# The importance of diffusion in surface reactions demonstrated with STM

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We have used STM to observe directly a process which can be described as two-dimensional, surface-mediated Ostwald ripening, occurring during the decomposition of methoxy intermediates on a Cu(110) surface. Some islands get bigger during the course of the reaction, at the expense of smaller ones, and it is shown that this diffusion is important for dictating the rate of methanol decomposition. This is proposed to occur from the dilute phase of methoxy existing in the inter-island region and the methoxy maintains a pseudo steady state there, supplied by diffusion from, and between, islands of adsorbate on the surface.

**Keywords:** scanning tunnelling microscopy; methanol oxidation; methoxy; surface diffusion; Ostwald ripening; atomic resolution

Scanning tunnelling microscopy (STM) has shown great utility in its application to studies of surface structures formed upon the adsorption of simple molecules, and has recently begun to probe surface reactions at the atomic scale [1,2]. The oxidation of methanol on Cu(110) has been reported in some detail [2–5] and in this communication we demonstrate the observation of a new phenomenon in surface reactions, namely the "sintering" of islands of adsorbate which occurs in this instance during methoxy decomposition on the surface.

The experiments were carried out in an Omicron UHV STM, and the results are shown in fig. 1. To obtain these images the methodology described previously [2,5] was followed, that is, the surface was predosed with a small amount of oxygen (to approximately 0.25 monolayers coverage), was then exposed to methanol at room temperature and imaging was then carried out in UHV after removal of the gas phase. Under such circumstances the methoxy ($CH_3O$) group is formed, and is fairly stable at 300 K, as amply demonstrated in our recent publications [2,4,5]. However, decomposition occurs slowly and with it fairly large islands of methoxy are produced, the exact size and form of which depends upon the extent of removal of preadsorbed oxygen and of decomposition of methoxy; such a surface is shown in fig. 1a, where a variety of islands of methoxy can be seen. Over a long period of time (200 min) this layer slowly decomposes and other work [2–5] shows this to occur as follows, yielding formaldehyde and hydrogen in the gas phase, with some methanol being reformed by methoxy recombination with liberated H atoms [3–5]:

$$CH_3O_{(a)} \rightarrow H_2CO_{(g)} + \tfrac{1}{2}H_{2(g)}$$

Here the subscripts a and g refer to adsorbed and gas phase species respectively.

It is clear from the images in fig. 1 that this is not a simple decomposition process and that surface diffusion plays an important part in the reaction. This is an inter-island diffusion which could be classified as "surface-mediated, two-dimensional Ostwald ripening". Ostwald ripening is used to describe a process (usually in reference to crystallisation from solution or the molten phase crystallisation) in which, in a distribution of particle sizes, during the kinetic loss of surface area which proceeds to reduce the total thermodynamic surface free energy, large particles get bigger at the expense of smaller ones (see fig. 2). This is a common problem in heterogeneous catalysis using supported metals, and is often a cause of efficiency decline of such materials in commercial operation due to loss of active area. Fig. 2 shows an example of this for the case of sintering of the Ag metal particles in a silver/$\alpha$-alumina catalyst after treatment of the reduced catalyst in an oxidising environment in a microreactor for several days.

The images in fig. 1 show this process occurring during overall methoxy decomposition. By the end of these experiments all the adsorbate has decomposed (fig. 1f). However, it is evident that between figs. 1a and 1c the island labelled A has decreased, whilst that that is labelled B has *increased* in size, while the total area of methoxy adsorbate continues to diminish. This must be due to mass transport of methoxy units from one island to another, as briefly discussed previously [6].

That methoxy is so mobile is not a total surprise since our earlier work showed that the active sites for methoxy formation are very limited in number; yet methoxy once formed can diffuse away from there to cover the whole surface [2,5]. Such diffusion has significant consequences for the kinetics of methoxy decomposition. It is the case that diffusion and mass transport occurs at a

