JOURNAL OF
Materials
CHEMISTRY
Communication

High oxide ion conductivity in Bi_2MoO_6 oxidation catalyst

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Received 26th July 2001, Accepted 17th October 2001
First published as an Advance Article on the web 16th November 2001

Both the low (γ)- and high (γ')-temperature polymorphs of Bi_2MoO_6 are oxide ion conductors. The γ' conductivity at 300 °C is comparable to that of yttria-stabilized zirconia (YSZ) while its activation energy, 0.510(2) eV, is much less than that of YSZ, 0.79 eV, and is lower than that of the best low temperature oxide ion conductor, BIMEVOX: $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$, 0.56 eV, thus suggesting that γ'-Bi_2MoO_6 contains a small number of highly mobile oxide ions. This may account for its usefulness as an oxidation catalyst.

Bismuth molybdates are useful oxidation catalysts in selective olefin oxidation and ammoxidation processes.[1] In the partial oxidation of olefins, superior catalytic activity appeared to be confined to the compounds Bi_2MoO_6 (γ) and $Bi_2Mo_2O_9$ (β).[2] $Bi_2Mo_2O_9$ produced the best catalyst in terms of activity and selectivity, but was unstable at temperatures above 400 °C.[3] Kumar and Ruckenstein[4] showed the decomposition products to be Bi_2MoO_6 and MoO_2 and suggested that Bi_2MoO_6 formed near the surface of the β phase and was responsible for the selective catalytic oxidation. Various studies on the selective oxidation of olefin using an ^{18}O-labelled catalyst have shown that diffusion of lattice oxygen of Bi_2MoO_6 (γ) played a major role in the catalytic process.[5–7] It was proposed[5] that during oxidation, a Bi-bound O^{2-} is removed, replaced by a nearby Mo-bound O^{2-} and the vacancy subsequently filled by an external O^{2-}. Galván *et al.*[3] reported that the high-temperature γ' form of Bi_2MoO_6 is a suitable catalyst in CO oxidation reactions, showing the same degree of catalytic activity as cobalt perovskites. The study showed that besides oxygen in the feed, oxygen from the lattice was consumed by the reaction, thus suggesting that a mechanism similar to olefin oxidation, in which reactive oxygen was provided by the catalyst, was in operation.

Bi_2MoO_6 exists in three polymorphic forms: γ, γ'' (or I) and γ', with transformation temperatures of 604 and 640–670 °C, respectively for the low to intermediate and intermediate to high temperature polymorphs.[8] The γ to I transition is reversible while the I to γ' transition is not, except when high pressures are applied. The temperature of the γ (or γ'') to γ' transition depends somewhat on heating conditions; transformation was reported to occur as low as 580 °C;[9] in this study we found the transformation occurred on prolonged heating at 600 °C. γ-Bi_2MoO_6 has a layered Aurivillius structure consisting of $Bi_2O_2^{2+}$ sheets alternating with MoO_4^{2-} perovskite layers;[10] in γ'-Bi_2MoO_6, the cation distribution forms a fluorite-related supercell with infinite channels of Bi polyhedra surrounded by Mo tetrahedra.[9] Despite the difference in crystal structure, similar mechanisms involving lattice oxygen appear to operate when these materials are used as oxidation catalysts. The anionic conductivity of the bismuth-rich fluorite-like phases in the Bi_2O_3–MoO_3 system has been reported.[11,12] However, there is only one report[13] on the conductivity of Bi_2MoO_6. Fixed frequency (1 kHz) conductivity data on γ and γ' polymorphs, combined with transport number measurements, led to the conclusion that the γ polymorph was an oxide ion conductor at low temperatures but became increasingly electronic above 300 °C, whereas the converse occurred for the γ' polymorph which became increasingly electronic for temperatures below 700 °C.[13] We became aware of this paper only at the conclusion of the present study and there are major discrepancies between the two sets of findings, as discussed below.

γ- and γ'-Bi_2MoO_6 were prepared by mixing and heating stoichiometric mixtures of high purity Bi_2O_3 and MoO_3 for 20 hours at 530 and 800 °C, respectively. The identities of the products were confirmed by their respective XRD patterns.

The electrical properties of Bi_2MoO_6 depended very much on the sample history and polymorph; powder X-ray diffraction, XRD, on crushed pellet fragments was carried out at the end of each set of conductivity measurements in order to establish whether or not any structural changes had occurred during the measurements. An impedance complex plane plot of γ-Bi_2MoO_6 sintered at 530 °C shows a broadened semicircle and a low frequency spike, Fig. 1a. The sintering temperature had to be kept below 600 °C to avoid phase transformation; hence it was difficult to obtain a dense ceramic for conductivity measurements; prolonged heating, 4 days, at 530 °C, did not lead to any noticeable change in conductivity. Total conductivity values were obtained from the low frequency intercept of the broadened semicircle.

