Reductive coupling desorption of methanol on reduced SrTiO₃(110)

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The adsorption and reaction of methanol with $SrTiO_3(110)$ has been studied using temperature-programmed desorption and X-ray photoelectron spectroscopy. The main organic products are methane and ethane, though the exact ratio of these depends on sample history and defect levels in the surface and bulk. It is likely that the methanol dissociates to form adsorbed methyl groups associated with reduced Ti^{3+} and Ti^{2+} centres which were formed by Ar^+ bombardment. We tentatively associate ethane formation with the latter sites and dialkyl formation, while methane production may be associated with the former sites and monoalkyl formation.

1 Introduction

The oxidative addition/reductive elimination process at a metal ion site is a crucial feature in some homogeneous catalysts system as has been demonstrated for Wilkinson's Rh catalyst¹ or for the Co catalyst in the oxo process.² This step can be described as follows:



In general terms, as a result of the oxidative addition, both the coordination number and the oxidation number of the metal centre increase by two units. The reductive elimination is the opposite process of the oxidative addition.

Whereas the importance of the above chemistry in homogeneous catalysis is established, the process has rarely been discussed in the area of heterogeneous catalysis for gas-solid systems. This may reflect either the difficulty in the heterogeneous case of characterising the adsorbate-solid interaction, or a difference in the chemistry involved in the catalytic cycles between the two systems. Gates³ states that "reactivity of metal clusters is not a good basis for prediction of the reactivity of ligands adsorbed on a surface. Nonetheless, the concept of isolated reactive sites on surfaces as molecular analogues is extremely valuable and borne out by a mass of experimental results." He stresses the importance of local structures for catalytic activity and surface reactivity, rather than the bulk properties, such as electronic structure.

The surface science approach, which examines the adsorbate-solid interaction under UHV conditions, could provide an insight into the chemistry shown above because of its "cleanliness". In this sense, transition metal oxides would be suitable for the investigation, since they are used as catalytic materials and transition metal ions can change their oxidation state and coordination number in such circumstances. Pierce and Barteau⁴ found cyclotrimerisation products on reduced TiO₂(001) and ascribed this reactivity to the presence of Ti²⁺. In the present study, a SrTiO₃(110) single crystal was chosen as the model surface and examined by XPS (X-ray photoelectron spectroscopy) and TPD (temperature-programmed desorption), and probed using a model reactant, methanol.

The structure of $SrTiO_3$ and the (110) surface is shown in Fig. 1. The bulk is of the perovskite type and the (110) plane consists of Ti, O and Sr. Although the coordination around Ti is identical, there are two types of O. It is widely accepted that Ti in the fully oxidised state is in the +4 oxidation state (d⁰) and in O is in the -2 oxidation state. Because of this, the fully oxidised surface could work as an acid-base centre for adsorbates at ambient conditions. In this work, we examine



Fig. 1 (a) Bulk structure of $SrTiO_3$ which is a perovskite lattice and (b) the (110) surface structure, showing the two types of oxygen which may exist on the perfect termination. The numbers in (b) correspond to those shown in (a).

the adsorption-desorption properties of methanol on the reduced surface prepared by *in situ* Ar^+ sputtering.

2 Experimental

2.1 Apparatus

All the experiments were carried in a conventional UHV chamber with a base pressure in the 10^{-10} mbar range. The main background masses in the chamber were 2 (hydrogen), 15,16 (methane) and 28 (carbon monoxide). SrTiO₃(110) (Pikem) was mounted without any pre-treatment. The back side and a small part of the front side was covered with gold foil. It was either heated by the radiation of a W filament from the back side or cooled by liquid nitrogen constant flow into the copper block mounted above it and connected to the gold foil. The temperature was monitored with a chromel–alumel thermocouple, which was sandwiched between the gold foil and the sample surface at the front side. A glass vial filled with methanol (99.8 + %, BDH) was connected to the dosing line of the main chamber, and purified *via* freeze–thaw cycles.

