Atom-resolved observation of Na ensembles activating CO₂ adsorption on a TiO₂(110)-(1 × 1) surface as the genesis of basic sites

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We have succeeded in observing the structure-sensitive reaction of CO₂ with TiO₂(110)-(1 × 1) surfaces modified with Na adatoms by scanning tunneling microscopy. At low coverages (0.4 atom/nm² or less) Na adatoms are ionized and adsorbed on the exposed Ti-rows of the substrate. A p(4 × 2) order locally appears at 0.6 atom/nm², and a c(4 × 2) order develops at 0.9 atom/nm². Those Na-modified surfaces are exposed to 10² L CO₂ at room temperature. Post-exposure observation finds chains of bright particles on the c(4 × 2) surface. The asymmetric topography of the individual particles is assigned to the distribution of the LUMO of the adsorbed carbonate. In contrast, dispersed Na adatoms at lower coverages are unable to react with CO₂ at all. The genesis of strong basic sites is thus suggested not to be linearly correlated with Na quantity, but to be correlated with the ordered structure of Na adatoms.

Keywords: acid-base catalysis; alkali additives; scanning tunneling microscopy; carbon dioxide; titanium oxide

1. Introduction

Alkali additives in metal-oxide catalysts have extensively been attracting attention. The base strength of doped catalysts are so remarkably enhanced that they are often termed "super-base" [1,2]. Acid-base reactivity is one of the important properties of metal-oxide catalysts, and its control is of interest in surface chemistry as well as in industrial applications [3,4]. In addition, the oxidative coupling reaction of methane has been found to proceed on oxide catalysts promoted by alkali additives [5,6]. To consider how the alkali additives promote the basic character and activity of metal-oxide catalysts, we have already studied Na-deposited TiO₂(110) single crystal surface by conventional photoelectron spectroscopic techniques [7]. Monolayer (ML) coverage was determined on a break observed in Na(ls) emission intensity plotted versus Na deposition time [7]. Chemisorption of CO₂, a typical acid-base reaction at surface, has further been tested to examine the reactivity of the modified surface [8]. XPS and UPS results have shown that submonolayer coverages of Na adatoms remarkably enhance the adsorption of carbon dioxide on the TiO₂ surface forming carbonate,

\[ \text{CO}_2 + \text{O}_2^- \rightarrow \text{CO}_3^{2-} \]  

where O₂⁻ represents an oxygen ion of the substrate. The enhanced adsorption is attributed to the promotion in the base strength of the oxygen ions by Na adatoms. The amount of carbonates thus formed varied with Na coverage exhibiting an S-shaped dependence, as shown in fig. 1 [8]. A critical coverage of 0.3 ML for carbonate formation coincided with the onset of a c(4 × 2) pattern in low energy electron diffraction (LEED), suggesting a strong structure-dependent character of the promotion.

In the present letter, we report the reaction of CO₂ with Na-promoted TiO₂(110) surface of different Na coverages observed by scanning tunneling microscopy (STM). This is an atomic-scale observation of the mechanism producing structural sensitivity in a reaction on a metal/metal-oxide model catalyst.

Rutile TiO₂ formally comprises Ti⁴⁺ and O²⁻ ions. Each Ti⁴⁺ ion is coordinated to an octahedron of six O²⁻ ions in the bulk crystal [9]. A TiO₂(110) surface prepared by argon ion sputtering and vacuum annealing exhibits a (1 × 1)-ordered structure. A stoichiometric model (fig. 2) is conceived for the (1 × 1) surface [10], where rows of Ti ions (Ti-rows) and ridges of O ions (O-ridges) are alternatively exposed. In recent STM studies [11–15] regular rows were found on the (1 × 1) surface and

