A study of "superacidic" MoO_3/ZrO_2 catalysts for methane oxidation

A.S.C. Brown [a], J.S.J. Hargreaves [a] and S.H. Taylor [b]

[a] *Catalysis Research Laboratory, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK*
[b] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Cardiff CF1 3TB, UK*

Received 22 September 1998; accepted 18 December 1998

A series of zirconia-supported molybdenum oxide catalysts with different molybdenum loadings prepared using conditions reported to generate "superacidity" have been evaluated for their performance as catalysts for methane oxidation. A marked dependence of Mo content on activity has been observed, with the most active material being that with intermediate molybdenum content. 5 wt% MoO_3/ZrO_2 compares favourably with $Zr_xCe_{1-x}O_2$ for methane combustion. The presence of MoO_3 is observed to stabilise the tetragonal polymorph of ZrO_2 and, as Mo content is increased, dispersed MoO_3 crystallites are formed as evidenced by Raman spectroscopy. Temperature-programmed reduction studies evidence differences in the reduction behaviour of the materials as a function of loading. The results indicate that molybdenum oxide supported on monoclinic zirconia gives rise to the most active catalyst. It is tentatively suggested that the formation of a MoO_3 monolayer during reaction may be of importance.

Keywords: superacid, zirconia, molybdenum oxide, methane, oxidation

1. Introduction

Molybdenum oxide is a component of some of the better selective methane oxidation catalysts [1]. It has been studied both in supported and unsupported form and issues such as structure sensitivity [2], support identity and loading [3,4], molybdenum oxide precursor [5] and the influence of impurities [4] have been addressed in the literature. In the following, we describe our studies of zirconia-supported molybdenum oxide catalysts which have been prepared using conditions reported to generate "superacidity" as evidenced in high efficacy for alkane isomerisation reactions [6]. We thought it of particular interest to investigate these systems, since their apparent high efficacy for alkane activation may lead to highly active catalysts for methane partial oxidation and/or combustion reactions.

To our knowledge, no previous studies of MoO_3-based "superacids" for methane oxidation have been reported in the literature. However, there have been several reports of the application of sulfated metal oxide "superacids" which suggest potential interest. Both Lin and Hsu [7] and Rezgui et al. [8] have reported that sulfated iron manganese zirconia catalyst is effective for the conversion of methane to ethane in the absence of oxidant. Murata et al. [9] have observed that lithium-doped sulfated zirconia is an effective catalyst for the oxidative coupling of methane at 800 °C. The addition of lithium was shown to be of major importance, since sulfation alone had little effect on performance. Some of the present authors have recently reported their studies on sulfated iron oxide catalysts for the partial oxidation of methane [10]. Although sulfation was observed to poison lower-temperature total oxidation activity, it enhanced methane conversion and methanol selectivity at higher temperatures.

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 $Zr(OH)_4$) 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 analysis 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.

Sulfated zirconia was prepared by calcining sulfated 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.

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

All materials were pelleted and sieved to yield 0.6–1.0 mm particles prior to activity testing.

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 in the 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 using Brooks 5850 TR mass-flow controllers. All lines 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.

Two reaction regimes were investigated. In the first, $CH_4:O_2:He$ in the ratio $46:4:12$ ml min^{-1} was flowed over the catalyst at a reaction pressure of 15 bar to yield a GHSV of ∼4600 h^{-1}. Reaction pressure was maintained using an in-line Tescom back-pressure regulator. These conditions are typical of those which we have previously applied in our studies of methane partial oxidation [10]. In the second regime, testing was conducted at ambient pressure using a feed ratio of $CH_4:O_2:He$ of $10:40:250$ ml min^{-1} to give a GHSV of ∼24000 h^{-1}. It is considered that these conditions are more appropriate for the evaluation of methane combustion activity and no background activity was observed in the absence of catalysts.

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. The carbon balances of all data reported were $100 \pm 3\%$.

2.3. Catalyst characterisation

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

Powder X-ray diffraction was performed using a Hiltonbrooks modified Phillips powder diffractometer using Cu K_α radiation operating at 42.5 kV and 18.0 mA. Samples were prepared by compaction into a glass-backed aluminium sample holder and were scanned in the range 5–80° 2θ using a step size of 0.02° and a count rate of 0.5 s/step.

