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Redox Properties of Various Bismuth Molybdate Phases in the Catalytic Oxidation of But-1-ene

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The redox properties of four bismuth molybdate catalysts (α, β and γ phases and a mixture of β and γ phases) have been investigated in atmospheres of oxygen and but-1-ene at different temperatures using the electrical-conductivity technique. It has been shown that these solids are intrinsic semiconductors in the oxidized state and become highly conductive when in contact with but-1-ene. The only source of active oxygen is the surface lattice anions of the solid, whose anionic vacancies are replenished by oxygen from the gas phase. The qualitative classification of the relative reduction rates found by conductivity measurements is identical to that found by kinetic measurements carried out in a pulse reactor ($\gamma > \alpha > \beta$).

Bismuth molybdates are used as selective industrial catalysts for the (amm) oxidation of olefins, and several reviews have been devoted to this system.[1,2] Although the unique rôle of lattice oxygen and not that of the adsorbed oxygen has been established for selective catalytic oxidations,[3] there are still problems about classification for the catalytic activity of the different Mo–Bi–O phases, either for propene oxidation and ammoxidation or for the oxidative dehydrogenation of butene.[4] The redox properties of the surface of bismuth molybdates and the lattice oxygen diffusivity are key parameters for the reactivity of these solids. Since redox processes are basically electronic, the electrical-conductivity technique appears to be a good method of following *in situ* the behaviour of the various Mo–Bi–O phases when in contact with reducing or oxidizing atmospheres. The solids have previously been studied for the oxidative dehydrogenation and/or isomerization of but-1-ene,[5,6] and so but-1-ene was chosen as the reducing agent for the various redox cycles.

EXPERIMENTAL

CATALYSTS

The Mo–Bi catalysts were prepared by coprecipitation starting with a mixture of an aqueous solution of ammonium heptamolybdate and a nitric acid solution of bismuth nitrate.[7–10] By choosing the correct proportions and controlling the basic parameters such as pH, temperature, stirring, concentration *etc*., different phases of bismuth molybdate were obtained: $Bi_2O_3 \cdot 3MoO_3$ (α phase), $Bi_2O_3 \cdot 2\,MoO_3$ (β phase), $Bi_2O_3 \cdot MoO_3$ (γ phase) and a Mo–Bi sample, denoted MJ, corresponding to *ca*. 25 and 75% of the β and γ phases, respectively. All samples had low surface areas (*ca*. 1 $m^2\,g^{-1}$) and were characterized by X-ray diffraction. Their structural evolution after oxidation–reduction sequences was followed by infrared spectroscopy.

ELECTRICAL CONDUCTIVITY

The electrical conductivity was measured in a static cell, specially designed for studying solid–gas electronic interactions at the surface of powdered oxides such as TiO_2,[11] Sn–Sb–O,[12] Fe–Sn–Sb–O[13] and metal catalysts deposited on semiconductors.[14] The procedure and limitations of the technique have been discussed previously.[11-14]

RESULTS AND DISCUSSION

SEMICONDUCTING BEHAVIOUR OF THE DIFFERENT PHASES

The four samples, whose physical properties are given in table 1, were tested in electrical measurements involving the influence of the oxygen pressure P_{O_2} and of the temperature. Fig. 1 (*a*) shows that the electrical conductivity, σ, of the four samples previously heated in oxygen to 450 °C is independent of P_{O_2}, at least in the range 2–160 Torr (1 Torr $\approx$ 133.3 Pa), which shows that the samples are intrinsic semiconductors. Consequently, according to theory, their respective activation energies of conduction, deduced from fig. 1 (*b*), correspond to half their band-gap energy, E_G, given in table 1. The α and γ phases, which are known to be stable, have the highest E_G, whereas the β phase, which is less stable, has a low band-gap energy ($E_G = 1.54$ eV) if compared by interpolation with those of the α and γ phases. The E_G value of the MJ-1/74 sample is intermediate between those of the γ and β phase, but closer to that of the β phase, although the amount of this phase in MJ is less.

The immediate consequence of the intrinsic semiconductor character of the Mo–Bi catalysts is that the concentration of free electrons will be very low and no oxygen ionosorption can occur on oxidized forms close to their stoichiometric composition. Thus, the only possible source of reacting oxygen will be surface or subsurface lattice anions O^{2-}.