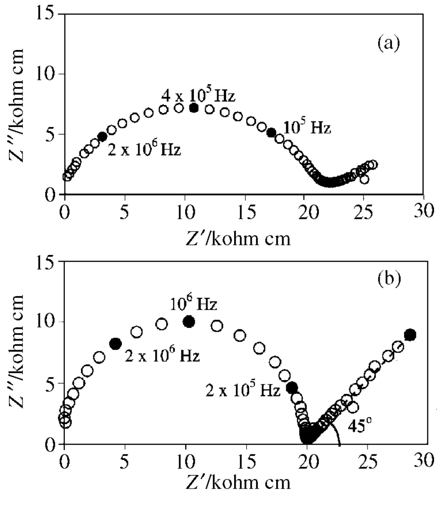

Fig. 1 Complex plane plots at 500 °C of (a) γ-Bi_2MoO_6 and (b) γ'-Bi_2MoO_6 sintered at 530 and 900 °C, respectively.

DOI: 10.1039/b106792n

Impedance data of the γ' polymorph were very dependent on sintering conditions. Impedance complex plane plots ranged from a slightly distorted high frequency semicircle for pellets sintered at 800 °C to an ideal, undistorted semicircle after repeated heat–cool cycles or sintering at higher temperature, Fig. 1b.

Arrhenius conductivity plots of the total pellet conductivity of γ'-Bi_2MoO_6 were very dependent on the sintering temperature with the highest conductivities observed after sintering at 928 °C, a temperature close to melting, Fig. 2. Linearity of the Arrhenius plots appeared to increase either with increasing sintering temperature or after repeated heat–cool cycles. The increases in conductivity on isothermal annealing at high temperature were irreversible and could not be reversed by isothermal annealing at lower temperature, *e.g.* on reheating overnight at 800 °C. There was also no evidence by either XRD or conductivity measurements that the $\gamma \rightarrow \gamma'$ transition could be reversed. These effects appear to be similar to those seen in $Ca_{12}Al_{14}O_{33}$,[14] which were attributed to an increase in grain size and increased area of contact between grains in well-sintered samples, giving rise to an overall increase in pellet conductivity. Consistent with this explanation, scanning electron micrographs (SEM) of pellets of γ'-Bi_2MoO_6 sintered at 800 °C, 850 °C and 900 °C, Fig. 3, show an increase in grain size, decreased porosity and increased contact between grains with increasing sintering temperature.

The conductivity Arrhenius plot of γ-Bi_2MoO_6 was reversible on cooling, with an activation energy of ~1.14 eV for temperatures up to 530 °C, Fig. 2. At higher temperatures (not shown), a sharp drop in the conductivity of γ-Bi_2MoO_6 was observed, within the temperature range 625–675 °C, as the sample transformed from the γ to the γ' polymorph; the conductivity of the resulting γ' polymorph was comparable to that of the γ' sample sintered at 800 °C. The conductivity–temperature dependence of γ-Bi_2MoO_6 is, therefore, very different to that of well-sintered γ'-Bi_2MoO_6, with much higher activation energy and lower conductivity, especially at lower temperatures.

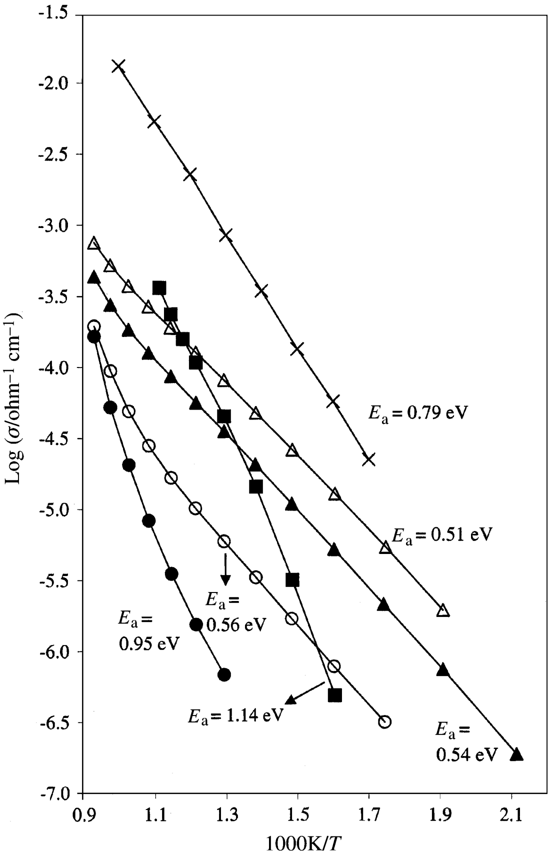

Fig. 2 Arrhenius plots of γ-Bi_2MoO_6 (■), γ'-Bi_2MoO_6 sintered at 800 °C (●), 850 °C (○), 900 °C (▲), 928 °C (△) and yttria-stabilized zirconia (×).

