Catalysis Today 59 (2000) 403–409

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The application of “superacidic” metal oxides and their platinum doped counterparts to methane combustion

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Abstract

A range of metal oxides have been compared as methane combustion catalysts. The effect of modification to generate “superacidic” behaviour on the activities of ZrO_2 and Fe_2O_3 systems has been studied. It has been shown that whilst sulphation lowers the activity of Fe_2O_3, sulphation and, particularly, molybdation enhance the performance of ZrO_2. Despite enhancing the activity of the unmodified base oxides, the addition of low levels of Pt has been demonstrated to poison the activity of “superacidic” zirconias. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Oxidation; Combustion; Superacids; Platinum

1. Introduction

The catalytic combustion of hydrocarbons is currently of widespread interest both as a means of power generation and exit stream purification without the concomitant creation of large amounts of nitrogen oxides, [1–3]. Methane, the most difficult alkane to activate, has been the subject of some attention and amongst the most successful catalysts reported to date have been perovskites [4], hexaluminates [5,6], supported noble metals [7], and zirconium doped ceria systems [8,9]. In this contribution, we present the results of our methane combustion activity studies of some of the so-called “superacidic” metal oxides and their platinum doped counterparts. These are of potential interest since such oxides are known to have very high efficacy for alkane activation, even catalysing the isomerisation of *n*-butane at near ambient temperature [10].

Two general types of “superacid” have been investigated — the more familiar sulphated metal oxides and a series of molybdated zirconias. In the former case, we have previously reported that sulphation of iron oxides modifies their high pressure methane oxidation performance [11]. Although at lower temperature ($<400°C$) total oxidation activity is suppressed by site blocking, the oxidation activity at higher temperature is enhanced. In the case of “superacidic” molybdena zirconia combinations, we have found the methane oxidation activity to be a strong function of MoO_3 content, being greatest at intermediate loadings, which we have related to differences in reducibility and the possible formation of an active monolayer during reaction [12]. In the present contribution, we have extended our previous studies to a wider range of “superacidic” metal oxide systems under conditions which are of greater interest for combustion application. The effects

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PII: S0920-5861(00)00305-9

of platinum doping on these systems has also been investigated, since supported platinum is a known effective hydrocarbon combustion catalyst in its own right [3].

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide was precipitated from a 0.5 M solution of zirconium basic carbonate (MEL Chemicals) in 1 l of a 1:1 HCl:distilled H_2O mixture by the addition of a 35% ammonia solution until pH 10 was achieved. The resultant precipitate was then filtered, washed with 4×1 l of distilled water and dried at 110°C overnight. Molybdenum oxide doping was performed using appropriate amounts of ammonium heptamolybdate tetrahydrate (Aldrich, 98%) in distilled water (0.445 ml g^{-1} $Zr(OH)_4$) to obtain loadings corresponding to 2, 5 and 10 wt.% MoO_3/ZrO_2. The samples were dried at 110°C overnight prior to calcination in static air at 800°C for 12 h. EDAX yielded Mo/Zr ratios of 0.13, 0.14 and 0.15 for the 2, 5 and 10 wt.% samples, respectively. ZrO_2 was prepared by calcination of zirconium hydroxide at 800°C for 12 h in static air. MoO_3 (Aldrich, 99.5%) was calcined at 800°C for 12 h in static air. Sulphated zirconia was prepared by calcining sulphated zirconium hydroxide (MEL Chemicals) at 800°C for 12 h in static air.

$Zr_xCe_{1-x}O_2$ was prepared as follows: 4 g of zirconium basic carbonate (MEL Chemicals) and 12 g of cerium carbonate (Aldrich, 99.9%) were added to a 1:1 solution of nitric acid (Fisons) in distilled water whilst stirring. A 35% ammonia solution was then added to form a purple coloured precipitate at pH 10. The precipitate was then filtered, washed with 4×1 l of distilled water and dried in an oven at 110°C overnight. It was then calcined at 925°C for 12 h in static air.

CeO_2/ZrO_2 was prepared as follows: A solution of 1.2 g of zirconium basic carbonate (MEL Chemicals) and 11 g of cerium carbonate (Aldrich, 99%) was prepared in 700 ml of a 1:1 ratio of distilled water and hydrochloric acid (Fisons). This solution was slowly added to 1.5 l of ammonia solution (Philip Harris 35% NH_3) to precipitate the product at pH 10. Fifty ml of hydrogen peroxide (Fisons 100 volumes) was then added to this solution. The precipitate was then filtered and washed with 4×1 l of distilled water and dried in an oven at 110°C overnight, prior to calcination at 800°C for 12 h in static air.