Temperature-programmed reduction was conducted using a flow rate of 40 ml min^{-1} of a 5% hydrogen in argon mixture (Air Products) with a ramp rate of 5 °C/min up to a temperature of 1000 °C. The data reported correspond to a sample mass of 0.26 g for 2 and 5 wt% MoO_3/ZrO_2 and 0.13 g of 10 wt% MoO_3/ZrO_2.

Laser Raman spectroscopy was performed with powder specimens using a Renishaw System 1000 laser Raman microscope. The spectrophotometer was a dispersive mode instrument using an argon ion laser (518 nm), which produces low power and minimises the effects of catalyst heating.

3. Results and discussion

The performance of the MoO_3/ZrO_2 materials for methane oxidation at elevated pressure and low space velocity has been determined and the results are presented in table 1. Their activity is in excess of the background which has been determined using a bed of α-Al_2O_3 chips. Only traces of selective oxidation products (CH_3OH and C_2H_6) were detected at the highest temperature studied. It is apparent that the activity of the 5 wt% MoO_3/ZrO_2 catalyst is generally greater than that of the other two over much of the temperature range investigated. This trend was also evident in the evaluation of catalysts under conditions which favour methane combustion. Figure 1 presents the mass-normalised conversion for a range of materials

Table 1
Methane oxidation performance of MoO_3/ZrO_2 materials at elevated pressure.

Material	Surface area ($m^2\,g^{-1}$)	Temperature (°C)	Conversion (%)		Selectivity (%)				Activity ($\times10^4$ mol CH_4 conv. $g^{-1}\,min^{-1}$)
			CH_4	O_2	CO_2	CO	CH_3OH	C_2H_6	
2 wt% MoO_3/ZrO_2	26	400	0.5	2.0	20	80	–	–	0.10
		450	0.9	7.6	46	54	–	–	0.17
		500	3.0	29.2	49	51	–	–	0.58
		550	8.1	84.8	65	34	Trace	1	1.59
5 wt% MoO_3/ZrO_2	33	400	0.6	3.9	21	79	–	–	0.11
		450	4.4	47.7	33	67	–	–	0.82
		500	7.5	57.4	62	38	–	–	1.39
		550	8.0	84.2	70	30	Trace	–	1.48
10 wt% MoO_3/ZrO_2	48	400	0.4	6.6	50	50	–	–	0.08
		450	1.7	20.3	53	47	–	–	0.33
		500	2.9	32.6	53	47	–	–	0.57
		550	7.1	73.7	59	40	–	1	1.40

at 800 °C. 2 wt% MoO_3/ZrO_2 has not been included, because there were no detected gas-phase products. However, the carbon balance and post-reactor characterisation studies suggest that an as yet unidentified carbon-containing species was being deposited on this material under these conditions. This is currently the subject of further investigation. With the exception of 10 wt% MoO_3/ZrO_2, which exhibited a selectivity of 30% to carbon monoxide, all the catalysts in figure 1 were 100% selective to carbon dioxide. It is especially interesting to note the comparative performance of 5 wt% MoO_3/ZrO_2, since Zanar et al. have recently reported $Zr_{0.2}Ce_{1.8}O_2$ catalysts to be very effective for methane combustion [11]. Although the activities of our catalysts are much lower, we find that the mass-normalised combustion activity of 5 wt% MoO_3/ZrO_2 is ca. 15 times that of $Zr_xCe_{1-x}O_2$ under our conditions. When normalised for surface area, 5 wt% MoO_3/ZrO_2 is second only to Fe_2O_3 in the activity series.

