

Support-mediated alkane activation over Pt–SO₄/Al₂O₃ catalysts

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Sulphate-promoted alkane combustion has been investigated over a series of Pt/Al₂O₃ catalysts using pre-sulphated alumina supports. Catalyst sulphation greatly enhanced ethane combustion over Pt/Al₂O₃, and also improved methane and propane light-off performance. Catalyst activity increased with Pt loading, however the magnitude of sulphate promotion was independent of Pt loading under oxidising conditions, but scaled with alkane chain length. Propane combustion activity was directly proportional to the surface coverage of aluminium sulphate sites; support-mediated alkane activation is the dominant process in sulphate promotion.

KEY WORDS: catalysis; platinum; alumina; oxidation; sulphate; alkane; ethane.

1. Introduction

The development of catalytic materials for the efficient combustion of light alkanes is of fundamental importance for automotive pollution control, and control of emissions produced from bio-fuel combustion [1,2]. While there are many detailed studies of methane and propane (for reviews see [3–5]) oxidation kinetics over supported platinum group metals (PGM), there are fewer investigations focussed on ethane combustion [6–12].

The rate-limiting activation step in alkane combustion is determined by the energy required to cleave the weakest C–H bond. Thus the relative reactivity would be expected to follow the order methane < ethane < propane, in accord with their respective C–H bond energies of 440, 420 and 401 kJ mol^{–1}. Indeed over PGM foils [13], the combustion light-off temperature for C₁–C₄ alkanes follows this trend, with the activation energy for combustion of >C₄ alkanes observed to be invariant of chain length [10]. In addition under fuel-lean conditions enhanced combustion activity is also correlated with low metal–oxygen bond strength with light off temperatures observed to increase from Pt < Pd < Rh < Ir. The optimum air fuel ratio thus depends on the relative sticking probability of O₂ and the corresponding alkane.

A recent study of sol–gel prepared Pt/Al₂O₃ catalysts has shown enhanced ethane combustion occurs over larger metallic Pt crystallites [12], which is in accord with trends observed for methane [14], and propane [15] combustion where higher catalytic activity is observed when the metallic phase prevails. Ethane combustion has largely been studied in conjunction with methane for control of emissions from Natural Gas Vehicles, and has

concentrated on the use of Pd based catalysts, which are more active than Pt in methane oxidation under air:fuel ratios typically employed, but also prone to sulphur poisoning [16].

Since the original report of SO₂-promoted propane combustion over Pt/Al₂O₃ [17] this phenomenon has been explored over both dispersed Pt catalysts [18–21] and model single-crystal systems [22–24]. However catalyst sulphation (*ex situ* or *in situ*) affects numerous physico-chemical changes, including the Pt oxidation state/particle size [25], Pt dispersion [20] and the support crystallinity [18,9,25] and porosity [25], hence various models have been advanced to explain this promotion. To date there have been no systematic efforts to isolate the respective roles of support and metal, and in particular identify which plays the dominant factor in sulphate-promoted alkane combustion. Here we address these issues using a range of well-defined Pt/SO₄–Al₂O₃ catalysts, and report the first observation of sulphate-promoted ethane combustion.

2. Experimental

2.1. Catalyst preparation

Sulphated aluminas were prepared by incipient wetness impregnation of 1 g of γ -Al₂O₃ (Degussa Aluminium Oxide C) with a 10 cm³ solution of 0.01–2.5 M H₂SO₄ (Fisher 98%). The resultant slurry was dried at 80 °C in air for 12 h and then calcined in flowing O₂ at 550 °C for 3 h. Samples were subsequently stored in air. Platinum was added *via* the incipient wetness technique using 1 cm³ of (NH₄)₄PtCl₂ (Johnson Matthey, 55.24 wt% Pt assay) as an aqueous solution per gram of support. The resultant paste was air-dried at 80 °C for 12 h and then calcined in flowing O₂ at 500 °C for 2 h. Catalysts were then reduced in flowing H₂ at 400 °C for 2 h.