Fe_2O_3 (Aldrich, 99%) was calcined at 800°C for 12 h in static air.

$SO_4{}^{2-}/Fe_2O_3$ was prepared via goethite as follows: 100 ml of a 1 M solution of iron(III) nitrate nonahydrate (Avocado, 98+%), prepared using distilled water, was added to a polythene screw top bottle. To this, 180 ml of a 5 M sodium hydroxide solution was added with stirring. This solution was then diluted to 500 ml with distilled water and aged in an oven at 70°C for 60 h. The resultant yellow precipitate was then filtered, washed with distilled water and dried in a vacuum oven for two days. X-ray diffraction analysis indicated the resultant material to be goethite (JCPDS 29-713). Two grams of this material was sulphated by immersion in 30 ml of a 0.5 M sulphuric acid for 30 min, following which the suspension was filtered and the filtrate was dried in an oven at 110°C overnight. The sample was then calcined at 550°C for 3 h and at 800°C for a further 12 h in static air.

CuO (Aldrich, 99%) was calcined at 800°C for 12 h in static air.

Platinum doping of samples was achieved using the wet impregnation of hexachloroplatinic acid (Aldrich 8 wt.% aqueous solution of Pt) corresponding to a 0.5 wt.% loading of Pt. The samples were then dried at 110°C overnight and were calcined in a 100 ml min^{-1} flow of helium (Air Products, 99.999%) at 300°C for 3 h prior to activity testing.

All materials were pelleted and sieved to yield 0.6–1.0 mm particles prior to activity testing. The surface areas prior to reaction of the materials tested are reported in Table 1.

2.2. Catalyst testing

Catalyst performance was evaluated in a fixed-bed microreactor. A stainless steel jacketed quartz reactor tube was used in which 0.75 ml of catalyst was held centrally within heated zone of a furnace between quartz wool plugs. Methane (Air Products, 99%), oxygen (Air Products, 99.6%) and helium (Air Products, 99.999%) were flowed over catalysts in the ratio 10:40:250 ml min^{-1} to give a GHSV of $\sim$24000 h^{-1} using Brooks 5850TR mass-flow controllers. All lines

Table 1
Catalyst surface areas

Material	Surface area ($m^2\,g^{-1}$)
ZrO_2	17
SO_4^{2-}/ZrO_2	17
2 wt.% MoO_3/ZrO_2	26
5 wt.% MoO_3/ZrO_2	33
10 wt.% MoO_3/ZrO_2	48
MoO_3	9
$Zr_xCe_{1-x}O_2$	27
10 wt.% CeO_2/ZrO_2	16
Fe_2O_3	5
CuO	2
0.5 wt.% Pt/ZrO_2	17
0.5 wt.% $Pt/SO_4^{2-}/ZrO_2$	17
0.5 wt.% Pt/5 wt.% MoO_3/ZrO_2	33
0.5 wt.% Pt/Fe_2O_3	5

downstream of the reactor were trace heated to a temperature in excess of 150°C to prevent condensation of products. Analysis was performed on-line using a Varian Saturn GCMS equipped with a thermal conductivity detector. Megabore Poraplot GS-Q and Megabore Molesieve columns were used to affect the separation.

In all cases, the reactor was allowed to stabilise for 1 h under the conditions reported and the results are the mean of three analyses made at steady state. Unless otherwise stated, the carbon balances of data reported were 100±3%. Methane conversion has been calculated on the basis of the difference in inlet and outlet concentration.

2.3. Catalyst characterisation

Surface areas were determined by application of the BET method to nitrogen physisorption isotherms determined at liquid nitrogen temperature.

3. Results and discussion

Fig. 1 presents the mass normalised oxidation activities at 800°C of the materials studied. With the exceptions of 10 wt.% MoO_3/ZrO_2 which showed a 30% selectivity to carbon monoxide, 2 wt.% MoO_3/ZrO_2 which gave a poor carbon balance and for which there is evidence for the formation of a carbonaceous deposit during reaction, and ZrO_2 where no activity was measured, the selectivity to carbon dioxide for all materials was total. A number of interesting features are evident in the data set.