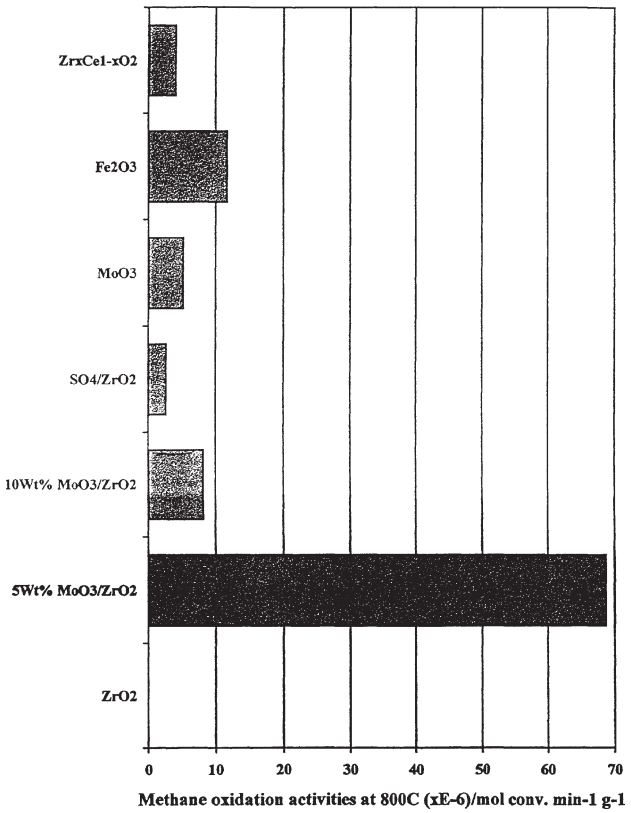

Figure 1. Mass-normalised methane oxidation activity at 800 °C.

The above studies demonstrate that there is a marked dependence upon MoO_3 content and catalytic activity for MoO_3/ZrO_2 "superacidic" catalysts in methane oxidation. Additionally, the methane combustion performance of the most active material, 5 wt% MoO_3/ZrO_2, has been found to compare well with materials expected to display high efficacy for this reaction. Accordingly, a comprehensive characterisation study of the MoO_3/ZrO_2 materials has been undertaken in an attempt to elucidate the origin of differences in activity and the results are reported below.

Powder X-ray diffraction has been applied to the materials prior to activity testing and the patterns are shown in figure 2. In all cases, no evidence of discrete molybdenum-containing phases was found. However, the addition of higher loadings of MoO_3 increased the proportion of tetragonal zirconia as evidenced by the reflection at ca. 30° 2θ.

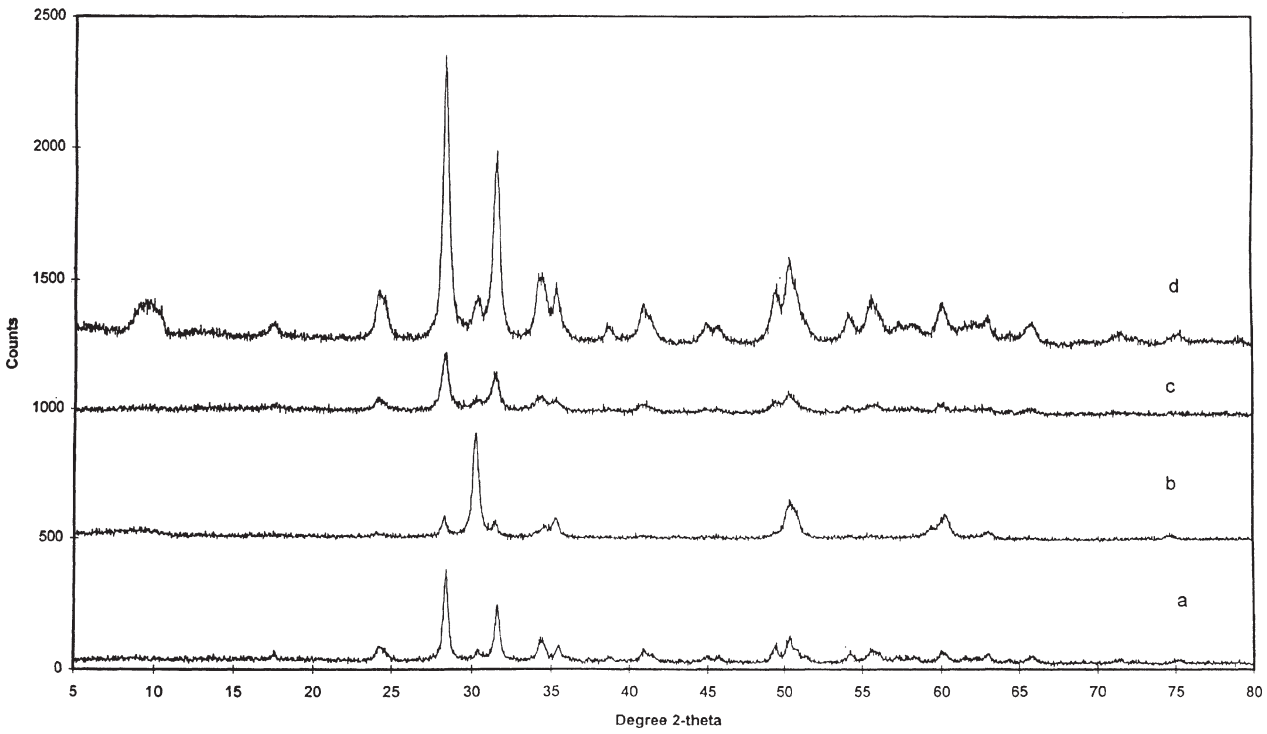

Figure 2. Powder X-ray diffraction patterns: (a) zirconia, (b) 10 wt% MoO_3/ZrO_2, (c) 5 wt% MoO_3/ZrO_2 and (d) 2 wt% MoO_3/ZrO_2.