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2.2. Catalyst characterisation

Porosity and surface area measurements were performed following the N₂ adsorption on a Micromeritics ASAP 2010 instrument. Surface areas were calculated using the BET equation over the pressure range $P/P_0 = 0.02$ – 0.2 , where a linear relationship was maintained. The final sulphur content was determined by elemental analysis using a Carlo Erba 1108 CHN/S instrument (quoted percentages refer to total S levels). Pt loadings were measured using a Perkin-Elmer P40 emission ICP-MS instrument. XRD spectra were acquired using a Siemens D5000 diffractometer and CuK α radiation. S 2p XP spectra were also measured using a Kratos AXIS HSi instrument, equipped with charge neutraliser and MgK α X-ray source, to identify the S species present in the final fresh catalysts. Two point energy referencing was employed using adventitious carbon at 285 eV and the valence band, and in all instances only SO₄ groups were observed with a characteristic binding energy of 170 eV.

2.3. Catalyst testing

Catalyst testing was performed in a fixed-bed quartz reactor using 100 mg catalyst. The total gas flow rate was 21 cm³ min⁻¹ and stoichiometric mixtures were employed using 1 cm³ min⁻¹ of alkane together with the appropriate oxygen flow with helium added as an inert diluent. This equated to gas mixes of 5 vol% HC and 10–25 vol% O₂ in He. Gases used were CH₄ (E&W 99.995%), C₂H₆ (E&W 99.5%) and C₃H₈ (E&W 99.9%). Light-off measurements were performed with a ramp rate of 5 °C min⁻¹ with the catalyst bed temperature measured with a coaxial thermocouple. Reaction was monitored on-line using a VG 200 amu quadrupole mass spectrometer. The sole reaction products were CO, CO₂ and H₂O. The systematic error in conversion was $\pm 2\%$. Blank runs showed negligible gas-phase contributions to alkane combustion below 700 °C.

3. Results and discussion

The effect of sulphate on alkane combustion was first investigated using Pt-doped catalysts prepared from a SO₄/Al₂O₃ support pre-sulphated with 0.1 M H₂SO₄. Figure 1a compares the resulting light-off curves for methane, ethane and propane combustion over sulphated and unsulphated 0.05 wt% Pt/Al₂O₃. The alkane light-off temperatures decrease in the order propane < ethane < methane over the unsulphated catalyst as expected; C–H bond activation is widely accepted as rate-limiting in alkane oxidation over Pt/Al₂O₃. Alkane combustion is sensitive to both metal dispersion and reaction conditions, and consequently literature T₅₀ values span a wide range. Our light-off temperatures are in good agreement with those reported for propane [19],