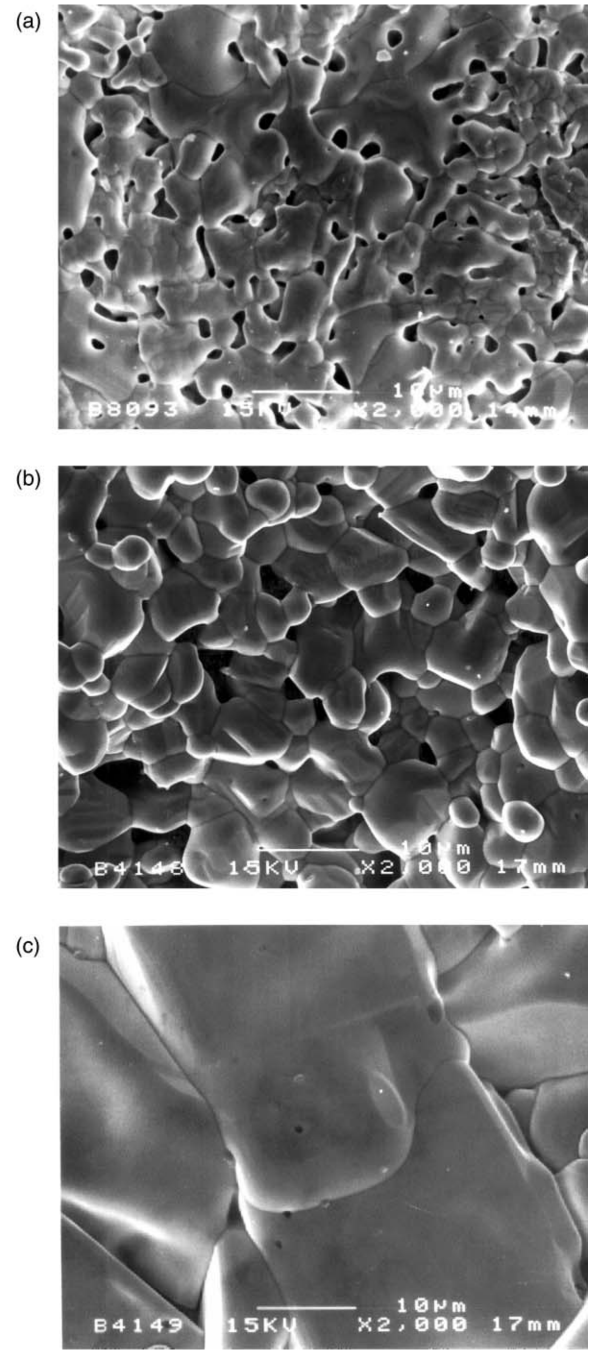

Fig. 3 SEM micrographs of γ'-Bi_2MoO_6 sintered at (a) 800 °C, (b) 850 °C and (c) 900 °C.

The decrease in conductivity associated with the $\gamma \rightarrow \gamma'$ transition and the subsequent increase on sintering γ' above ~800 °C are believed to have a common origin. From published data,[9,10] the unit cell volumes (densities) of γ'-Bi_2MoO_6 and γ-Bi_2MoO_6 are 2162.35 (7.493) and 489.23 Å^3 (8.28 g cm^{-3}), respectively. As the density of γ is ~9% greater than that of γ', the $\gamma \rightarrow \gamma'$ transition is likely to be accompanied by significant expansion of all the grains in the ceramics and a reduction in the area of the grain–grain contacts. Consequently, the conductivity of the resulting γ' pellet is comparable to that of the γ' sample sintered at 800 °C and whose density, and conductivity, had not been enhanced by heating >800 °C.

The conducting species appear to be oxide ions, for two reasons. First, the conductivity data (Z^* plots) were completely unaffected by changing the atmosphere during measurement from dry to wet air, and so there was no evidence of protonic conduction. Second, the impedance data show evidence at low frequencies of an inclined spike, seen clearly for γ'-Bi_2MoO_6 in Fig. 1b, at an angle of $\sim 45°$ to the Z' axis. Such a spike is characteristic of a diffusion-limited process represented by a Warburg impedance; in the present case, the origin is likely to be the diffusion of oxygen molecules towards/away from the electrode/sample contact and is a very strong indicator that the present materials are oxide ion conductors and not electronic semiconductors; in order to confirm this, emf measurements of an oxygen concentration cell containing Bi_2MoO_6 as the membrane are needed.