Table 2
Quantitative phase composition of zirconia-based materials as determined by Toroya's method.

Material	Volume (%)	
	Monoclinic phase	Tetragonal phase
ZrO_2	90	10
2 wt% MoO_3/ZrO_2	92	8
5 wt% MoO_3/ZrO_2	87	13
10 wt% MoO_3/ZrO_2	37	63

In itself, this effect is insufficient to explain the differences in activity, since quantitative analysis (table 2) performed using Toraya's method [12] indicates a similarity in the phase composition of the 2 and 5 wt% MoO_3/ZrO_2 samples.

Temperature-programmed reduction (TPR) measurements have been performed and the results are shown in figure 3. The supported systems were observed to undergo reduction at lower temperatures than bulk MoO_3, which is consistent with previous studies (e.g., [13]). Blank experiments demonstrated that no reduction of either monoclinic or tetragonal zirconia occurs under our conditions. The reduction profiles of the 2 and 5 wt% samples were similar in general terms, consisting of two maxima at similar temperatures (394 and 756 °C, and 397 and 742 °C for 2 and 5, respectively) implying similarity in the Mo species. In the case of the 10 wt% MoO_3/ZrO_2 sample, additional features occur. An asymmetry is evident in the lower-temperature maximum ($T_{max} = 408$ °C) and an additional higher-temperature maximum is apparent ($T_{max} = 700$ and 832 °C), which may indicate the presence of two types of molybdenum oxospecies. Since the experiments involving the 5 and 10 wt% samples were performed under the same experimental conditions involving the same mass of MoO_3 species, we can exclude the possibility that experimental artefacts may be complicating the TPR patterns [15]. The positions of the higher-temperature maxima generally decrease with increasing molybdenum content. Quantification of the total uptake indicates that the consumption of hydrogen is in the range 50–60% of that expected on the basis of Mo^{VI}–Mo^0 reduction in all three cases.

Due to its high sensitivity to surface molybdenum oxide species, the pre-reactor samples have been investigated using laser Raman spectroscopy and the results are shown in figure 4. Some spectra have been affected by cosmic interference which produces sharp bands such as that at 872 cm^{-1} in the 2 wt% MoO_3/ZrO_2 spectrum. The spectral region shown in figure 4 is that of most interest for the molybdenum oxospecies. Below ca. 650 cm^{-1}, spectra are dominated by components associated with the ZrO_2 polymorphs. It can be seen that bands at ca. 915 and ca. 870 cm^{-1} are evident in all three samples. These are in a similar region to those assigned to co-ordinated surface molybdate species by Smith et al. [15] in their study of MoO_3/SiO_2 catalysts. As molybdenum loading is increased, additional bands at ca. 988 and 816 cm^{-1} become apparent. These bands are in a similar region to those observed in bulk MoO_3 where they have been assigned to

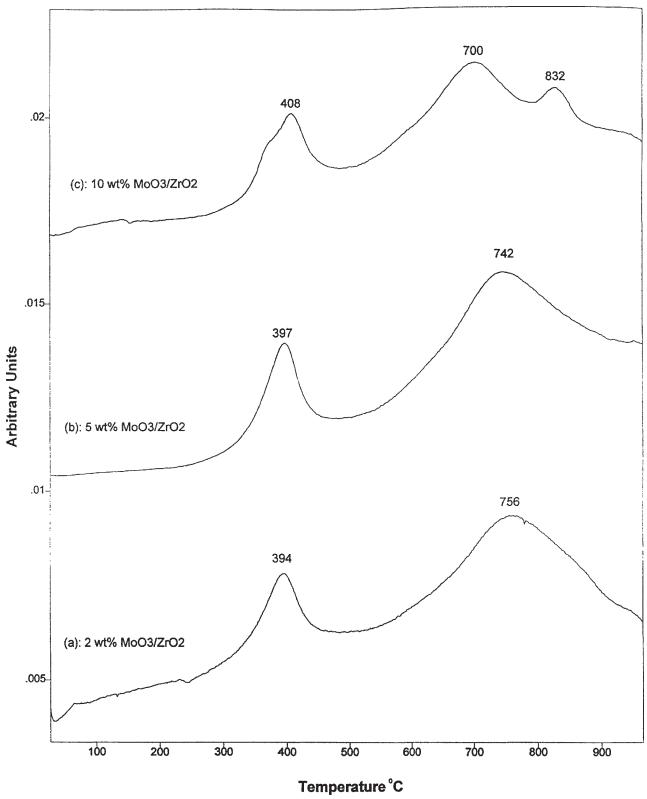

Figure 3. Temperature-programmed reduction profiles.