3.1. Non-Pt doped samples.

In the case of ZrO_2 based materials, it can be clearly seen that both the sulphation and molybdation procedures adopted to promote "superacidity" also have the effect of enhancing the methane oxidation performance. This is perhaps not surprising in view of the fact that such modifications are well known to promote reactions involving hydrocarbon activation which is generally the rate determining step in combustion. Although sulphate is a promoter, the effect of molybdation is more marked and the comparative activities of bare ZrO_2 and MoO_3 reveal this to be a synergistic effect. As we have previously reported, there is a very strong influence of MoO_3 content on combustion activity, the activity being highest at the intermediate loading studied [12]. We have related this to a greater ease of reduction of molybdenum containing species on the monoclinic phase of zirconia and have tentatively suggested that the active form of the catalyst consists of a MoO_3 monolayer species.

Enhanced methane oxidation activity due to electrophilic activation associated with the generation of "superacidic" sites seems an unlikely explanation for the influence of sulphate and molybdate modifications on ZrO_2. The consensus is increasingly emerging that the remarkable catalytic properties of SO_4^{2-}/ZrO_2 do not relate to very strong acidity [13], but possibly to an oxidation function which has implications in terms of our observed efficacy of such materials for oxidation reactions.

The inclusion of ceria in zirconia based catalysts, which is known to significantly modify their oxidation behaviour, also enhances the combustion activity, although at the levels used to a lesser extent than the addition of 5 wt.% MoO_3, which shows the greatest mass normalised activity of any of the non-platinum doped samples investigated. In the case of the reverse material, the more cerium rich $Zr_xCe_{1-x}O_2$, the activity is lower which is both disappointing and surprising in view of previous literature reports of the high efficacy of these materials for methane combustion [8]. We are currently not sure as to the origin of the differences between the studies, although it is