2.2 Sample treatment

The sample was oxidised by heating in 1×10^{-6} mbar O₂ (99.0%, ARGO) at 820 K for 10 min and subsequently cooled in oxygen to 353 K. Ar (99.999%, ARGO) ion sputtering (at 500 K, 4.0 kV-1 μ A in the scanning mode) was used for the reduction of the sample, and since the ion gun was differentially pumped the pressure in the main chamber was 5×10^{-7} mbar. Annealing at 820 K tended to reoxidise the surface sub-



Fig. 2 (A) Angle dependence of the Sr 2p and C 1s spectra of SrTiO₃(110) covered by the contaminant carbon species, measured at (a) 0°, (b) 20°, (c) 60°, (d) 70° and (e) 80° from the surface normal, showing the increase of the relative intensity of Sr/C at high angles. (B) Dependence of the C 1s/Sr $3p_{3/2}$ area ratio upon the angle emission with respect to the surface normal, calculated from Fig. 2(A) (C 1s cross section 1, Sr 4.4).

stantially; however, an almost completely oxidised surface was easily obtained by oxygen treatment at 820 K.

2.3 Experimental procedure

After the pre-treatment of the sample, methanol was dosed to the main chamber at a constant pressure in the range $5 \times 10^{-9} - 4 \times 10^{-6}$ mbar for varying lengths of time. TPD or XPS spectra were measured with the background pressure below 3×10^{-9} mbar.

2.4 XPS (X-ray photoelectron spectroscopy)

Al-K α (1486.6 eV) radiation was used for the photoemission measurements. The photoelectrons were collected by a conventional CHA analyser (100 mm ϕ , VSW Ltd) with a pass energy of 20 eV. During measurement, the sample was earthed through the thermocouple line.

In general, XPS has been shown to be useful for the analysis of chemical states due to the chemical shift of the core level binding energy for different valence states. The states chosen for the analysis were Ti $2p_{3/2}$, $2p_{1/2}$, O 1s, Sr $3p_{3/2}$, $3p_{1/2}$ and C 1s, respectively.

The binding energy reference for the peak position was either Sr $3p_{1/2}$ or $3p_{3/2}$ at 279.5 and 269.1 eV, respectively, on the assumption that the position in the binding energy scale would not change with the experimental conditions, since the spectral shapes were hardly affected throughout the treatments shown in Table 1. By doing this, the charging effect on the measured kinetic energy of photoelectrons is corrected. When the Au 4f (from the sample holder) was used as a reference, the peak positions were not consistent for the series of the spectra, which is owing to charging of the oxide, while the Au was truly earthed.

2.5 Angle dependence of XPS

XPS spectra were taken at a glancing emission angle in the present paper unless otherwise noted. This is to get precise information on the composition of the surface layer(s). The angle was adjusted by turning the manipulator connected to the sample support. The angle between the X-ray gun and the analyser was about 75° .

Fig. 2(A) demonstrates that the intensity both of C 1s and Sr 3p signals changed with variation of the electron take-off angle. As the C was on the surface, the change of the C 1s is mainly the result of the effect of the change of X-ray flux intensity. On the other hand, the change of the Sr signal would be affected by variation of both the inelastic mean free path of the photoelectrons and X-ray flux.

The angle dependence of the Sr/C atomic ratio normalised by $\cos \theta$ is shown in Fig. 2(B) and this supports the above consideration. The area of Sr $3p_{3/2}$ (normalised to C integral) changed by more than 6 times between glancing and normal angle. Consequently, as expected, the spectra taken at a glancing angle are much more surface sensitive than the normal angle analysis.

2.6 TPD (Temperature-programmed desorption)

The sample was radiatively heated from the back and was positioned 2 cm from the quadrupole mass analyser (VG). At the beginning of the heating, typically in the 300–350 K range, there was an induction period of non-linear heating which was followed by a constant heating rate, typically ~ 5 K s⁻¹, over the range 350–650 K.

3 Results

3.1 Sample pre-treatment

After the oxidation treatment, the XPS spectrum of Ti 2p showed a simple peak characteristic of the Ti⁴⁺ ion [Fig.