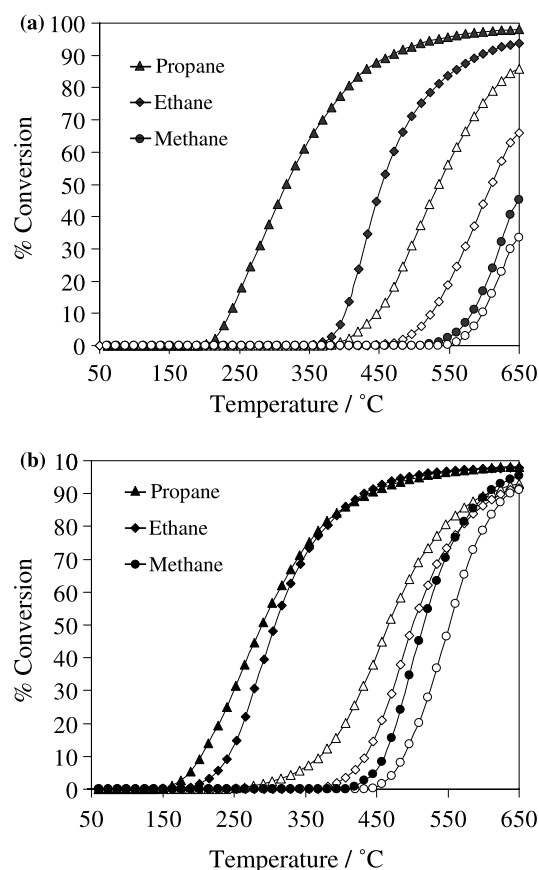


Figure 1. (a) Light-off curves for C1–C3 alkanes over 0.05 wt% Pt/Al₂O₃ and Pt-SO₄/Al₂O₃ catalysts. (●) Alumina pre-sulphated with 0.1 M H₂SO₄; (○) unsulphated alumina. (b) Light-off curves for C1–C3 alkanes over 5 wt% Pt/Al₂O₃ and Pt-SO₄/Al₂O₃ catalysts. Alumina pre-sulphated by 0.1 M H₂SO₄; (●) alumina pre-sulphated with 0.1 M H₂SO₄; (○) unsulphated alumina.

ethane [18] and methane [8] under fuel-lean conditions. Apparent activation energies derived over the kinetic (low conversion) regime are also in accord with previous estimates (table 1). These show a progressive rise in E_{act} with chain length, supporting C–H cleavage as the rate-limiting step.

Alumina pre-sulphation reduced the light-off temperature for *all light alkanes*, with the magnitude of

Table 1
Kinetic parameters for alkane combustion over a 0.05 wt% Pt/Al₂O₃ catalyst^a

Alkane	ΔE_{act} (± 2 kJ mol ⁻¹)		ln A	
	Fresh	Sulphated ^b	Fresh	Sulphated ^b
Methane	217	209	17.7	17.8
Ethane	108	115	13.6	15.9
Propane	78	79	9.7	14.8

^aReaction conditions: 100 mg catalyst with 5 vol% alkane under a stoichiometric air : fuel mix.

^bA 0.1 M H₂SO₄ impregnated SO₄/Al₂O₃ support (containing 2.5 wt% S) was used.

promotion increasing dramatically from methane to ethane, while ethane and propane exhibited similar enhancements of 178 and 153 °C respectively. This represents the first literature report of sulphate-promoted ethane combustion; previous studies have focused on enhanced propane combustion. Propane light-off is variously reported as lowered by between 50 and 250 °C over Pt/Al₂O₃ catalysts [18–21], consistent with our value of 178 °C, however no systematic correlations between catalyst structure, reaction conditions and degree of promotion have yet been identified. The only previous report of sulphate (SO₂) promoted methane combustion by Meeyoo *et al.* [26], over a Pt/Al₂O₃ cordierite monolith, noted a reduction of ~30 °C, in accord with our observation.

Activation energies over unsulphated Pt/Al₂O₃ are in good agreement with those reported for methane [8,14,15], ethane [8,27] and propane [8,18,20] combustion over Pt for which typical literature values range between 113–146, 80–114 and 71–104 kJ mol⁻¹ respectively. Catalyst pre-sulphation had little effect on these activation barriers (table 1) in accord with an earlier report by Hubbard *et al.* [18] on SO₂ promoted propane combustion, but contrary to that of Burch *et al.* [20] who noted an increase in E_{act} from 78.5 to 129 kJ mol⁻¹ following high temperature sulphation under heavily oxidising conditions. The similar apparent activation energies are compensated by greatly increased pre-exponential factors. This suggests alkane oxidation proceeds *via* a common reaction pathway over both fresh and sulphated Pt/Al₂O₃, with sulphation generating a vast number of new surface sites active towards C–H activation.

We have previously shown that sulphate enhances the dissociative sticking probability of alkanes over model Pt{111}/Al₂O₃ single-crystal surfaces *via* propylsulphate formation [23], with the enhancement directly correlated with interfacial sulphate formation. Such alkylsulphate intermediates may provide a general alternative low energy pathway to C–H bond activation. This hypothesis is supported by observations which show SO₂ does not enhance combustion of long chain alkanes (e.g., hexane) [5] which have intrinsically higher sticking probabilities over platinum surfaces.