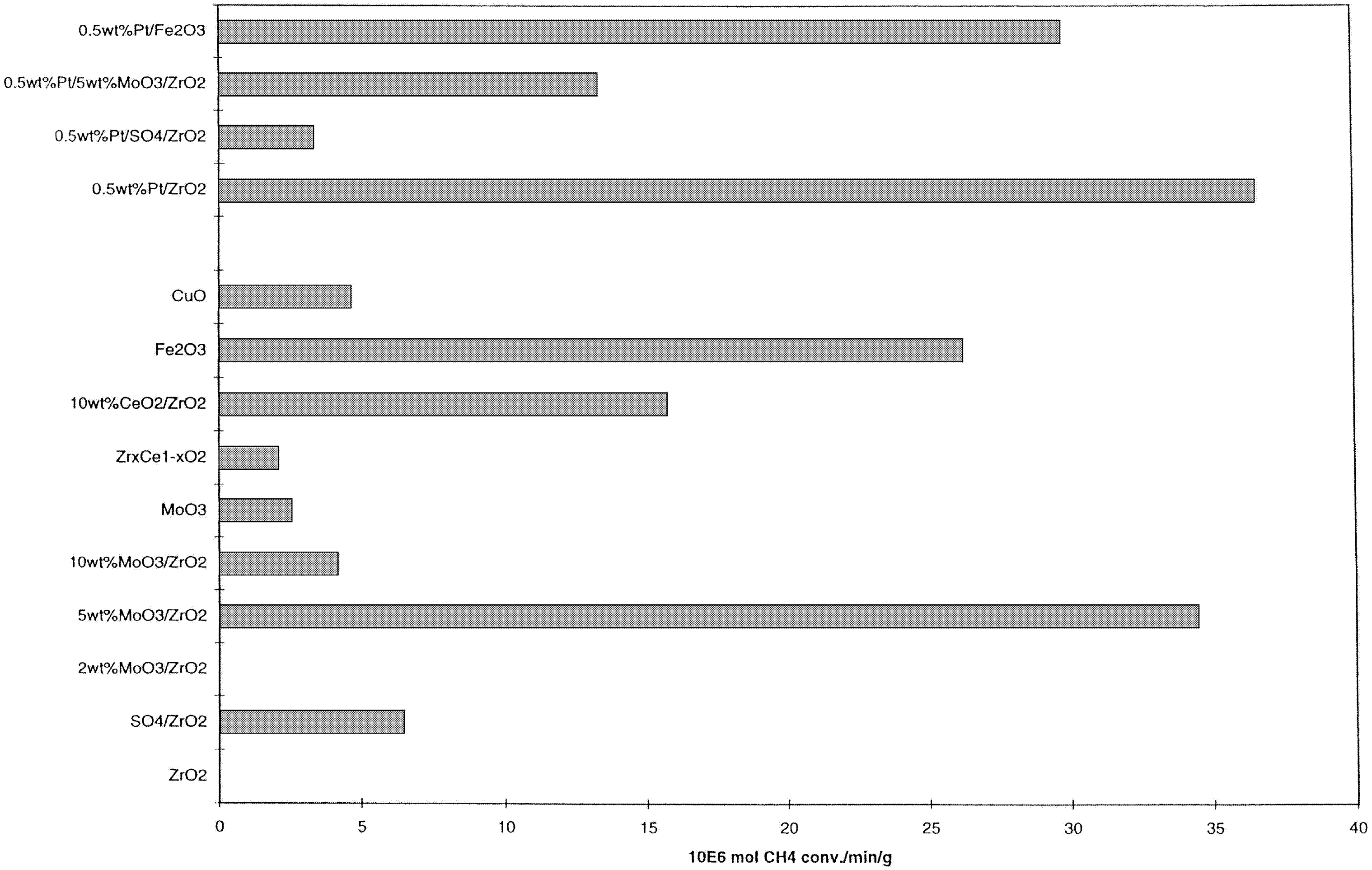

Fig. 1. Mass normalised methane conversion at 800°C.

possible that the composition of the two sets of materials differs.

Fe_2O_3 has also been studied and compares favourably with the majority of the non-platinum doped materials. In terms of its stability, McCarty et al. [14] have suggested that it is a suitable methane combustion catalyst. However, unlike ZrO_2, its activity is poisoned by sulphation. Forms of sulphur are well known poisons of catalytic activity [15], and it is possible that the effect observed here originates by a site blocking mechanism in which sulphate reduces the intrinsically higher activity of iron oxide. This suggestion is supported by the data shown in Fig. 2, which demonstrates that the surface area normalised activity is also reduced by sulphation. In previous studies of methane oxidation performed at higher pressure and with a different feed ratio [11], we have reported that sulphation retards lower temperature ($<400°C$) total oxidation activity of iron oxides prepared from different routes, although at higher temperature (i.e. up to 500°C) the overall activity is enhanced by the formation of new types of active site. CuO, which has been well studied as a methane combustion catalyst and which is reported to display very high activity [16], has been included in this study for purposes of comparison. Although it can be seen in Fig. 1 that the activity is lower than many of the other materials studied, surface area normalisation (Fig. 2) shows that this material is second only to Fe_2O_3 amongst the non-promoted samples, suggesting that provided a high enough dispersion can be maintained, this material would be superior in performance to the majority of oxides investigated in this study.

3.2. Pt doped samples

Some of the oxides have been modified by the addition of 0.5 wt.% Pt. Although Pd is often the noble metal of choice for methane combustion [3], the effect of Pt has been studied, because it has been shown to strongly enhance the “superacidic” properties of sulphated zirconia catalysts [17,18] and the combination of sulphate species with Pt particles on the surface of alumina supported catalysts has been proposed to be of significance for the origin of sulphur dioxide promotion of propane oxidation in Pt/Al_2O_3 systems [19–22]. On inspection of the data, it is apparent that the addition of Pt has two general effects — either enhancement or suppression of activity depending upon the nature of the system. In the case of the base oxides, i.e. those which have not been modified to generate “superacidic” behaviour, Pt is found to enhance the activity. Indeed, ZrO_2 which does not show any activity under our conditions, is promoted by the presence of Pt and becomes best overall in our data set in terms of mass normalised activity. A promotional effect on the activity of iron oxide is also observed, although it is to a much smaller degree than in the case of zirconia. However, surprisingly, Pt addition has a detrimental effect on the activity of the molybdated or sulphated zirconias. The reason for the apparent paradox is at present not clear, although a possible explanation relates to differences in the oxidation state of the Pt in the different zirconia based systems. There is currently some controversy as to the active form of noble metals for combustion, with some authors favouring zero valent forms [23,24] whilst others suggest oxidic forms of the metal to be active [9,25,26].

Although, we would expect the platinum to be in the zero valent state under the conditions of our experiments (i.e. at 800°C), studies of platinum sulphated zirconia systems pre-treated at lower temperatures suggest that metal support interactions modify the Pt reduction characteristics, with contradictory evidence being presented for greater ease of reduction [27], stabilisation of higher oxidation state [28] and the formation of platinum with chemisorbed sulphur species [29]. Without additional characterisational studies, it is difficult for us to definitively differentiate between these suggestions. However, Pt present in the base oxides would generally be expected to be in the zero valent state, at least initially, under the conditions of our experiments, whilst it seems that in the case of “superacidic” materials Pt addition has removed some of the sites originally active for combustion. A plausible explanation for this may be that higher oxidation states of Pt are stabilised in these systems and that inactive phase formation between the Pt moieties and sulphate and molybdate promoters occurs under the conditions of our studies. Poisoning of activity by the co-products of hexachloroplatinic acid decomposition also cannot be ruled out.