Fig. 3 XPS spectra of $SrTiO_3$ for oxidised and sputtered surfaces: (a) Sr 3p, (b) Ti 2p, (c) O 1s.

3(b)]. The peak features for each element are summarised in Table 1. The values of FWHM (full-width half-maximum) were 2.1 and 3.0 eV for Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, for FAT (fixed analyser transmission) 44 mode and each peak could be fitted with a single Gaussian. From the results of

quantitative peak analysis in Table 2, it was apparent that the topmost layer(s) were richer in oxygen than the sublayers (No. 1, 2). This might suggest that the top layer on a nearly fully oxidised surface is, at least partially, covered by oxygen.

As a result of Ar^+ ion sputtering, the Ti 2p spectrum changed its shape as shown in Fig. 3(b). Broadening of the spectrum indicates the creation of new valence states, owing to some conversion of Ti⁴⁺ into lower oxidation state(s). The peak area was estimated to be decreased by about 20%. The O 1s [Fig. 3(c)] spectrum has become broader with asymmetric tailing to a higher binding energy region, and could not be fitted with a single Gaussian. The intensity of O signal has decreased by about 30%, indicating that oxygen species were preferentially removed by sputtering. The Sr $3p_{3/2}$ spectral shape (FWHM) was almost unchanged by the treatment as shown in Fig. 3(a) and Table 1.

3.2 TPD of methanol on highly reduced SrTiO₃(110)

Thermal desorption after methanol dosing was carried out on the reduced SrTiO₃(110) crystal. After the reduction by Ar⁺ sputtering, methanol was dosed at room temperature with a base pressure in the machine of around 5×10^{-10} mbar. Fig. 4 shows a typical TPD example after dosing 4×10^{-6} mbar for 1800 s. The main features were the desorption of ethane, methane and some hydrogen around 400 K, and carbon monoxide/hydrogen around 700 K. A broad feature was observed for methanol over a wide range of temperature, possibly owing to background desorption from the sample support assembly. Ethane was identified by its cracking pattern which has major masses in the order 28, 27, 30, 26 and 29. In the figure only mass 27 and 28 are shown. The profiles of CO and hydrogen at high temperatures have a similar shape, suggesting coincident desorption.

3.3 XPS

The analysis of the reaction pathway was attempted by XPS. Fig. 5 shows the XPS spectra at several points in the TPD



Fig. 4 TPD spectrum following methanol adsorption on reduced $SrTiO_3(110)$ at room temperature. The numbers refer to the relative molecular mass of the species desorbed.

Table 1 Binding energy ^a and FWHM (eV) of each component (FAT 44)							
Element chemical state	Sr		Ti(rv)	0			
	3p _{3/2} /eV	3p _{1/2} /eV	2p _{3/2} /eV	$2p_{1/2}/eV$	1s/eV		
Oxidised ^b Oxidised ^d Sputtered ^e	269.1(3.2) ^e 269.1(3.2) 269.1(3.3)	279.5(3.2) 279.5(3.2) 279.5(3.3)	458.8(2.1) 458.6(2.1) 458.4 ^f	464.4(3.0) 464.5(3.0) 464.2 ^f	530.7(2.2) 530.5(2.2) 530.2 ^f		

^{*a*} Peak position. ^{*b*} Treated in oxygen at 820 K, analysed at $+20^{\circ}$. ^{*c*} The value of FWHM is shown in parentheses. ^{*d*} Treated in oxygen at 820 K, analysed at $+80^{\circ}$ (glancing angle). ^{*e*} Sputtered, analysed at $+80^{\circ}$ (glancing angle). ^{*f*} Results by Gaussian function fitting.