![Fig. 1. The amount of adsorbed carbonate on the Na-modified TiO₂(110) surface as a function of Na coverage [8].](image)
assigned to the exposed Ti-rows. In those STM studies also a protruding row-like species containing double strands was found. When the double-strand reconstruction covered the surface, a (1 x 2) pattern accordingly appeared in LEED. Quite recently, Murrey et al. have observed p(4 x 2)-ordered Na adatoms deposited on the TiO$_2$(110)-(1 x 2) surface by STM [16]. The interpretation of the double-strand topography on the reconstructed surface remains controversial: an added Ti$_2$O$_3$ row model (fig. 2) [12], and three types of missing-oxygen row models [11,14,17] have been proposed. An STM study of a DCOO-covered TiO$_2$(110) surface [15], where Ti ions on the surface were titrated by imaging individual formate ions, revealed the absence of Ti ions exposed on the double-strand row. This gives strong evidence for the added Ti$_2$O$_3$ row model as a surface-limited phase of titanium oxide. In the present study on the unreconstructed TiO$_2$(110)-(1 x 1) substrate, we have resolved individual Na atoms in the c(4 x 2)-ordered adlayer responsible for the CO$_2$ adsorption.

2. Experimental

The experiments were performed in a scanning tunneling microscope (STM4500VT, JEOL) with a base pressure of $2 \times 10^{-8}$ Pa. Constant current topography was observed with a Pt-Ir tip. A polished TiO$_2$(110) wafer of 6.5 x 1 x 0.25 mm$^3$ (Earth Chemicals) was cleaned with cycles of argon-ion sputtering (3 keV, 0.3 µA, 3 min) and vacuum annealing at 900 K [12,15]. An IR radiation thermometer (IR-FBP, Chino) monitored surface temperature. The annealed crystal was deep blue and gave a (1 x 1) LEED pattern. An oxygen deficiency of 0.001% was estimated from electrical resistivity of the crystal [18]. Sodium atoms were deposited with a dispenser source (Saes Getters) resistively heated in the microscope. Sodium dosage was controlled by deposition time. Sodium deposition, CO$_2$ exposure, and STM observation were done on the (1 x 1) surface cooled for 1 h after the annealing. Surface temperature of the cooled crystal was below the lower limit of the thermometer and estimated to be 300–350 K.

3. Results and discussion

3.1. Deposited Na adatoms

Fig. 3 shows constant current topography of Na adatoms deposited on a TiO$_2$(110)-(1 x 1) surface. Regular rows of contrast on the clean surface, shown in fig. 3a, have been assigned to the exposed Ti-rows along the [001] direction [12,15]. Individual Ti ions were resolved as axial corrugations on the rows. When the substrate was exposed to the Na flux for 90 s, bright spots of 0.1 nm height randomly appeared on the Ti-rows. Sodium coverage of the surface in fig. 3b corresponded to 0.1 ML in the scale of fig. 1. Forty one spots were counted in fig. 3b. The number of spots increased in proportion to deposition time. Hence, we assume that a spot represents a Na adatom. The absolute coverage of Na at the surface in fig. 3b was 0.2 atom/nm$^2$ on this assumption. The dispersed geometry in the dilute adlayer indicates repulsive force between the adatoms. The electrostatic repulsion among ionized adatoms is responsible for the structure. Indeed, an oxidation shift of 0.9 eV in Na(ls) XPS emission demonstrated that Na adatoms of 0.1 ML were ionized to the Na$^+$ state [7]. The resultant electron transport from the adatoms to the substrate caused a substantial decrease in work function of the Na-modified surface [7].

A p(4 x 2) order was locally formed on the surface exposed to the Na flux for 420 s. A rectangular lattice of the p(4 x 2) order was observed at the center of fig. 3c, where Na coverage was determined as 0.6 atom/nm$^2$ based on the surface density of imaged particle. This p(4 x 2) order did not develop over the surface being replaced by the c(4 x 2) order at higher coverages. The instability of the p(4 x 2)-ordered ensemble is consistent with the absence of the according pattern in LEED observation [7]. A similar p(4 x 2)-ordering of Na adatoms has been observed on a (1 x 2)-reconstructed TiO$_2$(110) surface [16]. Fig. 3d shows a nearly completed c(4 x 2)-ordered overlayer of 0.9 Na atom/nm$^2$. The structure of these dense overlayers fluctuated even at room temperature. A model for the ordered structures is illustrated in fig. 4. We assume in the model that a bright spot in the images represents a Na adatom adsorbed on a Ti-row, though the Ti-row could not be resolved under the dense Na-layers shown in figs. 3c and 3d. Thus, our previous model for the c(4 x 2) surface [7,8] should be revised on the results by STM. We may have failed in the accurate estimation of analyzer transmission character-