In line with the documented structure sensitivity of alkane combustion over unsulphated Pt/Al₂O₃ catalysts [15], the light-off temperatures for all alkanes decreased with increasing Pt loading (figure 1b). In contrast the magnitude of sulphate promotion for methane, ethane and propane was loading invariant, as shown in figure 2, and clearly exerts a greater influence on alkane light-off than achievable through varying metal loading alone over a pure alumina support. This is particularly significant as it suggests that *support-mediated chemistry plays the dominant role in sulphate-promotion*.

In order to explore this hypothesis a series of catalysts with a common 0.05 wt% Pt loading were prepared from Al₂O₃ supports pre-sulphated with H₂SO₄ of

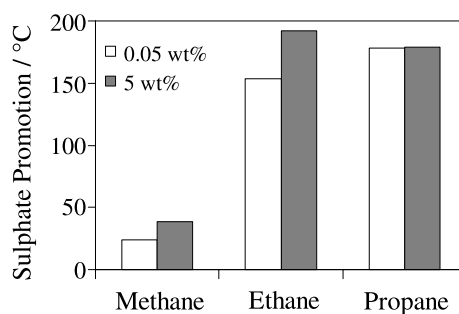


Figure 2. Magnitude of SO₄ promotion for 0.05 and 5 wt% Pt/Al₂O₃ catalysts in C1–C3 alkane combustion.

varying molarity between 0.01 and 2.5 M. Elemental and surface analysis (S 2p XP spectra) confirm that increasing the concentration of impregnating solution results in progressive S incorporation into the alumina surface (figure 3), with a small bulk contribution for strong acids. The S 2p oxidation state and DRIFTS measurements (not shown) confirm the presence of surface SO₄ species. Figure 4 shows the resulting light-off curves for propane combustion under stoichiometric conditions. The T₅₀ values are a strong function of alumina pre-sulphation, falling progressively with increasing H₂SO₄ concentration to reach a minimum of 390 °C for 0.1 M impregnated alumina. Higher acid molarities actually reverse this trend, i.e. afford less promotion, with the propane T₅₀ light-off attaining 420 °C for 2.5 M H₂SO₄.

This variation in alkane activation performance with support pre-sulphation is fully explicable in terms of the accompanying morphological changes. The surface areas of sulphated aluminas shown in figure 5 remain essentially constant ~130 m² g⁻¹ for H₂SO₄ concentrations below 0.1 M. However further increases in acidity produce a continuous and dramatic fall in area down to 13 m² g⁻¹ for 2.5 M H₂SO₄. This decrease reflects S incorporation into the alumina bulk and corresponding support crystallisation, evidenced by the emergence of

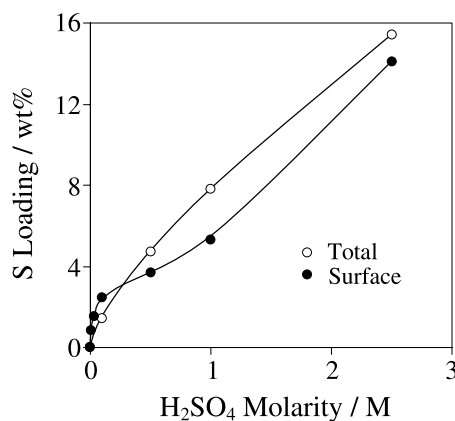


Figure 3. Bulk and surface S content of 0.05 wt% Pt-SO₄/Al₂O₃ catalysts as a function of H₂SO₄ impregnating solution molarity.

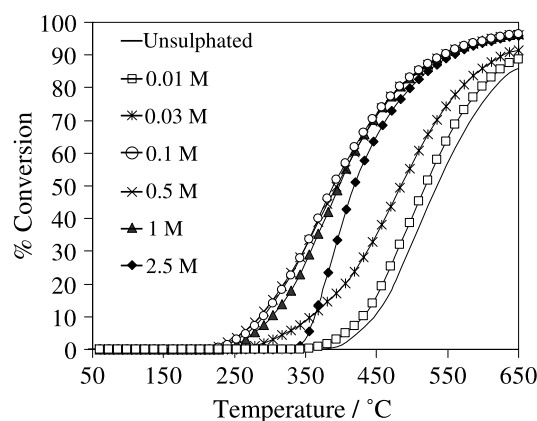


Figure 4. Propane light-off curves over 0.05 wt% Pt-SO₄/Al₂O₃ catalysts as a function of support presulphation.