OXIDATION–REDUCTION IN BUT-1-ENE–OXYGEN SEQUENCES

Since these Mo–Bi catalysts are known to oxidize but-1-ene to butadiene or isomerise it into *cis*- or *trans*-but-2-ene with two distinct patterns of behaviour depending on the temperature range (one pattern starting from 280 °C and the other ending at 350 °C),[5, 6, 15, 16,] these two limit temperatures were chosen for the measurement of σ during but-1-ene–oxygen sequences.

BUT-1-ENE–OXYGEN RUNS AT 280 °C

The influence upon σ of the reduction at 280 °C by but-1-ene is given in fig. 2, with a sharp initial increase followed by a slower one, especially for the α and γ phases. Simultaneously, the solids become dark and behave as n-type semiconductors with the formation of anionic vacancies $V_{O^{2-}}$:

$$C_4H_8 + O_S^{2-} \rightarrow C_4H_6 + V_{O^{2-}} + H_2O. \qquad (1)$$

Vacancies are generally singly ionized in the ordinary thermal conditions of catalysis, thus explaining the increase of conductivity:

$$V_{O^{2-}} \rightleftharpoons (V_{O^{2-}})^+ + e^-. \qquad (2)$$

The amplitude of the initial σ variations, expressed in orders of magnitude by log (σ/σ_0), are indicative of the relative initial rates of reduction of the various bismuth molybdates. Actually, log (σ/σ_0) values are in the order: $\gamma > \alpha \approx$ MJ $> \beta$. This order is identical to that obtained for the rates of reduction measured in a pulse reactor,[15] as shown by fig. 3 (*a*). Similarly, the total amplitude σ over *ca.* 2 h varies with the mean rate of reduction rates of Mo–Bi by but-1-ene [fig (3*b*)] in the order $\gamma > \alpha >$ MJ $> \beta$.

Table 1. Physical characteristics of Mo–Bi samples

formula	catalyst phase	Bi/Mo	structure	colour	$\frac{d \log \sigma}{d \log P_{O_2}}$	E_c/kJ mol^{-1}	E_G/eV
$Bi_2O_3 \cdot 3MoO_3$	α	2/3	scheelite	pale yellow	0	130	2.67
$Bi_2O_3 \cdot 2MoO_3$	β	1	—	pale yellow	0	75	1.54
$Bi_2O_3 \cdot MoO_3$	γ	2/1	koechlinite	bright yellow	0	146	3.04
$75\% \gamma + 25\% \beta$	MJ-1/74	—	—	bright yellow	0	102	2.12

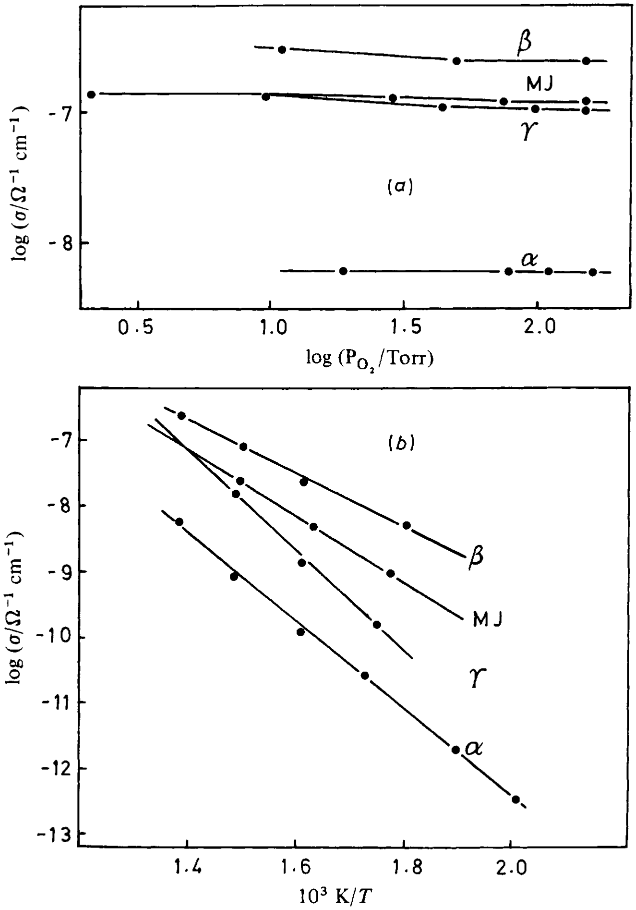

Fig. 1. (*a*) Conductivity isotherms: plots of log σ against $f(\log P_{O_2})$ at 450 °C. (*b*) Arrhenius plot of log σ against $f(10^3/T)$ at $P_{O_2} = 160$ Torr.