Mo=O and Mo–O–Mo stretches, respectively [16]. Therefore, we conclude that surface non-XRD evident MoO_3 species are present in both the 5 and 10 wt% materials. In their study of MoO_3/ZrO_2 superacids, Zhao et al. [17] have assigned a broad band at 814 cm^{-1} to Mo=O stretches associated with strongly acidic Mo–O–Zr species. However, we feel that the simultaneous presence of the 988 cm^{-1} band makes the assignment to MoO_3 species more reasonable in our case. An important conclusion from the Raman studies is that there is not a unique molybdenum oxospecies associated with the 5 wt% material. Comparison of the relative intensities of the 816 and 988 cm^{-1} bands in the 5 and 10 wt% samples suggests that differences in pre-reactor dispersion are small, since Mo=O species are preferentially associated with the side planes and Mo–O–Mo with the basal planes of MoO_3 [2].

Taking the TPR and Raman results together, it appears that although the form of molybdenum oxide in the 5 and 10 wt% samples is similar, its reducibility is different. It is probable that this relates to the phase composition of the zirconia substrate, with reduction occurring at lower temperatures on the monoclinic form. This correlates with the higher activity of the 5 wt% sample, since a relationship between reducibility and oxidation activity has previously been observed [13]. Although one of the higher-temperature maxima occurs at lower temperatures in the 10 wt% sample, the remaining maxima both occur at higher temperatures compared to the 2 and 5 wt% samples. An important consideration is whether the forms of molybde-

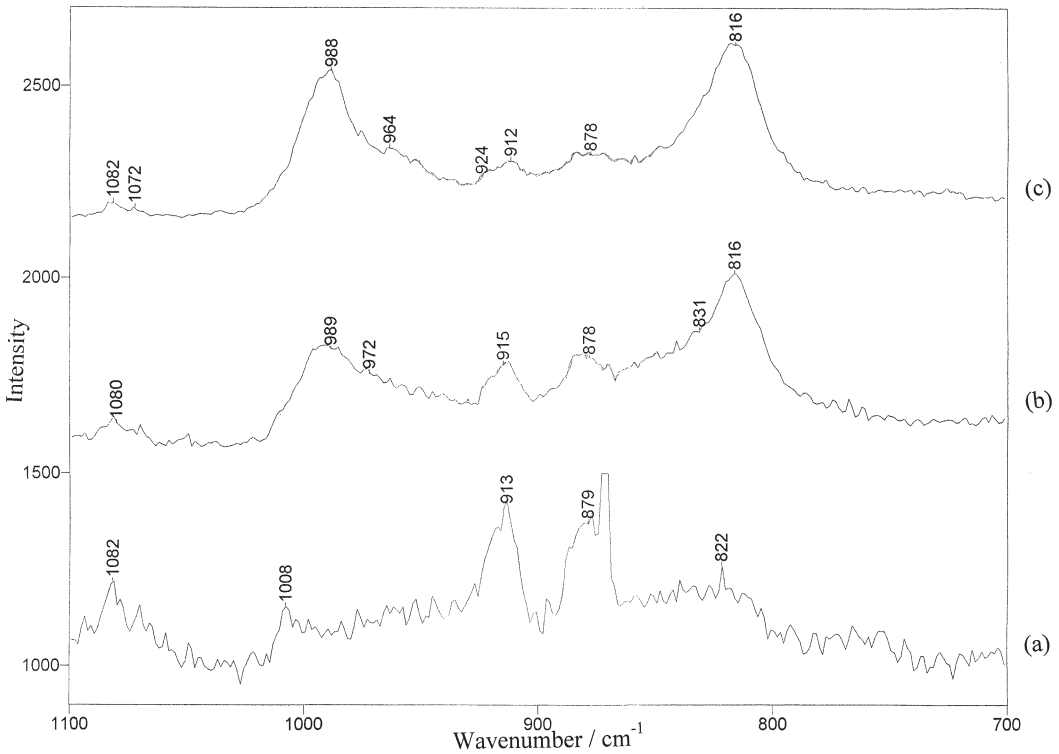

Figure 4. Raman spectra: (a) 2 wt% MoO_3/ZrO_2, (b) 5 wt% MoO_3/ZrO_2 and (c) 10 wt% MoO_3/ZrO_2.