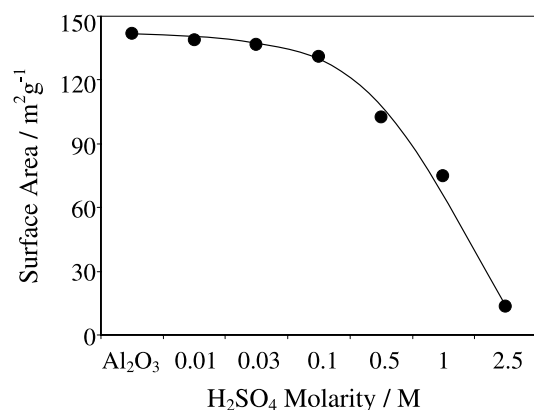


Figure 5. BET surface areas of SO₄/Al₂O₃ supports as a function of support pre-sulphation.

aluminium sulphate X-ray diffraction features [28], figure 6. Crystallisation affects the light-off profile of the most heavily sulphated sample which is much sharper than for all lower loadings; indeed the activation barrier rises from a constant value of $\sim 79 \pm 2 \text{ kJ mol}^{-1}$ for 0.1–1 M SO₄/Al₂O₃ to over $112 \pm 2 \text{ kJ mol}^{-1}$ for the 2.5 M SO₄/Al₂O₃. This increased activation energy is consistent with the observation of Burch *et al.* [20], and compensated by a greatly increased pre-exponential factor, presumably reflecting the formation of vast numbers of new, but low activity, crystalline aluminium sulphate sites. Pure aluminium sulphate is catalytically inert for propane combustion.

It is important to note that these support transformations are unaffected by subsequent Pt doping; perhaps unsurprising since the associated metal calcination/reduction steps involve lower temperatures than those employed during support pre-sulphation. Increasing the degree of alumina sulphation above 3 wt% (0.1 M H₂SO₄) is thus accompanied by a decrease in the overall support surface area. Figure 7 compares the total accessible surface sulphate and the corresponding propane T₅₀ light-off values. This plot shows a remark-

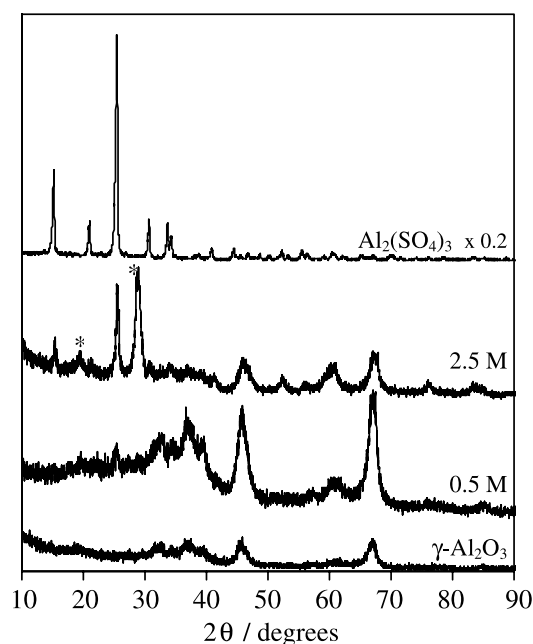


Figure 6. X-ray diffractograms of SO₄/Al₂O₃ supports as a function of support pre-sulphation. Anhydrous Al₂(SO₄)₃ is shown for comparison while additional peaks due to Al₂(SO₄)₃ · 14H₂O and Al₂(SO₄)₃ · H₂O are also indicated (*).