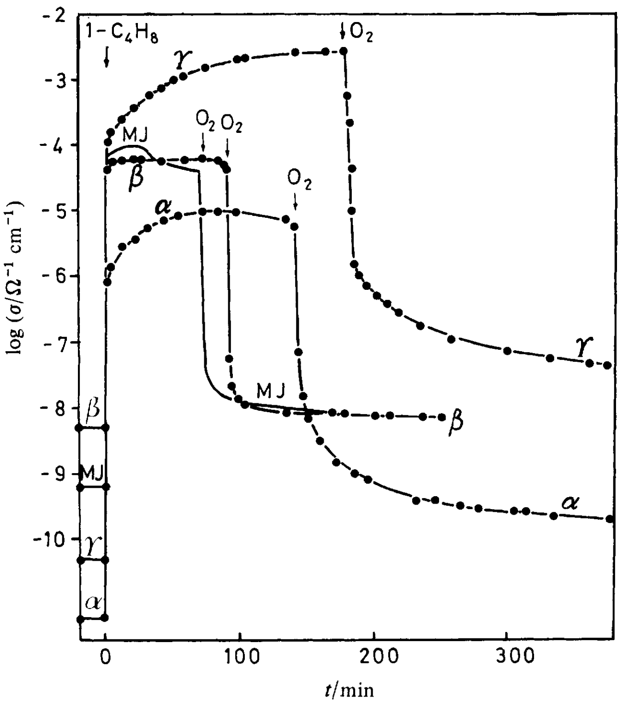

Fig. 2. Plot of electrical conductivity (log σ) against time with but-1-ene (60 Torr) and oxygen (160 Torr) at 280 °C.

After prompt outgassing, the introduction of oxygen at the same temperature causes a sharp decrease of σ, corresponding to the fast filling of surface anionic vacancies:

$$\tfrac{1}{2}O_2(g)+(V_{O^{2-}})^{+}+e^{-}\rightleftharpoons O_S^{2-}. \qquad (3)$$

An electrical steady state is reached rapidly in the case of the β phase and the MJ sample. The slower σ variations found for the α and γ phases, for reduction as well as for reoxidation (fig. 2), seem to be indicative of deeper oxidation–reduction processes affecting the subsurface lattice oxygen. By comparing the variations of σ in but-1-ene and in oxygen, it appears that only the β phase is reoxidized completely in O_2 at 280 °C.

BUT-1-ENE–OXYGEN RUNS AT 350 °C

The same sequences were repeated at 350 °C (fig. 4), which corresponds to the higher temperature used for catalytic tests. As with low-temperature experiments, the initial electrical conductivity variations ($\log \sigma/\sigma_0$) provide the relative, initial rate of reduction. These are determined on the vertical axis at time $t = 0$ and vary according to the nature of the Mo–Bi phases in the same order as obtained for initial rates of reduction measured at 350 °C in pulse reactor:[15] $\gamma > \alpha >$ MJ $> \beta$. For the mean rates of reduction, determined for $t \approx 100$ min, electrical-conductivity estimates always parallel the kinetic data obtained in the pulse reactor, but with an inversion between the α and γ phases: $\alpha > \gamma >$ MJ $> \beta$.

After rapid evacuation, the introduction of oxygen causes a sharp drop in the electrical conductivity and a simultaneous change in the colour of the catalysts from

