

# The Adsorption of Butene, Butadiene, and Ammonia on $\text{UO}_3\text{-Sb}_2\text{O}_3$ Catalysts

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The adsorption equilibria of butene-1, butadiene, and ammonia were studied on antimony-uranium oxide catalysts. On  $\text{UO}_3$  and  $\text{U}_2\text{O}_7$ , which are nonselective oxidation catalysts, there is strong and irreversible adsorption of butene-1. However, butene-1 was found to be adsorbed rapidly but weakly and reversibly on  $\text{USb}_3\text{O}_{10}$  which proved to be active and selective for the oxidation of olefines.

Similar types of adsorption sites for butene-1, butadiene and ammonia on  $\text{Bi}_2\text{MoO}_6$  were observed on  $\text{USb}_3\text{O}_{10}$ . From these results a surface reaction site model is proposed which refers to special mobile bulk oxygens in rows on  $\text{USb}_3\text{O}_{10}$  and is very similar to that given earlier for  $\text{Bi}_2\text{MoO}_6$ . On the basis of this model the mechanism of the ammoxidation of propene to acrylonitrile was discussed.

## INTRODUCTION

The SOHIO U-Sb oxide catalyst (1) is one of the most selective catalysts for the ammoxidation of propene to acrylonitrile and is moreover a quite selective oxidation catalyst for olefins. Grasselli and Callahan (2) reported that there are two different U-Sb oxide compounds,  $\text{USbO}_5$  and  $\text{USb}_3\text{O}_{10}$ , of which only the former proved to be active and selective for the ammoxidation. Simons, Houtman, and Schuit (3) reported that  $\text{USbO}_5$  is an active catalyst for the combustion of butene but that  $\text{USb}_3\text{O}_{10}$  is selective for its oxidation to butadiene. Recently Aykan and Sleight (4) and independently Grasselli and Suresh (5) proposed crystal structures for  $\text{USbO}_5$  and  $\text{USb}_3\text{O}_{10}$  that are closely related to the  $\alpha\text{-UO}_3$  structure. They concluded for  $\text{USb}_3\text{O}_{10}$  that there is one type of uranium but two crystallographically different types of antimony and four types of oxygen. Grasselli and Suresh (5) suggested that the more labile but less abundant oxygen participates in the selective oxidation and also

that depleted oxygen sites are supplied from oxygen in the lattice.

On  $\text{Bi}_2\text{MoO}_6$  catalyst Matsuura and Schuit (6) found two types of adsorption sites, namely *B-sites* which adsorb butene weakly and *A-sites* which adsorb butadiene strongly. An *A-site* is supposed to be a special  $\text{O}^{2-}$ -ion connected to a  $\text{Bi}^{3+}$  (or  $\text{Bi}^{5+}$ ) ion. This oxygen is selectively removed by partial reduction of the catalyst. The catalytic activity was found to be proportional to the *A-site* surface concentration and to the second power of that of the *B-sites*, leading to the assumption that the reaction site is a combination of one *A-site* and two *B-sites*. In the experimental results of butene oxidation on  $\text{Bi}_2\text{MoO}_6$  catalyst and on  $\text{USb}_3\text{O}_{10}$  catalyst as given by Batist *et al.* (7) and Simons *et al.* (3), there appear to be many similarities. Therefore it may be expected that on  $\text{USb}_3\text{O}_{10}$  catalyst two different types of centers might also exist.

It is the purpose of this paper to describe the adsorption of butene, butadiene, and ammonia on the selective olefin oxidation

catalyst  $USb_3O_{10}$ , and also on  $USbO_5$ ,  $UO_3$ ,  $U_3O_8$ , and  $Sb_2O_4$ , and to propose a model for the surface site.

EXPERIMENTAL PROCEDURE

$USb_3O_{10}$  and  $USbO_5$  were prepared by method I as described by Simons *et al.* (3).  $UO_3$  was prepared by precipitation from a solution of uranyl acetate with ammonia solution and calcination at  $300^\circ C$  for 4 hr.  $U_3O_8$  was obtained by calcining  $UO_3$  in air at  $750^\circ C$  for 16 hr.  $UO_2$  was prepared by reduction of  $U_3O_8$  by hydrogen at  $450^\circ C$  for 2 hr.  $Sb_2O_4$  was obtained by oxidating  $Sb_2O_3$  (from Merck Inc.) in air at  $725^\circ C$  for 16 hr. The surface areas of these catalysts were measured by the BET method using nitrogen, and the results are summarized in Table 1.