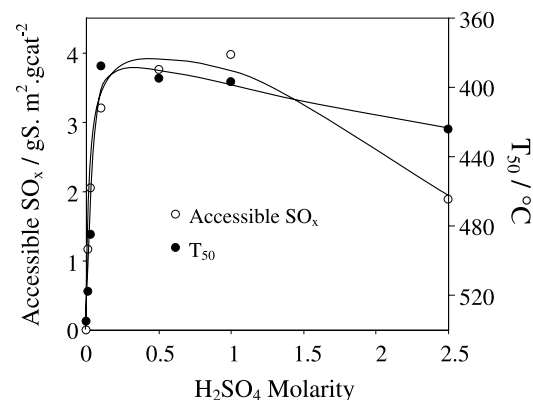


Figure 7. Propane T₅₀ light-off values for 0.05 wt% Pt-SO₄/Al₂O₃ as a function of accessible alumina surface sulphate. Accessible sulphate is defined as the product of the surface S loading (g S g cat⁻¹) × surface area (m² g⁻¹).

able correlation between these structural and reaction parameters, which both pass through a maximum for ~ 0.1 – $0.5 \text{ M H}_2\text{SO}_4$. For the first time we are able to demonstrate the degree of *alumina surface sulphation* plays a crucial role in the subsequent overall catalyst alkane activation performance, irrespective of Pt morphology/oxidation state.

Although these measurements were performed under stoichiometric reaction conditions this phenomenon appears general over a wide range of reactant compositions. Indeed, the magnitude of support-mediated, sulphate-promoted propane combustion increased by a further 45 °C when using the 0.1 M H₂SO₄ pretreated

alumina under fuel-lean operation. This additional enhancement probably arises from complete oxidation of SO_x species at defective alumina sites and inhibited SO₄ reduction to site-blocking S adatoms over Pt sites.

The use of pre-sulphated Al₂O₃ supports has facilitated greater control over the degree of catalyst sulphation and allowed separation of sulphate-induced changes to the support from those associated with dispersed Pt clusters. The magnitude of sulphate-promoted propane combustion correlates with the coverage of surface aluminium sulphate groups, but is roughly independent of the number of Pt sites. Such findings are in excellent agreement with earlier model studies over a Al₂O₃/Pt{111} single-crystal catalyst [23] which, in the absence of particle-size effects, unequivocally identified interfacial SO_x as responsible for C–H activation. This is an interesting phenomenon that bridges both the structure and pressure gap in heterogeneous catalysis. Although our previous studies of SO₄ on Pt{111} evince direct propane activation is possible over metal sites alone [22], the low coverage ($\theta_{\text{SO}_4} = 0.25$ ML) and thermal stability of such species, which decompose >230 °C, suggests this is a minor pathway. Thus we propose the promotional mechanism involves C–H activation and concomitant alkyl-sulphate formation across the sulphated alumina support [29]. Alkyl-sulphate intermediates generated at the periphery of Pt clusters spillover hydrocarbon fragments onto bare metal sites where they are subsequently oxidised (scheme 1).

4. Conclusions

The phenomenon of sulphate-promoted combustion over Pt/Al₂O₃ catalysts extends across C1–C3 alkanes, with the magnitude increasing with chain length but independent of Pt loading under lean conditions. Similar apparent activation barriers suggest a common rate-limiting step, i.e. C–H bond scission in alkane combustion over untreated and sulphated Pt/Al₂O₃. Alumina pre-sulphation by simple wet impregnation affords an efficient means of tuning the support surface sulphate coverage. The degree of promotion (reduced light-off temperature) for propane combustion directly correlates with the number of accessible surface aluminium sulphate sites. This suggests support-mediated effects, *via* alkylsulphate formation, are the dominant factor in sulphate-promoted propane combustion, although spillover of alkyl fragments onto bare metallic Pt sites remains essential for subsequent (fast) oxidation steps.

