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Tin-119 Mössbauer Investigations of Mixed Oxide Catalysts

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Tin-119 Mössbauer spectra show that the cationic oxidation states and crystal structures of some mixed oxide catalysts remain unaltered by the adsorption of acidic or basic molecules. Reaction of the oxides with either hydrogen or butenes gives reduced catalysts in which the retention of the tin atom with an oxidation state of (IV) is accompanied by an attenuation of the electric field gradient at the tin nuclei. The results are related to the catalytic properties of these materials.

Introduction

The potential value of Mössbauer spectroscopy for the study of catalysts has been demonstrated during investigations of supported microcrystallites [1] and is also reflected in the rapid development of Conversion Electron Mössbauer Spectroscopy for the specific examination of solid surfaces [2]. The direct investigation of the electronic environment of bulk nuclei by conventional transmission Mössbauer spectroscopy has also been shown to be informative in the study of the fundamental properties of catalytically active materials [3]. Tin–antimony oxides containing less than 10% antimony and calcined at 600 °C were found to be single phased materials for which the tin-119 Mössbauer parameters could be correlated with the catalytic character of the material. No evidence was found for the formation of reduced tin species. The samples containing more than 10% antimony appeared to contain an additional antimony oxide phase.

Although the catalytic properties of tin-antimony oxides in the selective oxidation, oxidative dehydrogenation and ammoxidation of hydrocarbons have provoked several investigations there seems to be little unanimity as to the nature of the active sites and whether or not any changes in oxidation state and lattice structure accompany the adsorption and catalytic processes [4]. The power of Mössbauer spectroscopy in the elucidation of such matters is well established and this work reports some tin-119 Mössbauer investigations of tin–antimony oxides and tin–molybdenum oxide catalysts when used in adsorption and catalytic reactions.

Experimental

Stannic oxide, tin–antimony- and tin–molybdenum-oxides of the type $Sn_{1-x}M_xO_2$ (M = antimony or molybdenum) were prepared by methods which have been previously described [3]. The samples were calcined at 600 °C and treated by (*a*) pyridine at 200 °C or acetic acid at 150 °C until a steady rate of adsorption and desorption was obtained; (*b*) a 10% hydrogen/90% nitrogen gas mixture at 480 °C; (*c*) a 5% butene/10% oxygen/85% nitrogen gas mixture at 400 °C.

Tin-119 Mössbauer spectra were recorded at 77 K using a conventional constant acceleration spectrometer with a $Ca^{119m}SnO_3$ source and samples containing 10 mg Sn/cm^2. The drive velocity was calibrated with a ^{57}Co/Rh source and iron foil. Spectra of stannic oxide were also recorded at frequent intervals to provide both a means of internal calibration and a standard to which the isomer shift data have been referred.

Results

The tin–antimony oxides were reduced by the hydrogen/nitrogen gas mixture by 4%, 10% and 30%. The tin-119 Mössbauer parameters of the tin–antimony oxides after reaction with hydrogen and following their use in the catalytic oxidation of butene are given in Table I.

Discussion

The adsorption of acetic acid (up to 4.31 μmol m^{-2}) and pyridine (up to 2.69 μmol m^{-2}) on oxides of formula $Sn_{1-x}Sb_xO_2$ (x = 0.00, 0.02, 0.10, 0.75)

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TABLE I. Tin-119 Mössbauer Parameters for Tin–Antimony Oxides ($Sn_{1-x}Sb_xO_2$) Following Reduction with Hydrogen and Catalysis of the Oxidation of Butene.

x	Treatment	$\delta(SnO_2) \pm 0.03$/mm s^{-1}	$\Delta \pm 0.03$/mm s^{-1}
0.20	–	0.15	0.75
	Reduced by 4%	0.18	0.72
	10%	0.18	0.69
	30%	0.11	0.66
	Oxidation of butene	0.04	0.67
0.02	–	0.05	0.66
	Oxidation of butene	–0.05	0.56

gave no significant alteration to the Mössbauer parameters of the pure materials. It is clear therefore that despite infrared evidence for the adsorption of bases to Lewis acid sites on metal oxides [5, 6] the processes are unlikely to involve the bulk tin cations in tin(IV) oxide or mixed tin–antimony oxide catalysts in a charge balancing role or give any significant modification to the rutile type lattice structures.