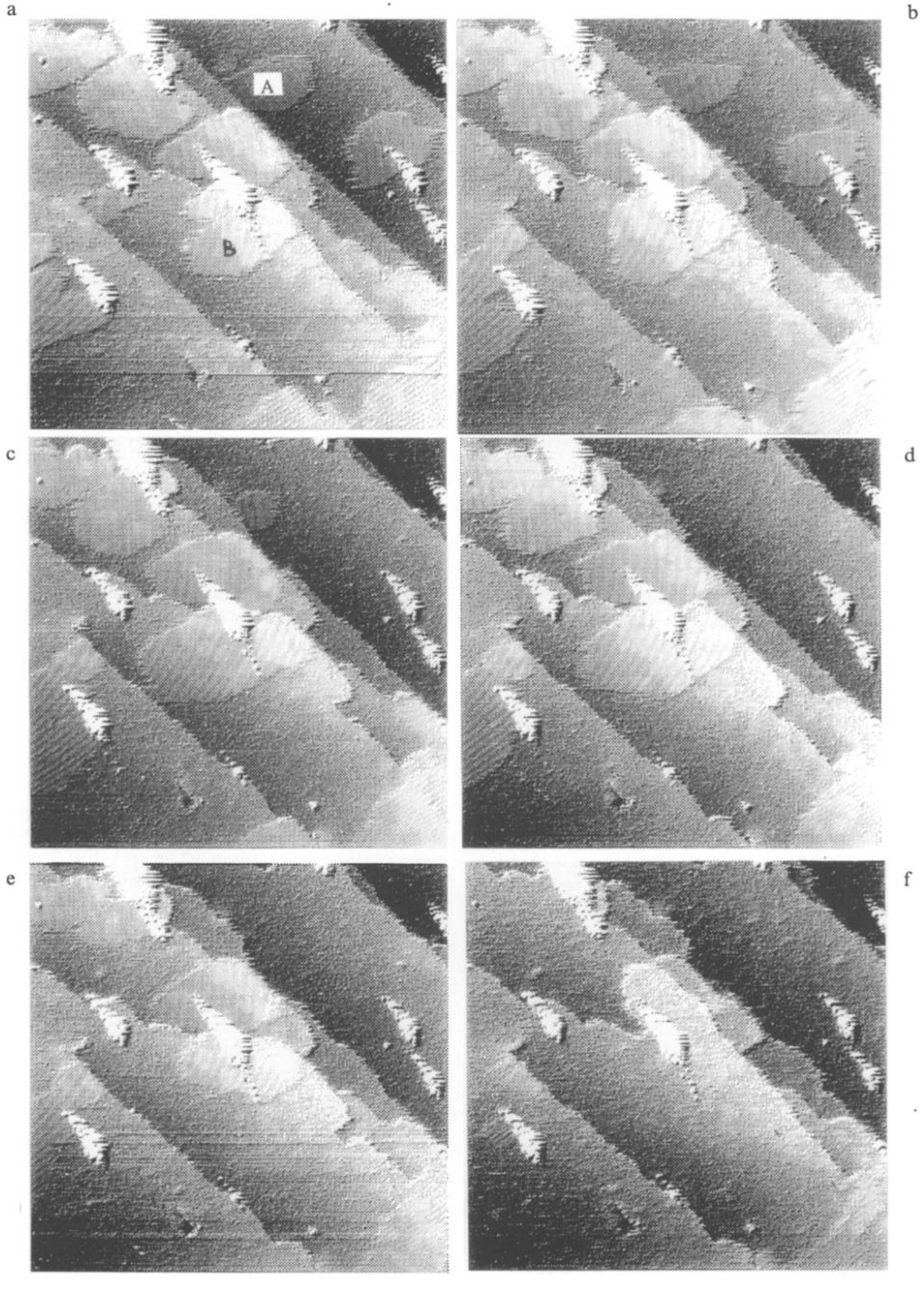

Fig. 1. Successive STM images of methoxy islands on Cu(110), showing the diffusion and loss of total area as time progresses. The time between images is approximately 5 min. These are 200 nm × 200 nm scans.