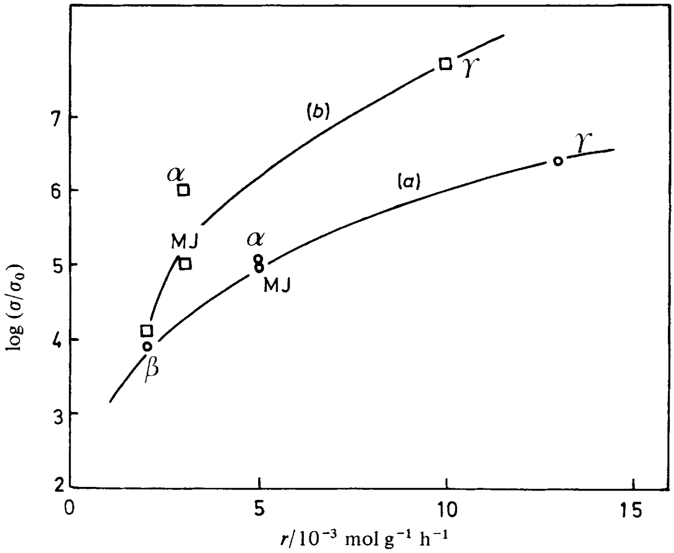

Fig. 3. Plot of relative electrical conductivity (log σ/σ_0) as a function of rate of reduction determined in a pulse reactor: (*a*) initial variation of σ as a function of initial reduction rates and (*b*) total variation of σ within *ca.* 100 min as a function of the mean reduction rate. $T = 280$ °C.

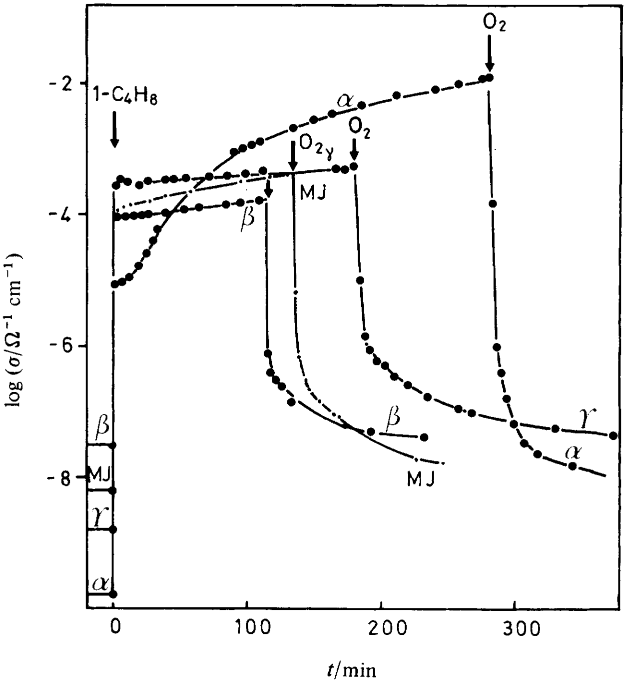

Fig. 4. Same as in fig. 2 but at 350 °C.

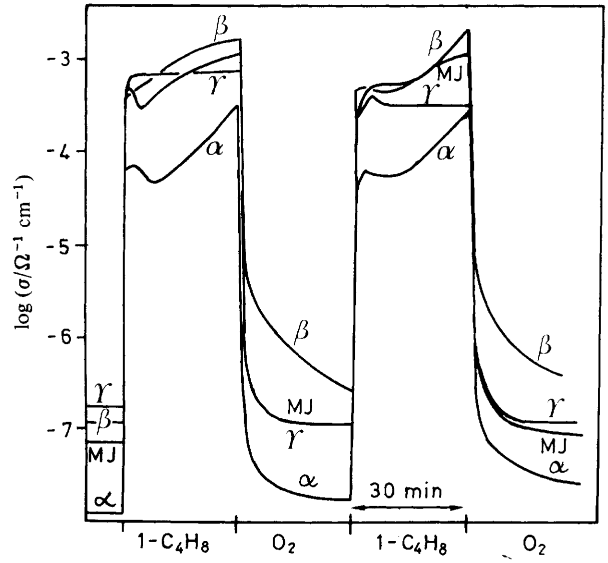

Fig. 5. Plot of log σ for but-1-ene–oxygen sequences at 450 °C.

black to yellow. This corresponds to the filling of peripheral anionic vacancies [reaction (3)]. Note that the initial slopes $(\mathrm{d}\log\sigma/\mathrm{d}t)_0$ are smaller for oxidation than for reduction. Their relative ratios (red/ox) are always higher than unity (4.4, 1.1, 8.7 and 3.8 for α, β, γ and MJ, respectively). This means that the rate of surface reduction of Mo–Bi by but-1-ene is higher than the rate of reoxidation by gaseous O_2, as was found for the same solids in the presence of an ammoxidation reacting mixture of propene, ammonia and oxygen.[17] Consequently, we conclude that the Mo–Bi catalysts are in a partially reduced surface state during the reaction. The redox process, which involves the participation of lattice oxygen ions, is described mathematically by the Mars and Van Krevelen mechanism.[18]