A tin–molybdenum oxide ($Sn_{0.98}Mo_{0.02}O_2$) which can be used for the catalytic oxidation of propylene to acrolein gave a tin-119 Mössbauer spectrum (δ 0.03 mm s^{-1}) which showed that the tin(IV) species is not reduced to tin(II). The result is therefore compatible with esr investigations [7] which described the material as one in which pentavalent molybdenum ions took up substitutional sites in the rutile stannic oxide lattice. The quadrupole splitting (Δ 0.68 mm s^{-1}) is comparable with that recorded for the tin–antimony oxide of analogous composition (Table I) and reflects similar distortion of the stannic oxide lattice by the replacement of tin(IV) ions with different cations of similar size. Subsequent Mössbauer spectra showed the oxide to be unaffected by the adsorption of 1.6 μmol m^{-2} of pyridine at 400 °C despite the reported reduction of tin and iron during the chemisorption of hydrocarbons on tin–molybdenum- and iron–molybdenum-oxide catalysts [8–10].

The tin–antimony oxide containing 20% antimony when reduced by hydrogen gave chemical isomer shifts which were, within the limits of experimental accuracy, identical to those of the pure mixed oxide. It may be surprising that reduction by as much as 30% gives no evidence for the formation of tin(II). Separate Mössbauer experiments showed that tin(II) in stannic oxide is easily detectable when present in quantities above 2 mol%. The decrease in quadrupole splitting which accompanied the increased reduction is also significant since it reflects a diminishing electric field gradient at the tin nuclei. The two tin-119 Mössbauer parameters are therefore consistent with the reduction of antimony to a lower charged species causing an attenuation of the valence contribution to the electric field gradient at the tin nuclei.

The tin–antimony oxides containing either 20% or 2% antimony when used as catalysts for the oxidation of butene gave more negative chemical isomer shifts and smaller quadrupole splittings than the pure mixed oxides. The process therefore resembles the hydrogen reduction of the tin–antimony oxides although the diminution of the electric field gradient during the catalytic reaction is accompanied by a simultaneous decrease in the electron density at the tin nuclei. The compound containing 20% antimony may be described in terms of the rutile tin(IV) oxide with antimony in substitutional sites plus an additional Sb_6O_{13} phase [3]. Since hydrogen reduction of the tin–antimony oxides does not involve the tin species the tin-119 Mössbauer data for the reaction of the mixed oxide containing 20% antimony under catalytic conditions can be associated with either the reduction of antimony in the rutile phase or the reduction of Sb_6O_{13} to antimony(III) oxide. The compound $Sn_{0.98}Sb_{0.02}O_2$ is quite different since it represents the single phase material containing antimony in the tin oxide rutile lattice. It is significant that the tin-119 Mössbauer parameters of this material following its use in the catalytic process are remarkably similar to those of pure tin(IV) oxide. This decrease in electron density at the tin nuclei and the apparent recovery of the lattice structure implies a decrease in both the lattice and valence contribution to the electric field gradient at the tin nucleus as a result of the reduction of antimony(V). It seems therefore that the formation of materials in which $x < 0.10$ involves the substitution of antimony(V) for tin(IV) in the stannic oxide lattice and, if confirmed, would provide further evidence for the achievement of charge balance in tin–antimony oxides by the delocalisation of electrons into conduction bands [11] as suggested by the previous Mössbauer and esr study [3]. The failure of tin-119 Mössbauer spectroscopy to identify any reduction of tin(IV) to tin(II) and the presumed reduction of substitutional antimony(V) during the catalytic reaction may be correlated with mechanisms which have been proposed for the chemisorption and catalytic reactions of olefins on tin–antimony oxides [12, 13] which have involved partial reduction of antimony(V) to antimony(III) and the formation of a π allyl intermediate species [14]. A similar mechanism has been postulated for the reaction of propylene on tin–molybdenum oxide catalysts [15].

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