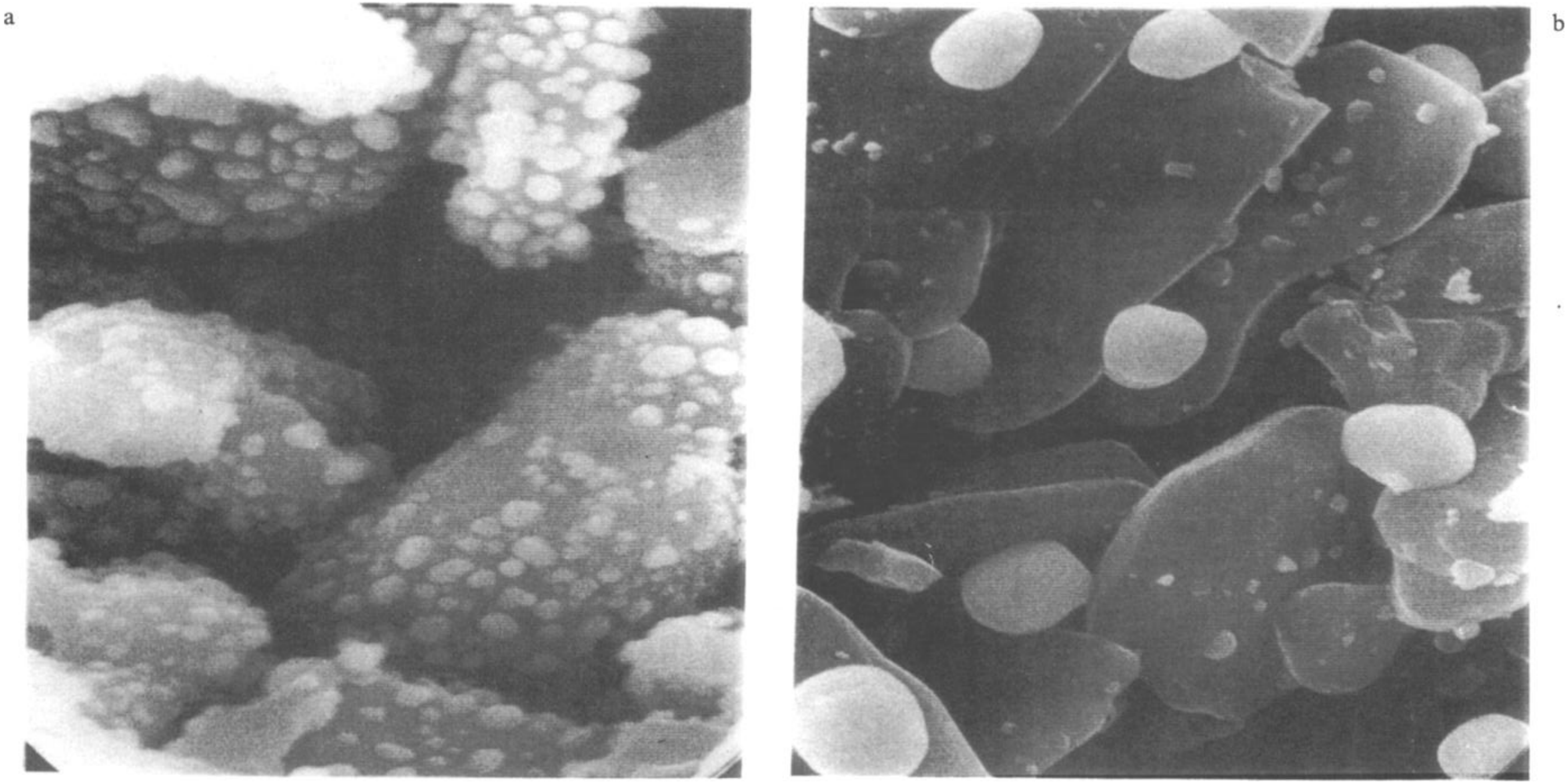

Fig. 2. An example of the sintering of metal particles, in this case occurring by both Ostwald ripening and coalescence. (a) Ag particles supported on a $\alpha$-aluminia support before reaction. (10 k magnification.) (b) After being used in ethylene epoxidation catalysis in a microreactor for 7 days at 250°C. There are mainly large Ag particles, plus a few very small ones. (10 k magnification.)

faster rate than decomposition in this system. Thus the mechanism of methoxy reaction should be more properly written as follows:

$$CH_3O^1_{(a)} + S^2 \underset{-1}{\overset{1}{\rightleftharpoons}} CH_3O^2_{(a)} + S^1 \qquad (1)$$