In conclusion, a well-sintered sample of γ'-Bi_2MoO_6 is a better oxide ion conductor than the low temperature γ polymorph at temperatures below 500 °C. It has an activation energy of 0.510(2) eV (average of three conductivity sweeps on a pellet sintered at 928 °C) and conductivity of 7.3×10^{-6} ohm^{-1} cm^{-1} at 300 °C. Its conductivity at 300 °C is comparable to that of yttria-stabilized zirconia (YSZ), Fig. 2, while its activation energy is much less than that of YSZ, 0.79 eV. The activation energy of γ'-Bi_2MoO_6 is, in fact, less than that of the BIMEVOX family, which contains materials with the highest known oxide ion conductivity for temperatures below ~500 °C, *e.g.* 0.56 eV for $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$[15] and 0.57 eV for $Bi_4V_{1.5}Sb_{0.5}O_{11}$.[16] This indicates that γ'-Bi_2MoO_6 contains a small number of mobile oxide ions. The relatively high oxide ion conductivity of γ-Bi_2MoO_6 at low temperatures and, especially, the low activation energy, may account for its usefulness as an oxidation catalyst where migration of lattice oxygen from the bulk to the surface appears to be of paramount importance.

The results presented here contrast significantly with those in ref. 13, which showed a low conductivity for both γ and γ' polymorphs which was comparable to that of our data for γ'-Bi_2MoO_6 sintered at 800 °C; however, the data in ref 13 which were fixed frequency data, may not have represented true bulk conductivities and were not presented in conventional Arrhenius format, thus making comparison difficult. It appears that those data were for poorly sintered samples, and therefore the conductivities were 1 to 2 orders of magnitude lower than those of our well-sintered samples.

C. K. L. thanks the RSC for a Journals Grant for International Authors.

Notes and references

1 Y. Moro-Oka and W. Ueda, *Adv. Catal.*, 1994, **40**, 233.

2 Ph. A. Baptist, A. H. W. M. Der Kinderen, Y. Leeuwenburgh, F. A. M. G. Metz and G. C. A. Schuit, *J. Catal.*, 1968, **12**, 45.

3 D. H. Galván, S. Fuentes, M. Avalos-Borja and L. Cota-Araiza, *Catal. Lett.*, 1993, **18**, 273.

4 J. Kumar and E. Ruckenstein, *J. Solid State Chem.*, 1980, **31**, 41.

5 D. B. Dadyburjor and E. Ruckenstein, *J. Phys. Chem.*, 1978, **82**, 1563.

6 H. Miura, T. O. Otsubo, T. Shirasaki and Y. Morikawa, *J. Catal.*, 1979, **56**, 81.

7 L. C. Glaeser, J. F. Brazdil, M. A. Hazle, M. Mehicic and R. K. Grasselli, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2903.

8 H. Kodama and A. Watanabe, *J. Solid State Chem.*, 1985, **56**, 225.

9 D. J. Buttrey, T. Vogt, U. Wildgruber and W. R. Robinson, *J. Solid State Chem.*, 1994, **111**, 118.

10 R. G. Teller, J. F. Brazdil, R. K. Grasselli and J. D. Jorgensen, *Acta Crystallogr., Sect. C*, 1984, **40**, 2001.

11 T. Takahashi, T. Esaka and H. Iwahara, *J. Appl. Electrochem.*, 1977, **7**, 31.

12 G. Chiodelli, A. Magistris, G. Spinolo, C. Tomasi, V. Antonucci and N. Giordano, *Solid State Ionics*, 1994, **74**, 37.

13 V. I. Utkin, Yu. E. Roginskaya, R. P. Kayumov and Yu. N. Venevtsev, *Zh. Fiz. Khim.*, 1980, **54**, 2953.

14 M. Lacerda, J. T. S. Irvine, E. E. Lachowski, F. P. Glasser and A. R. West, *Br. Ceram. Trans. J.*, 1988, **87**, 191.

15 F. Abraham, J. C. Boivin, G. Mairesse and G. Nowogrocki, *Solid State Ionics*, 1990, **40**, 934.

16 O. Joubert, A. Jouanneaux, M. Ganne, R. N. Vannier and G. Mairesse, *Solid State Ionics*, 1994, **73**, 309.