num oxide species observed in the Raman studies are representative of those under reaction conditions. Since the Tamman temperature of MoO_3 is only 534 K [18], the highly dispersed MoO_3 crystallites will be mobile during reaction. One possibility is that they disperse and spread over the surface of the support, forming a monolayer like species. Taking the cross-sectional area of an MoO_3 unit to be 15 $Å^2$ [19], we calculate that the amount of MoO_3 in the catalysts synthesis mixture corresponds to 48, 95 and 131% of a monolayer for the 2, 5 and 10 wt% samples, respectively, based on the surface areas reported in table 1. If activity is associated with monolayer like species, an additional possibility is that the presence of excess molybdenum oxide in the 10 wt% sample could inhibit activity by blocking active sites.

Acknowledgement

We gratefully acknowledge MEL Chemicals for the generous provision of materials and in particular Drs. Peter Moles and Gary Monks and Mr. Colin Norman. We would like to thank Mr. D. Lacey, Faculty of Science and Mathematics, Nottingham Trent University, for his kind assistance with EDAX measurements.

References

[1] T.J. Hall, J.S.J. Hargreaves, G.J. Hutchings, R.W. Joyner and S.H. Taylor, Fuel Proc. Technol. 42 (1995) 151.
[2] M.R. Smith and U.S. Ozkan, J. Catal. 141 (1993) 124.
[3] A. Parmaliana, F. Frusteri, A. Mezzapica, M.S. Scurrell and N. Giordano, J. Chem. Soc. Chem. Commun. (1993) 751.
[4] A. Parmaliana, F. Frusteri, D. Micelli, A. Mezzapica and M.S. Scurrell, Appl. Catal. 78 (1991) 33.
[5] M.A. Banares, B. Pawelec and J.L.G. Fierro, Zeolites 12 (1992) 882.
[6] K. Arata, Appl. Catal. A 146 (1996) 3.
[7] C.-H. Lin and C.-Y. Hsu, J. Chem. Soc. Chem. Commun. (1992) 1479.
[8] S. Rezgui, A. Liang, T.-K. Cheung and B.C. Gates, Catal. Lett. 53 (1998) 1.
[9] K. Murata, T. Hayakawa and K.I. Fujita, J. Chem. Soc. Chem. Commun. (1997) 221.
[10] A.S.C. Brown, J.S.J. Hargreaves and B. Rijniersce, Catal. Lett. 53 (1998) 7.
[11] F. Zanar, A. Trovarelli, C. de Leitenburg and G. Dolcetti, J. Chem. Soc. Chem. Commun. (1995) 965.
[12] H. Toraya, M. Yoshimura and S. Somiya, J. Am. Ceram. Soc. 67 (1984) C-119.
[13] A. Parmaliana, F. Arena, F. Frusteri, G. Martra, S. Coluccia and V. Sokolovskii, Stud. Surf. Sci. Catal. 110 (1997) 347.
[14] G. Fierro, M. Lo Jacono, M. Inversi, G. Morretti, P. Porta and R. Lavecchia, in: *Proceedings 10th International Congress Catalysis*, eds. L. Guczi et al. (Elsevier, Amsterdam, 1993).
[15] M.R. Smith, L. Zhang, S.A. Driscoll and U.S. Ozkan, Catal. Lett. 19 (1993) 1.
[16] E.M. Gaigneaux, D. Herla, P. Tsiakaras, U. Roland, P. Ruiz and B. Delmon, in: *Heterogeneous Hydrocarbon Oxidation*, Am. Chem. Soc. Symposium Series, Vol. 638, eds. B.K. Warren and S.T. Oyama (1996).
[17] B. Zhao, X. Wang, H. Ma and Y. Tang, J. Mol. Catal. A 108 (1996) 167.
[18] Y. Chen and L. Zhang, Catal. Lett. 12 (1992) 51.
[19] M. Del Arco, M.F.M. Sanfelipe, V. Rives, P. Malet and M.A. Ulibarri, J. Mater. Sci. 27 (1992) 2960.