$$CH_3O^1_{(a)} \xrightarrow{2} H_2CO_{(g)} + H_{(a)} \qquad (2)$$

$$CH_3O^2_{(a)} \xrightarrow{3} H_2CO_{(g)} + H_{(a)} \qquad (3)$$

$$CH_3O^1_{(a)} + H_{(a)} \xrightarrow{4} CH_3OH_{(g)} + S^1 \qquad (4)$$

$$CH_3O^2_{(a)} + H_{(a)} \xrightarrow{5} CH_3OH_{(g)} + S^2 \qquad (5)$$

Here, superscripts 1 and 2 refer to methoxy adsorbed at island edges and in the region between islands respectively and similarly $S^1$ and $S^2$ refer to metal sites in the same positions. Now the exact kinetics of decomposition will involve the decomposition and diffusion processes. However, in terms of the rate-determining step, it is possible that the reaction may be dominated, in some temperature regions, by one or other of these steps. The rate is given by

$$\frac{-\mathrm{d(Mt)}}{\mathrm{d}t} = R_2 + R_3 + R_4 + R_5 , \qquad (6)$$

where Mt represents the methoxy held in the islands, assumed to be by far the dominant surface species. If we ignore the rates of steps 4 and 5 (methanol yields are small [3–5] and are rate limited by the decomposition steps), then the full rate equation is

$$\frac{-\mathrm{d(Mt)}}{\mathrm{d}t} = k_2[CH_3O^1_{(a)}] + k_3[CH_3O^2_{(a)}][1 - \theta_{\mathrm{Mt}}] . \qquad (7)$$

However, it is clear from the data that surface diffusion is occurring. Furthermore, the order of the reaction in the amount of adsorbed methoxy (proportional to the methoxy island area) is expected to be 0.5, if the first term of eq. (7) (step 2) were dominant. It is clear however from fig. 3 that the process is apparently zero order, from the independence of rate upon time. The conclusion from this must be that the decomposition is dominated by the second term of eq. (7), that is by reaction in the dilute phase of the phase separated system. In this phase we must assume that a steady state is established with a low coverage of $CH_3O^2_{(a)}$ existing throughout the course of most of the reaction. This steady state is established in steps 1, −1 and 3 and the pseudo equilibrium of step 1, −1 determines the Ostwald ripening effect on the methoxy islands, while step 3 determines the total loss of island area.

The sample of the surface area here is relatively small and so some care must be taken in inferring how statistically meaningful such a sample is. However, the number of methoxy units in fig. 1a is high at around $4 \times 10^4$ and the deviation of the data in fig. 3 is very low with a least-squares fit giving a correlation factor of 0.994. The number of islands is small and so quantification of the diffusion is much more difficult than quantification of the total loss of methoxy. Thus, the sintering effect can only be qualitatively described at this stage.

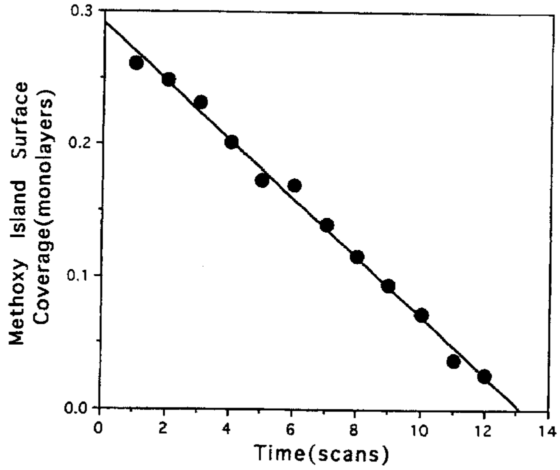

Fig. 3. The loss of methoxy island area as a function of time, showing a linear dependence characteristic of zero order behaviour.

In terms of desorption experiments care must be taken in directly comparing these data to desorption data. Firstly, the desorption data in the literature [3–5] are complicated, possibly showing more than one type of methoxy decomposition. Secondly, differences in experimental conditions could be very important. For instance, the formation of large methoxy islands is likely to be strongly methanol adsorption temperature dependent, and many of the results in the literature use low temperature adsorption (here it is carried out at 300 K). Furthermore, and depending on the heating rate, the decomposition of both the inter-island (step 3) and the island methoxy (step 2) may occur, with the latter being more stable and likely to proceed at slightly higher temperatures. This may be the source of the two peaks in TPD spectra for methoxy decomposition reported by Wach and Madix [3].

In conclusion, we have shown we believe for the first time, that a two-dimensional form of surface diffusion mediated Ostwald ripening can occur in layers of adsorbed intermediates which can exist as islands. Such processes can have great significance in determining the rates of surface reactions.

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