 Table 2
 Quantitative XPS peak analysis^a of the methanol dosed surface

	O/Ti (1)	Sr/Ti (2)	O/Sr (3)	(1)–(2) (4)	A.O.N. [(4) × 2] (5)	(Curve-fitting) (6)	(6)–(5) (7)	Conditions
1^b	3.05	1.05	2.90	2.00	4.00	4	0	Ox. ^c
2	3.18	1.09	2.92	2.09	4.18	4	-0.18	Ox., ^c gl. ^d
3-A ^e	2.70	1.25	2.07	1.45	2.90	3.05	0.15	Sp., ^f gl. ^d
3-B ^e	3.23	1.33	2.43	1.89	3.79	3.22	-0.57	$\operatorname{Sp.}^{f} \operatorname{gl.}^{d}$

^{*a*} See details in the Section 4.4 (A.O.N. = average oxidation number). ^{*b*} Analysed at $+20^{\circ}$ sensitivity factors were decided based on this data, cross section, Sr: 4.4, Ti: 7.9, O: 3.4. ^{*c*} Treated in oxygen at 820 K. ^{*d*} Analysed at $+80^{\circ}$ (glancing angle). ^{*e*} Symbol A: pre-treated by Ar⁺ bombardment, B: after methanol dose. ^{*f*} Sputtered.



Fig. 5 XPS spectrum after methanol TPD: (a) Sr 3p, C 1s, (b) Ti 2p, (c) O 1s.

experiment, *i.e.* after pre-treatment, after methanol dosing and after TPD.

After methanol dosing, a C 1s peak centred around 286.5 eV has appeared with FWHM of 2.2 eV, and a high binding energy shoulder has appeared in the O 1s, owing to the adsorbed species. The Ti 2p region has changed, the peak becoming narrower with the adsorption of methanol. This means that some of the reduced Ti has been oxidised (oxidative addition). The Sr 3p peak shape was almost unaffected by this adsorption.

After TPD, the C 1s intensity decreased to the background level. Almost all the C species were desorbed by heating. The shoulder of the O 1s, which had been formed by methanol adsorption, disappeared and the oxygen species are therefore either desorbed or incorporated as lattice oxygen. The Ti 2p spectrum has become broader again, suggesting that the rereduction of Ti species has occurred. This effect is not merely due to heating. The oxidation of Ti proceeds by the diffusion of oxygen from the bulk to the surface. Therefore, the broadening of the Ti 2p was accompanied by desorption of the C-containing species. Since no significant C peak was found after TPD, we can safely say that reductive-elimination has occurred.

3.4 Curve-fitting of Ti 2p

The deconvolution of the Ti 2p spectrum of the reduced sample is complex. First of all, the titanium ion can take several oxidation states, which are supposed to be separated by a few eV. Each oxidation state has two peaks, which are 5-6 eV apart in the spectrum due to spin-orbit interaction in the photo-emission process. Therefore the position and the shape (FWHM) corresponding to each species has to be decided to deconvolute the Ti 2p spectrum. Secondly, owing to the large step in background signal on each side of the peak envelope, the correct background subtraction is essential for this analysis. Nevertheless, we attempt here to quantify the nature of the reduced surface. The identification of the peak positions of lower valence states of Ti was done by several other workers^{5–9} and is summarised in Table 3. It is possible to assign the oxidation states to Ti²⁺, Ti³⁺ and Ti⁴⁺ for the reduced SrTiO₃(110).

Table 3 Ti $2p_{3/2}$ peak positions $(eV)^a$ for lower oxidation states

Ti ²⁺	Ti ³⁺	Ref.
-3.7	-1.8	5
-3.5	-1.7	6
-3.9	_	7
_	-1.5	8
-3.8	_	9
-3.9	-1.8	This work

⁴ Referenced to Ti⁴⁺ peak position.

Table 4 Comparison of the deconvolution reults for Ti 2p spectra taken at different FAT modes

	FAT 22	FAT 22		FAT 44	FAT 44	
Resolution	2p _{3/2} /eV ^a	$2p_{1/2}/eV$	Relative ratio $(\%)^b$	2p _{3/2} /eV ^a	$2p_{1/2}/eV$	Relative ratio $(\%)^b$
Ti ²⁺	454.4(2.2)	460.1	27.6	454.5(2.6)	460.0	28.6
Ti ³⁺	456.5(2.1)	462.0	24.8	456.6(2.4)	462.2	25.5
Ti ⁴⁺	458.4(1.9)	464.2	47.6	458.4(2.1)	464.2	45.9
		1 hall.				