Surface area normalisation, which allows direct comparison of the relative activity of catalysts independently of the influence of varying surface area,

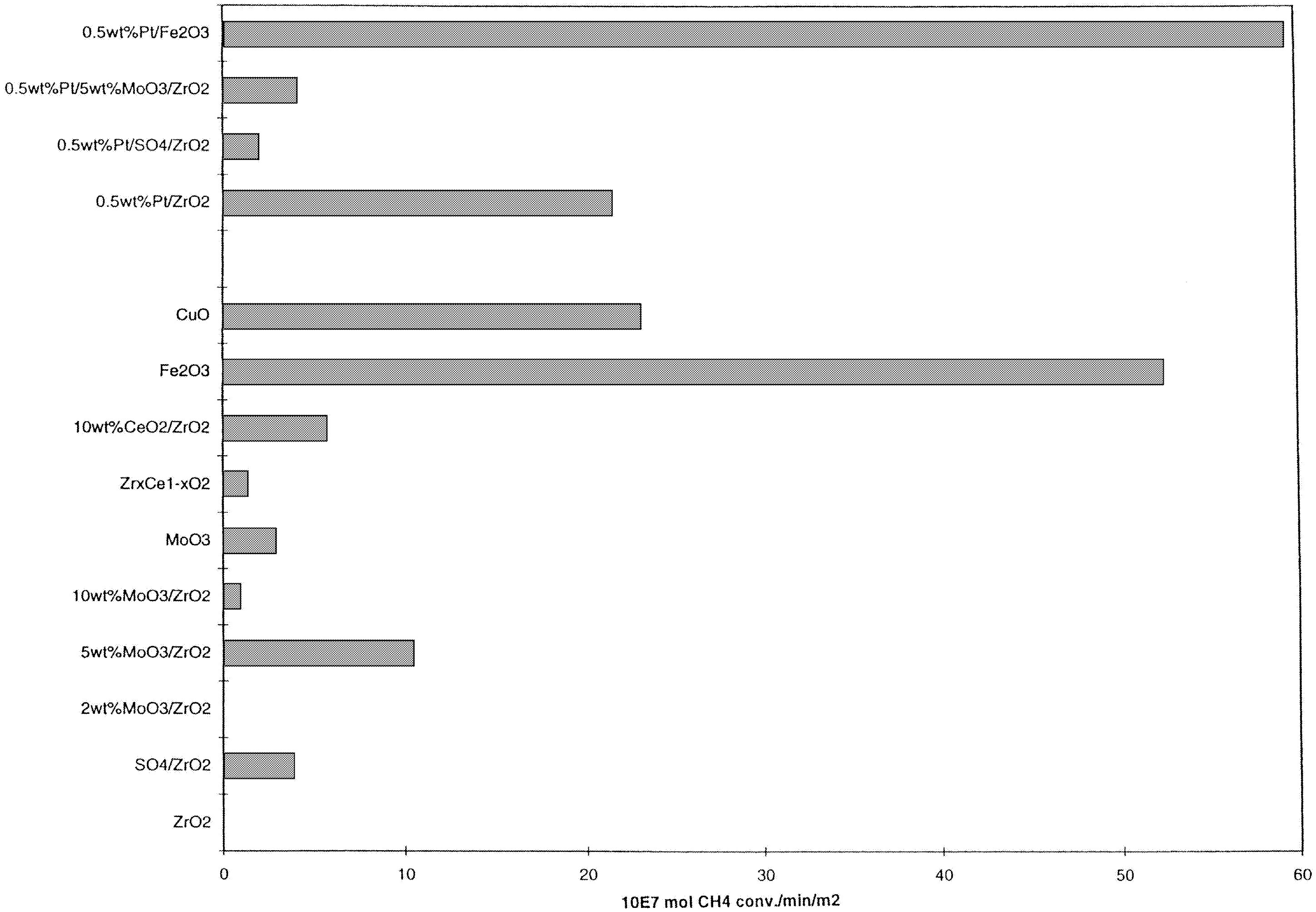

Fig. 2. Surface area normalised methane conversion at 800°C.

has been performed on the data set and the results are shown in Fig. 2. It is apparent that the intrinsic activity of the base oxides Fe_2O_3 and CuO, and Pt doped Fe_2O_3 and ZrO_2 are clearly much higher than the "superacidic" materials, the activity of which is poisoned by Pt addition. However, as the surface areas of our materials is likely to be representative of those used in practice, the present study does show that zirconia catalysts modified so as to enhance their "superacidic" properties, particularly by molybdation, are candidates worthy of further study for methane combustion.

