxidation sites are generated on nanocrystalline Co_3O_4 and the same sites are not apparent to the same extent on other Co_3O_4 catalysts. Activity for propane deep oxidation is stable with extended time on stream and it is also stable for temperature cycles.

Acknowledgments

The authors would like to thank Cardiff University for funding and the Spanish Ministry of Education and Science for the “Ramón y Cajal” Program (B. Solsona and T. García contracts).

References

[1] B.J. Finlayson-Pitts and J.N. Pitts, Science 276 (1997) 1045.

[2] M.J. Molina and F.S. Rowland, Nature 249 (1974) 810.

[3] H. Rodhe, Science 248 (1990) 1217.

[4] T.V. Choudhary, S. Banerjee and V.R. Choudhary, Appl. Catal. A: Gen. 234 (2002) 1.

[5] V.R. Choudhary and G.M. Deshmukh, Chem. Eng. Sci. 60 (2005) 1575.

[6] T. Davies, T. Garcia, B. Solsona and S.H. Taylor, Chem. Commun. 32 (2006) 3417.

[7] J. Haber and W. Turvk, J. Catal. 190 (2000) 320.

[8] H. Yang, Y. Hu, X. Zhang and G. Qiu, Mater. Lett. 58 (2004) 387.

[9] L.F. Liotta, G. Di Carlo, G. Pantaleo, A.M. Venezia and G. Deganello, Appl. Catal. B: Environ. 66 (2006) 217; F.E. Trigueiro, C.M. Ferreira, J.-C. Volta, W.A. Gonzalez and P.G. Pries de Oliveria, Catal. Today 118 (2006) 425.

[10] G. Busca, M. Daturi, E. Finocchio, V. Lorenzelli, G. Ramis and R.J. Willey, Catal. Today 33 (1997) 239.

[11] G.K. Boreskov, in *Catal. Sci. Technol.*, Vol. 3, eds. J.R. Anderson and M. Boudart, (Springer-Verlag, New York, 1982), p. 39.

[12] E. Finocchio, G. Busca, V. Lorenzelli and V. Sanchez Escribano, J. Chem. Faraday Trans. 92 (1996) 1587.

[13] I. Yuranov, N. Dunand, L. Kivi-Minsker and A. Renken, Appl. Catal. B: Environ. 36 (2002) 183.
[14] N.A. Merino, B.P. Barbero, P. Grange and L.E. Cadus, J. Catal. 231 (2005) 232.
[15] A.C. Gluhoi, N. Bogdanchikova and B.E. Nieuwenhuys, Catal. Today 113 (2006) 178.
[16] Y. Yazawa, H. Yoshida, S. Takagi, N. Komai, A. Satsuma and T. Hattori, J. Catal. 187 (1999) 15.
[17] C.P. Hubbard, K. Otto, H.S. Gandhi and K.Y.S. Ng, Catal. Lett. 30 (1995) 41.
[18] T.F. Garetto, E. Rincón and C.R. Apesteguía, Appl. Catal. B: Environ. 48 (2004) 167.
[19] M. Alifanti, J. Kirchnerova, B. Delmon and D. Klvana, Appl. Catal. A: Gen. 262 (2004) 167.
[20] A.F. Lee, C.R. Seabourne and K. Wilson, Catal. Commun. 7 (2006) 566.
[21] R. Burch, E. Halpin, M. Hayes, K. Ruth and J.A. Sullivan, Appl. Catal. B: Environ. 19 (1998) 199.
[22] G. Corro, J.L.G. Fierro and V.C. Odilon, Catal. Commun. 4 (2003) 371.
[23] K. Ruth, M. Hayes, R. Burch, S. Tsubota and M. Haruta, Appl. Catal. B: Environ. 24 (2000) L133.