^a The value of FWHM is shown in parentheses. ^b Calculated figures based on the peak area.



Fig. 6 Deconvoluted Ti 2p spectra of Fig. 5(b): (a) sputtered surface, (b) methanol dosed surface.

Table 5 Ti 2p deconvolution results for methanol adsorption

No.ª	Ti ²⁺ (%)	Ti ³⁺ (%)	Ti ⁴⁺ (%)	A.O.N. ^b	Δx^{c}	C/Ti ^d
3-A	34.2	26.6	39.3	3.05		
3-B	26.0	26.0	48.0	3.22	0.17	0.75

^{*a*} No. corresponds to that of Table 2. ^{*b*} Average oxidation number, calculated by the eqn. (3). ^{*c*} The change of A.O.N. after methanol dose. ^{*d*} Atomic ratio of C to Ti based on C 1s and Ti 2p area (cross section C: 1.0, Ti: 7.9).

Background subtraction was carried out according to the procedure of Procter and Hercules.¹⁰ After background subtraction, the spectrum was found to fit well with the above assumption, *i.e.* Ti 2p consisted of three paired species as shown in Fig. 6. The extreme low and high binding energy edge shape is informative, because it may reflect the signal of a single species. In the present case, it was concluded that one species exists, since the edges were found to fit with a single Gaussian function for different resolution measurement (FAT 44 and 22). The results are summarised in Table 4. The peak envelope could not be fitted by two contributing states (*i.e.* Ti³⁺ and Ti⁴⁺). The lowest binding energy peak was assigned to Ti²⁺, because it is located 3.9 eV lower than that of Ti⁴⁺ (Table 3). The possibility of the existence of Ti¹⁺ or Ti⁰ species was excluded by these considerations.

These deconvolution procedures were applied to the spectra after methanol dosing and the results are shown in Fig. 6 and Tables 5 and 6. It is clearly demonstrated in Table 5 that, after the adsorption, the Ti^{4+} proportion has increased with a decrease in the amount of Ti^{2+} after methanol adsorption, whereas the ratio of Ti^{3+} species remained constant. The result therefore indicates that methanol adsorption is accompanied by the oxidation of Ti^{2+} species to Ti^{4+} species.

3.5 Estimation of the analysis depth of XPS

The escape depth, λ , which is the distance from the surface at which the signal intensity decreases to (1/e) of that from the surface layer, can be expressed in eqn. (1).

$$S \propto \int e^{(-X/\lambda)} dx$$
 (1)

where, S = XPS peak area, $\lambda = \text{escape}$ depth and X = distance from the surface. This equation can be applied to the results of angle variation measurements by replacing λ with $\lambda \cos \theta$, since the Sr/C data showed the $\cos \theta$ dependence in Fig. 2(B). The analysis depth at the glancing angle (80°) was calculated from the escape depth at a normal angle. The results are shown in Fig. 7 for three different escape depths, namely 20, 30 and 40 Å. The analysis depth at the glancing angle would range between 3.4–6.8 Å for these escape depths. As the distance between the (110) planes is 2.8 Å in the ideal crystal, the analysis depth would be *ca.* 2–3 layers from the

 Table 6
 Ti 2p deconvolution results for various amount of methanol adsorption

No. ^a	Ti ²⁺ (%)	Ti ³⁺ (%)	Ti ⁴⁺ (%)	A.O.N. ^b	Δx^{c}	C/Ti ^d	MeOH dose ^e /L
$\begin{array}{c} 4\text{-}\mathrm{A}^{f} \\ 4\text{-}\mathrm{B}^{f} \end{array}$	32.4 29.9	26.5 25.8	41.2 44.3	3.09 3.14	0.05	0.49	6
5-A 5-B	41.2 34.9	25.4 27.4	33.3 37.7	2.92 3.03	 0.11	0.78	<u> </u>
6-A 6-B	39.5 33.3	27.7 26.3	32.8 40.4	2.93 3.07	0.14	0.77	50
7-A 7-B	36.4 26.7	27.1 27.8	36.4 45.6	3.00 3.19	0.19	0.88	500



Fig. 7 Simulated photoelectron decay curve based on eqn. (1), for three escape depths: (a) 20, (b) 30, (c) 40 Å; (a'), (b') and (c'): simulation for angle variation ($\theta = 80^{\circ}$) for the three escape depths, showing the increase of the first layer contribution to the total at glancing exit.

surface. Therefore, by using eqn. (1) the contribution of the first layer to the XPS peak was estimated as 25-45% on the assumption that first layer depth is 2 Å. It should be noted that the actual surface would have a roughness, by Ar^+ bombardment, that would affect the decay features of photoelectrons to some extent.