OXIDATION–REDUCTION SEQUENCES AT 450 °C AND STRUCTURAL EVOLUTION

Previous X-ray diffraction studies[19, 20] have shown that pure Mo–Bi–O phases react under the reducing influence of but-1-ene according to

$$Bi_2O_3\cdot 3MoO_3(\alpha) \rightarrow Bi_2O_3\cdot MoO_3(\gamma) + 2MoO_2 + 2O$$

$$Bi_2O_3\cdot 2MoO_3(\beta) \rightarrow Bi_2O_3\cdot MoO_3(\gamma) + MoO_2 + O$$

$$BI_2O_3\cdot MoO_3(\gamma) \rightarrow 2Bi + MoO_2 + 4O.$$

Moreover, when the β phase is reduced to metallic Bi and MoO_2, subsequent reoxidation with oxygen does not restore the initial structure and some formation of the α-phase occurs.

The results of the successive but-1-ene–oxygen sequences on the α phase at 280, 350 and 450 °C (fig. 2, 4 and 5) show a fast initial redox process followed by a slower one, as mentioned in ref. (17), which has to be related to its close-packed structure. At lower temperature the β phase is only superficially reduced, while α phase sublayers are involved even at 280 °C.

In the reoxidation cycle the initial α phase structure is not restored, at low

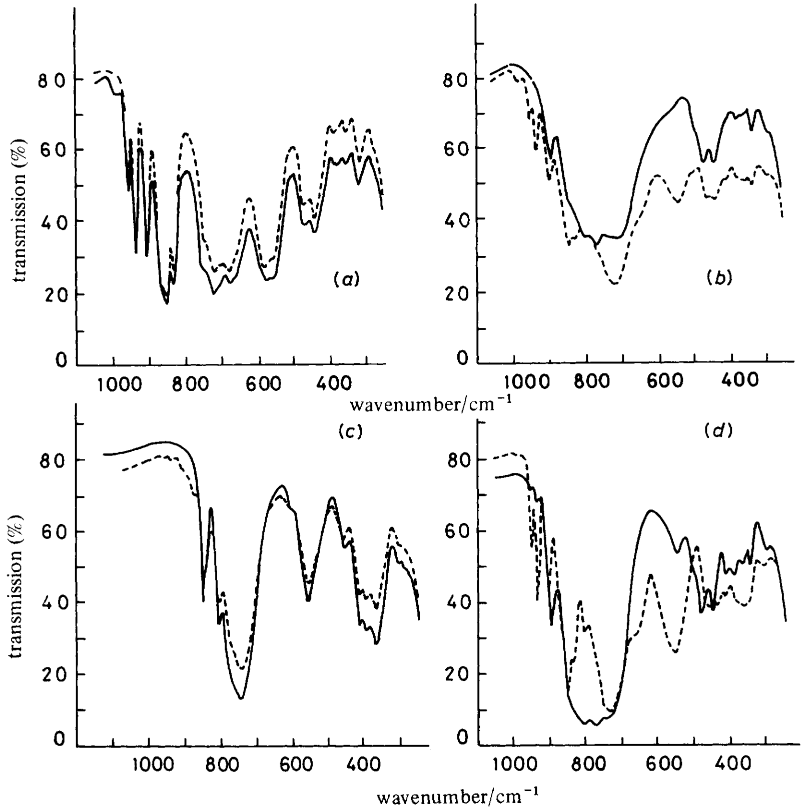

Fig. 6. I.r. spectra of (*a*) α, (*b*) β, (*c*) γ and (*d*) MJ samples (——) before and (– – –) after redox cycles at 450 °C.

temperature, during the analysed time, oxygen diffusion in the lattice being very slow: reversibility was observed at 450 °C [fig. 5 and 6(*a*)]. In β-phase reoxidation, reversibility was not achieved when sublayers were involved (450 °C), as shown in fig. 6(*b*) where characteristic i.r. bands of the α and γ phases are also visible.

The results obtained with the γ phase (fig. 2,4 and 5) show good agreement with previous data,[15] suggesting that this phase is the most reducible and the most promptly stabilized: the reduction–reoxidation process is reversible at high temperatures [fig. 5 and 6(*c*)].

The multiphase MJ sample, composed by β and γ phases, presents intermediate behaviour: the electrical conductivity at high temperatures is similar during reduction to that of its less reducible component (β phase). and is similar during reoxidation to that of its more easily oxidized component (γ phase) [fig. 5 and 6(*d*)].