Acknowledgments

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References

- [1] F. Klingstedt, A.K. Neyestanaki, R. Byggningsbacka, L.E. Lindfors, M. Lunden, M. Petersson, P. Tengstrom, T. Ollonqvist and J. Vayrynen, *Appl. Catal.* 209 (2001) 301.
- [2] J. Carno, M. Berg and S. Jaras, *Fuel* 75 (1996) 959.
- [3] T.V. Choudhary, S. Banerjee and V.R. Choudhary, *Appl. Catal. A* 234 (2002) 1.
- [4] P. Gelin and M. Primet, *Appl. Catal. B* 39 (2002) 1.
- [5] R. Burch and M.J. Hayes, *J. Mol. Cat. A* 100 (1995) 13.
- [6] S. Trautman and M. Baerns, *J. Catal.* 136 (1992) 613.
- [7] A. Pisanu and C.E. Gogola, *Appl. Catal. B* 11 (1996) 137.
- [8] Y-F. Yu Yao, *Ind. Eng. Chem. Prod. Res. Dev.* 19 (1980) 293.
- [9] R. Burch, P.K. Loader and F.J. Urbano, *Catal. Today* 27 (1996) 243.
- [10] A. Schwartz, L.L. Holbrook and H. Wise, *J. Catal.* 21 (1971) 199.
- [11] F.J. Gracia, J.T. Miller, A.J. Kropf and E.E. Wolf, *J. Catal.* 209 (2002) 341.
- [12] L. Khelifi, A. Ghorbel, E. Garbowski and M. Primet, *J. Chim. Phys. PCB* 94 (1997) 2016.
- [13] G. Vesper, M. Ziauddin and L.D. Schmidt, *Catal. Today* 47 (1999) 219.
- [14] R.F. Hicks, H. Qi, M.L. Young and R.G. Lee, *J. Catal.* 12 (1990) 280.
- [15] K. Otto, J.M. Andino and C.L. Parks, *J. Catal.* 131 (1991) 243.
- [16] J.K. Lampert, M.S. Kazi and R.J. Farrauto, *Appl. Catal. B* 14 (1997) 211.
- [17] G. Sadowski and D. Treibmann, *Z. Chem.* 19 (1970), 189.
- [18] C.P. Hubbard, K. Otto, H.S. Ghandi and K.Y.S. Ng, *J. Catal.* 144 (1993) 484.
- [19] H.C. Yao, H.K. Stepien and H.S. Gandhi, *J. Catal.* 67 (1981) 231.
- [20] R. Burch, E. Halpin, M. Hayes, K. Ruth and J.A. Sullivan, *Appl. Catal. B* 19 (1998) 199.
- [21] M. Skoglundh, A. Ljungqvist, M. Petersson, E. Fridell, N. Cruise, O. Augustsson and E. Jobson, *Appl. Catal. B* 30 (2001) 315.
- [22] K. Wilson, C. Hardacre and R.M. Lambert, *J. Phys. Chem.* 99 (1995) 13755.
- [23] K. Wilson, A.F. Lee, C. Hardacre and R.M. Lambert, *J. Phys. Chem. B* 102 (1998) 1736.
- [24] D.E. Gawthrope, K. Wilson and A.F. Lee, *Phys. Chem. Chem. Phys.* 5 (2003) 3299.
- [25] A.F. Lee, K. Wilson, R.M. Lambert, C.P. Hubbard and H.S. Ghandi, *J. Catal.* 184 (1999) 491.
- [26] V. Meeyoo, D.L. Trimm and N.W. Cant, *Appl. Catal. B* 16 (1998) L101.
- [27] L. Hiam, H. Wise and S. Chaiken, *J. Catal.* 10 (1968) 272.
- [28] H. Moselhy, G. Pokol, F. Paulik, M. Arnold, J. Kristóf, K. Tomor, S. Gál and E. Pungor, *J. Therm. Anal.* 39 (1993) 595.
- [29] S.B. Ushko, Z.G. Osipova, V.D. Sokolovskii and S.V. Ketchik, *Kinet. Catal.* 29 (1988) 195.