4 Discussion

The significant features of the reaction of methanol with the reduced $SrTiO_3(110)$ surface can be summarised as follows:

- 1. Methanol is adsorbed on the reduced $SrTiO_3$ surface at room temperature.
- Ethane was formed during TPD (C-C bond formation).
 A part of the reduced Ti was reoxidised by the adsorp-
- tion process (oxidative-addition).
- 4. The desorption process resulted in the reduction of Ti (reductive-elimination).

4.1 Adsorption of methanol on Ti²⁺

From the deconvolution results of Ti 2p XPS spectra, new insights for the methanol adsorption process at room temperature can be derived. A two-electron transfer from Ti^{2+} to methanol moieties has occurred during the adsorption process. In general, Ti^{2+} species are strong reducing agents, which are known to be able reduce even water. The presence of Ti^{2+} is the result of preferential removal of oxygen by Ar^+ sputtering and this also would decrease the coordination number of Ti. Therefore the Ti^{2+} ion, having both a low coordination number and high reduction potential, would have a strong affinity for the oxygen in the methanol molecule and appears to reduce it during the adsorption, as shown by the alkane products in TPD. This is discussed further in the next section.

4.2 C-C bond formation

C-C bond formation is a well-known reaction in organometallic compound decomposition. It often proceeds by an intramolecular reductive-elimination process as shown in Scheme 2.

Ethane is the coupling product of methanol-derived C species. To the best of our knowledge, this is the first observation of ethane as a main TPD product from methanol on single crystal metal oxides. Carrizosa *et al.*¹¹ observed ethane as one of the TPD products of methanol adsorption on pow-



dered anatase. They proposed dialkyl species as the ethane precursor formed at temperatures greater than 723 K as shown in species (I) below. By analogy with the organometallic compounds, in the present case a dialkyl species or dinuclear species I(b), would be a possible precursor, and this is formed at room temperature in these experiments (lattice oxygen is not shown in species I).



The binding energy (286.5 eV) of the C species is lower than that of molecular methanol (287.1 eV, dosed and measured at 170 K), and higher than that of carbidic carbon at 285 eV. On the other hand, the binding energy of the oxygen "shoulder" formed by room temperature adsorption was ~ 2 eV lower than that of methanol adsorbed at 170 K. This indicates that the oxygen species are more basic than methanol oxygen (assuming that at 170 K methanol is physisorbed). Therefore, it would have an anionic character similar to the hydroxide or methoxide ion. Thus, the C species is either a methyl or methoxy species. These considerations support the above precursors (I). [Methyl and hydroxy groups can be replaced by methoxy and hydrogen in species (I).] The fact that the desorption spectra of ethane showed first-order features, namely an asymmetric shape, would also lend some support to this proposal.

4.3 Quantification of the amount of desorbed ethane

By using eqn. (2) the amount of ethane desorbed was estimated.

$$\theta = (v/RT)A \tag{2}$$

where θ = surface coverage, v = pumping capacity, R = gas constant, T = temperature and A = area of the TPD spectrum

In the case of Fig. 4, the amount of desorbed ethane was estimated as 2.5×10^{13} molecules. On the other hand, the number of Ti cations on the fully oxidised $SrTiO_3(110)$ surface is estimated at 1.6×10^{14} atoms based on the assumption that the surface has no cation defects. The number of Ti cations on the sputtered surface was estimated to be 20% less than that of the oxidised surface (Section 3.1). The ratio of ethane molecules desorbed to surface Ti atoms is then 0.20 on the assumption that the top layer has an equivalent Ti concentration to the analysed region. The amount of methanol desorbed as ethane therefore corresponds to 40% of the number of surface Ti cations.