The adsorption method was described in an earlier report by Matsuura and Schuit (7).

On several catalysts butene was found to be adsorbed strongly and irreversibly. At higher temperatures a gas was desorbed that was further investigated by the following method. First, the amount of irreversibly adsorbed butene was obtained as follows. Butene was dosed at a relatively

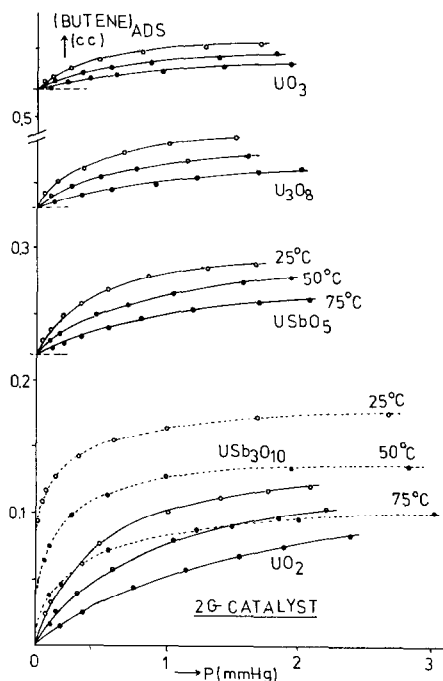


FIG. 1. Adsorption of butene-1 on  $UO_3$ - $Sb_2O_3$  catalysts.

high pressure (about 10 mmHg) at  $25^\circ C$  for 24 hr to obtain equilibrium. A known amount of gas was then withdrawn from the system until the gas pressure fell be-

TABLE 1  
ADSORPTION DATA OF  $C_4H_8$ ,  $C_4H_6$ , AND  $NH_3$

Catalyst	Surface area ( $m^2 g^{-1}$ )	Composition	Type of isotherm	$V_m$ ( $cm^3 g^{-1}$ )	$\log P_0^0$ (mmHg)	$Q$ (kcal mole $^{-1}$ )	$-\Delta S_{ads}$ (e.u. at $25^\circ C$ )
$USb_3O_{10}$	22	$C_4H_8$	DS <sup>a</sup> (W)	0.10	10.01	15.8	32.0
			DS (W)	0.10	9.88	14.8	32.3
			SS <sup>b</sup> (S)	0.045	9.18	23.3	34.2
		$NH_3$	SS (W)	0.09	3.60	5.3	4.2
			DS (S)	0.09	9.46	28.8	31.0
$USbO_5$	15	$C_4H_8$	SS (W)	0.04	3.35	5.2	7.2
			— (S)	0.11	irreversible		
$U_3O_8$	10		SS (W)	0.03	3.32	4.9	6.8
			— (S)	0.15	irreversible		
$UO_3$	20		SS (W)	0.02			
			— (S)	0.35	irreversible		
$UO_2$	9		SS (W)	0.07	3.34	5.3	7.1
$Sb_2O_4$	29		no adsorption				

<sup>a</sup> DS: dual-site adsorption.

<sup>b</sup> SS: single-site adsorption.

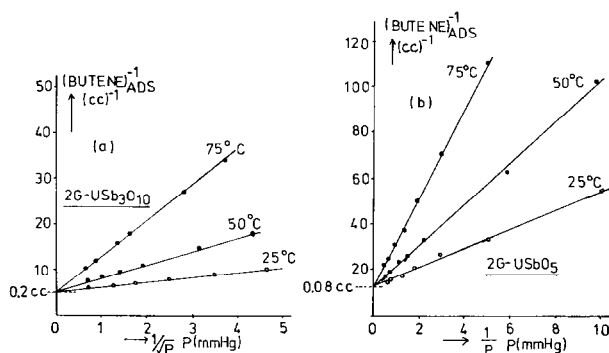


Fig. 2. Adsorption isotherm of butene-1 on  $\text{UO}_3\text{-Sb}_2\text{O}_3$  catalysts. (a) Dual-site adsorption on  $\text{USb}_3\text{O}_{10}$ ; (b) single-site adsorption on  $\text{USbO}_5$ .

low  $10^{-3}$  mmHg at  $50^\circ\text{C}$ . The remaining adsorbed butene cannot be recovered as such, because it is oxidized by the catalyst. In the next step, the catalyst was heated at a constant rate ( $5^\circ\text{C}/\text{min}$  from 50 to  $550^\circ\text{C}$ ), the gas desorbed being condensed successively every 5 min in traps cooled in liquid nitrogen. After termination of the experiment the condensed gas was analyzed. It was found to be  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by gas chromatography. For each experiment 10 g of catalyst was used.