Acknowledgements

We gratefully acknowledge MEL Chemicals for kindly providing some of the materials used in this study. In particular, we wish to thank Mr. Colin Norman and Drs. Peter Moles and Gary Monks.

References

[1] D.L. Trimm, Appl. Catal. 7 (1983) 249.
[2] M.F.M. Zwinkels, S.G. Jaras, P.G. Menon, Catal. Rev. Sci. Eng. 35 (1993) 319.
[3] J.W. Geus (Ed.), Catal. Today, Vol. 47, No. 1.
[4] D. Ferri, L. Forni, Appl. Catal. B 16 (1998) 119.
[5] G. Groppi, M. Bellatto, C. Cristiani, P. Forzatti, P.L. Villa, Appl. Catal. A 104 (1993) 101.
[6] M. Machida, E. Eguchi, H. Arai, J. Catal. 120 (1989) 377.
[7] M. Lyubovsky, L. Pfefferle, Appl. Catal. A 173 (1998) 107.
[8] F. Zanar, A. Trovarelli, C. de Leitenburg, G. Dolcetti, J. Chem. Soc., Chem. Commun. (1995) 965.
[9] A. Primavera, A. Trovarelli, C. de Leitenburg, G. Dolcetti, J. Llorca, Stud. Surf. Sci. Catal. 119 (1998) 87.
[10] C.-Y. Hsu, C.R. Heimbuch, C.T. Armes, B.C. Gates, J. Chem. Soc., Chem. Commun. (1992) 1645.
[11] A.S.C. Brown, J.S.J. Hargreaves, B. Rijniersce, Catal. Lett. 53 (1998) 7.
[12] A.S.C. Brown, J.S.J. Hargreaves, S.H. Taylor, Catal. Lett. 57 (1999) 109.
[13] A.S.C. Brown, J.S.J. Hargreaves, Green Chem. 1 (1999) 17 and references therein.
[14] J.G. McCarty, M. Gusman, D.M. Lowe, D.L. Hildebrand, K.N. Lau, Catal. Today 47 (1999) 5.
[15] M.V. Twigg (Ed.), Catalyst Handbook, Wolfe, Frome, UK, 1989.
[16] P. Artizzu, E. Garbowski, M. Primet, Y. Brulle, J. Saint-Just, Catal. Today 47 (1999) 83.
[17] M. Hino, K. Arata, J. Chem. Soc., Chem. Commun. (1995) 789.
[18] M. Hino, K. Arata, Catal. Lett. 30 (1995) 25.
[19] H.C. Yao, H.K. Stepien, H.S. Ghandi, J. Catal. 67 (1981) 231.
[20] G.P. Ansell, S.E. Golunski, H.A. Hatcher, R.R. Rajaram, Catal. Lett. 11 (1991) 183.
[21] K. Wilson, C. Hardacre, R.M. Lambert, J. Phys. Chem. 99 (1995) 13755.
[22] R. Burch, E. Halpin, M. Hayes, K. Ruth, J.A. Sullivan, Appl. Catal. B 19 (1998) 199.
[23] S.H. Oh, P.J. Mitchell, R.M. Siewert, J. Catal. 132 (1991) 287.
[24] M. Lyubovsky, L. Pfefferle, Catal. Today 47 (1999) 29.
[25] R. Burch, F.J. Urbano, Appl. Catal. A 124 (1995) 121.
[26] R.J. Farrauto, J.K. Lampert, M.C. Hobson, E.M. Waterman, Appl. Catal. B 6 (1995) 263.
[27] A. Sayari, A. Dicko, J. Catal. 145 (1994) 561.
[28] J.C. Yori, M.A. D'Amato, G. Costa, J.M. Parera, J. Catal. 153 (1995) 218.
[29] Z. Paal, M. Muhler, R. Schlogl, J. Catal. 143 (1993) 318.