4.4 Average oxidation number (A.O.N.) of Ti

The A.O.N. can be defined in the following way. From the results of the deconvolution of Ti 2p spectrum, the relative ratio of each species was calculated based on the peak area in Table 5. The sensitivity factor for each state was assumed as equal.

Average oxidation number of Ti^{x+}

$$x = \sum_{i} n_i \times C_i \tag{3}$$

where n_i is the oxidation number of species i (2–4) and C_i is the relative concentration of species i.

$$x = (C_{\rm O} - C_{\rm Sr}) \times n_0 / C_{\rm Ti} \tag{4}$$

where C_i is the concentration of species *i*, n_0 is the absolute value of the oxidation number of oxygen.

Although the oxygen species in a reduced sample consists of more than one species as was suggested by the O 1s shape, n_0 was assumed to be 2. Cross sections for each element were decided based on the spectrum area for the nearly fully oxidised sample measured at a 20° emission angle. The values tabulated by Scofield¹² were modified to fit the stoichiometry. The results are summarised in Tables 2 and 7. The two definitions for the A.O.N. of Ti were in good agreement, indicating the average oxidation state of Ti ion on the reduced surface to be around +3.0.

4.5 Analysis of the scheme with the quantified data

By combining the data discussed so far, the process for ethane desorption can be proposed (semi)quantitatively. The amount of ethane is 20% (40% methanol) of Ti atoms in the first layer (Section 4.3). The first layer contribution to the total signal would be in the range 25-45% (Section 3.5). Two views can be drawn for the extremes of our estimate with an assumption that Ti^{x^+} species in the subsurface region do not change their oxidation state by methanol adsorption. For the 45% case, since about 8% of Ti²⁺ is converted into Ti⁴⁺ as a whole, the amount of Ti²⁺ reacted in the first layer is 18% by the above assumption. In this case, 16% of Ti^{x+} ions in the first layer still remains as Ti²⁺. The number of reacted Ti²⁺ and ethane evolved are then in good agreement. This would support the precursor species to be that illustrated in species I(a) above. On the other hand, for the 25% case, since reacted Ti²⁺ would be about 32%, almost all the Ti^{2+} species on the surface would have been converted to Ti^{4+} species. In this case, the precursor species would be I(b). For both cases, ethane molecules will be desorbed as the decomposition product from isolated metal centre(s).

4.6 The application of A.O.N. definitions for methanol dosed surfaces

Although the two definitions of A.O.N. are in agreement for the clean sputtered surface, the results differed greatly when it was applied to the surface with adsorbed methanol. The results are summarised in Tables 2 and 7. The differences of the two definitions range between 0.5 and 1.0 and this large difference can not be explained by either the shielding effect of the adsorbed species (hence the increase in the O/Ti ratio), or by the difference of the escape depth for each element (assuming that all the adsorption is accompanied by oxidation of surface Ti). Therefore, it is suggested that there are other type(s) of adsorption, which do not accompany the oxidation of surface Ti. The adsorption would be either acid-base or molecular type, probably on both Ti³⁺ and Ti⁴⁺ sites as shown below [(II), acid-base type]. The possibility of adsorption on a Sr²⁺ site cannot be excluded, but the fact that the Sr/Ti ratio has increased about by 10% after the adsorption of methanol may suggest the preferable adsorption on Ti sites.

4.7 The reaction pathway for desorption of ethane, methane, CO and hydrogen

Another example of the TPD which was obtained in this work is shown in Fig. 8. This is a typical example which was observed at the beginning of the series of experiments. The results of Fig. 4 were towards the end of the series of experiments (four months later). In Fig. 8 hydrogen and methane desorption were clearly observed around 400 K. Therefore it



Fig. 8 TPD spectrum following the adsorption of methanol on reduced $SrTiO_3(110)$ from early in the experimental period. Methane is more prevalent and appears at a low temperature than ethane. The numbers refer to the relative molecular mass of the species desorbed.