CONCLUSIONS

From the electrical-conductivity data for the four bismuth molybdates studied (α, β and γ phases and mixed β+γ phases) the following points can be deduced. (1) In oxygen, after preoxidation, the solids behave as intrinsic semiconductors with low conductivities, independent of oxygen pressure in the range 2–160 Torr, as would be consistent with the stoichiometric composition and the absence of anionic vacancies in equilibrium with P_{O_2}. (2) In the presence of but-1-ene the solids become highly conductive because of the formation of singly ionized vacancies due to the oxidative dehydrogenation of C_4H_8 into C_4H_6 [reaction (1)]. The rates of reduction of the solids, deduced from variations of σ, vary in the same way as those obtained from pulse-reactor kinetics ($\gamma > \alpha >$ MJ $> \beta$). (3) Reoxidation of butene-treated samples by O_2 at 280 and 350 °C causes the conductivity to decline towards values originally observed for oxygen-pretreated samples, consistent with reconstitution of surface lattice anions from anion vacancies caused by reduction. (4) From conductivity cycles in butene and oxygen it was observed that the initial rates of reduction are higher than the initial rates of oxidation, which shows that the surfaces of the solids are in a slightly reduced state (Mars and Van Krevelen mechanism). (5) Electrical-conductivity measurements and infrared spectroscopy gave complementary results showing that the α and γ phases undergo reversible surface structural changes in redox sequences at 450°, in contrast to the β phase.

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[1] G. W. Keulks, L. D. Krenzke and T. M. Notermann, *Adv. Catal.*, 1978, **27**, 183.

[2] R. K. Grasseli and J. D. Burrington, *Adv. Catal.*, 1981, **30**, 133.

[3] A. Bielanski and J. Haber, *Catal. Rev.*, 1979, **19**, 1.

[4] D. Carson, G. Coudurier, M. Forissier, J. C. Védrine, A. Laarif and F. Théobald, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 1921.

[5] M. M. Oliveira, M. F. Portela, M. J. Pires and F. R. Ribeiro, *Can. J. Chem. Eng.*, 1983, **61**, 87.

[6] M. F. Portela, M. J. Pires and M. M. Oliveira, *Proc. 8th Iberoamer. Symp. Catal.*, Huelva, Spain, 1982, p. 374.

[7] M. J. Pires, M. F. Portela, M. M. Oliveira, A. Saraiva and T. Miranda, *Proc. 7th Iberoamer. Symp. Catal.*, La Plata, Argentina, 1980, p. 189.

[8] G. W. Keulks, J. Hall, C. Daniel and K. Suzuki, *J. Catal.*, 1974, **34**, 79.

[9] P. A. Batist, J. F. H. Bowens and G. C. A. Schuit, *J. Catal.*, 1972, **25**, 1.

[10] C. R. Adams, H. H. Voge, C. Z. Morgan and W. E. Armstrong, *J. Catal.*, 1964, **3**, 379.

[11] J-M. Herrmann, *J. Chim. Phys.*, 1974, **73**, 474; 479.

[12] J-M. Herrmann, J-L. Portefaix, M. Forissier, F. Figueras and P. Pichat, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1346.

[13] J-M. Herrmann and B. Benaïchouba, *React. Kinet. Catal. Lett.*, 1983. **22**, 209.

[14] J-M. Herrmann and P. Pichat, *J. Catal.*, 1982, **78**, 425.

[15] M. M. Oliveira, M. F. Portela, M. J. Pires, *5th Portug. Nat. Conf. Chem.*, Porto, Portugal, 1982.

[16] M. F. Portela, M. M. Oliveira, M. J. Pires, F. M. S. Leonos and L. Ferreira, *Proc. 8th Int. Congr. Catal.*, West Berlin, (Verlag Chemie, Weinheim, 1984), vol. II, p. 533.

[17] J. F. Brazdil, D. D. Suresh and R. K. Grasselli, *J. Catal.*, 1980, **66**, 347.

[18] P. Mars and D. W. Van Krevelen, *Chem. Eng. Sci. Suppl.*, 1954, **3**, 41.

[19] M. Egashira, H. Sumie, T. Sakamoto and T. Seyama, *Kogyo Kageku Kyokai-Shi*, 1970, **73**, 860.

[20] M. F. Portela, *Proc. 8th Iberoamer. Symp. Catal.*, Huelva, Spain, 1982, p. 315.

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