 Table 7 Quantitative XPS peak analysis of the methanol dosed surface^a

	O/Ti (1)	Sr/Ti (2)	O/Sr (3)	(1)–(2) (4)	A.O.N. [(4) × 2] (5)	A.O.N. (curve-fitting) (6)	(6)–(5) (7)
4-A	2.76	1.25	2.21	1.51	3.02	3.09	$0.07 \\ -0.50$
4-B	3.20	1.38	2.32	1.82	3.64	3.14	
5-A	2.70	1.19	2.27	1.51	3.02	2.92	$-0.10 \\ -0.93$
5-B	3.17	1.19	2.66	1.98	3.96	3.03	
6-A	2.54	1.16	2.19	1.38	2.76	2.93	$0.17 \\ -0.85$
6-B	3.23	1.27	2.54	1.96	3.92	3.07	
7-A	2.60	1.14	2.28	1.46	2.92	3.00	$0.08 \\ -0.93$
7-B	3.32	1.26	2.63	2.06	4.12	3.19	
^a See captio	ons of Tables 2 and	d 6.					

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can be deduced that methane is the product of the reaction between a CH_3 moiety and hydrogen according to reaction (III). It may be that the onset of hydrogen mobility dictates the formation of methane.

$$CH_3(a) + H(a) \rightarrow CH_4$$
 (III)

$$H(a) + H(a) \rightarrow H_2$$
 (IV)

When the methane desorption was distinct, little CO and hydrogen desorption at high temperature could be observed. High temperature CO and hydrogen desorption would be the sequential decomposition products of the CH_3 moiety perhaps because of a shortage of available hydrogen on the surface (or in the subsurface) in reaction (III). The precursor species could be methoxide on Ti or methyl on lattice O and be identical with $CH_3(a)$ in the above reaction scheme.

$$CH_3O \rightarrow CO + H_2$$
 (V)

Alternatively, it can be written as

$$CH_3(a) + O(a) \rightarrow CO + H_2$$
 (VI)

The path for the production of ethane is likely to parallel that of methane. The difference between them is that hydrogen is required for methane production, but not for ethane (Figs. 4, 6). The reason for the change with time during the experimental period is most likely to be owing to slight changes in the bulk reduction state of the sample, which in turn would affect its semiconducting properties and its surface reactivity. Upon removal from the system the sample was a blue colour, indicative of bulk reduction, whereas initially it was pale opaque yellow.

4.8 Small dose of methanol

To examine the surface reactivity, the dosed amount was varied. The results of XPS analyses are shown in Tables 6 and 7 and Fig. 9. Even for a few Langmuirs dose of methanol, its adsorption was confirmed by changes in the XPS spectrum.



Fig. 9 Relationship between the increment (Δx) of the average oxidation number of Ti and that of C/Ti per unit change.

This suggests that the reactivity of the surface relates to the degree of the reduction (No. 4, 5) and the reduced $SrTiO_3(110)$ was almost saturated with less than 50 L of methanol dosed. The change of A.O.N. at low coverage (4-B) is smaller than expected. This may imply that the adsorption at the early stage was mainly the type shown in reaction (II) in Section 4.6.

5 Conclusion

The adsorption of methanol on SrTiO₃(110) has been studied using TPD and XPS. On the highly reduced surface Ti²⁺ was present and ethane was a major product from methanol coupling. As a result of the deconvolution of the Ti 2p XPS spectra, it is suggested that two kinds of adsorption sites are involved in methanol adsorption. Ti²⁺ is ascribed to be the oxidative adsorption (addition) site. On the other hand, Ti³⁺ or Ti⁴⁺ is suggested to be active for acid-base adsorption of methanol. As the reduction of Ti was observed after the desorption, the whole process for ethane production can be written as oxidative-addition and reductive-elimination. This type of process is well-known in the field of organometallic chemistry; however, this is the first clear example of this type of reaction and shows the change in the oxidation number at the metal centre involved. Oxygen removed from methanol is incorporated into the surface as lattice oxygen, filling vacancies in the bulk structure.

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