## EXPERIMENTAL RESULTS

### Adsorption of Butene-1

Figure 1 shows that there are two types of butene adsorption on  $\text{UO}_3$ ,  $\text{U}_3\text{O}_8$ , and  $\text{USbO}_5$ , one being weak and nondissociative

(see Fig. 2b), the other being strong and irreversible. For  $\text{UO}_2$  and  $\text{USb}_3\text{O}_{10}$  there is only one type of adsorption (see Fig. 2a). It is weak and nondissociative for  $\text{UO}_2$  and similar to that for the above mentioned catalysts. On  $\text{USb}_3\text{O}_{10}$  it is dissociative with a heat of adsorption of  $15.8 \text{ kcal mole}^{-1}$  higher than the value of  $12.0 \text{ kcal mole}^{-1}$  on  $\text{Bi}_2\text{MoO}_6$ . For  $\text{Sb}_2\text{O}_4$  no adsorption was observed. The strong and irreversibly adsorbed butene can be removed as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  above  $100^\circ\text{C}$ . The evolution of  $\text{CO}_2$  is shown for the three catalysts in Fig. 3. The temperature of maximum  $\text{CO}_2$  evolution is  $250^\circ\text{C}$  for  $\text{UO}_3$ ,  $310^\circ\text{C}$  for  $\text{U}_3\text{O}_8$ , and  $380^\circ\text{C}$  for  $\text{USbO}_5$ , which is close to the temperature of  $350^\circ\text{C}$  at which the oxidation of butene on  $\text{U}_3\text{O}_8$  and  $\text{USbO}_5$  increases steeply (see Simons *et al.* (3)).

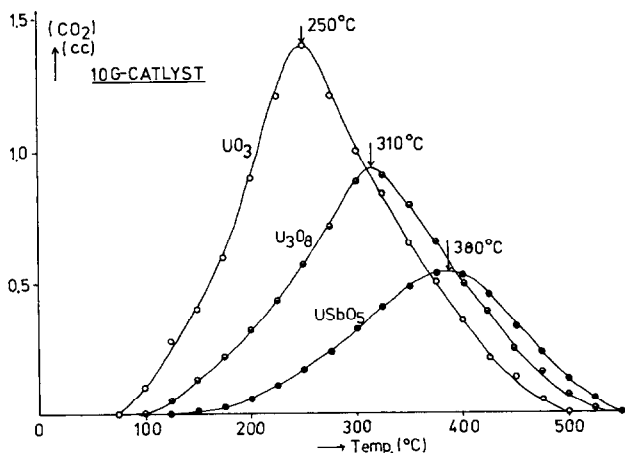


Fig. 3.  $\text{CO}_2$  formation from adsorbed butene-1 on  $\text{UO}_3\text{-Sb}_2\text{O}_3$  catalysts.

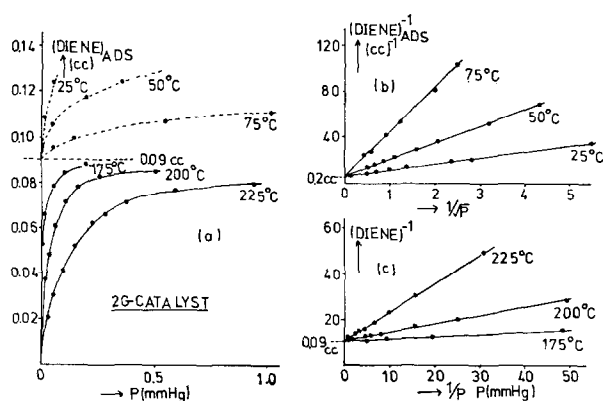


FIG. 4. Adsorption of butadiene on  $USb_3O_{10}$ . (a) Adsorption equilibria; (b) weak and dual-site adsorption isotherm; (c) strong and single-site adsorption isotherm.

From Fig. 3, the activation energy of  $CO_2$  evolution can be calculated in the following way. The rate of evolution of  $CO_2$  at any given temperature  $T$  was approximated by  $(\Delta CO_2/\Delta t)_T$  where  $\Delta CO_2$  is the amount of  $CO_2$  evolved during a time period  $\Delta t$  between two measurements, and  $T$  the average temperature in this period. The rate evidently depends on the amount of carbonaceous material still present at the beginning of the period. If the total amount of this material at the beginning of the run is represented by the total amount of  $CO_2$  evolved at the end of the run ( $q_0$ ) and that removed during preceding periods, denoted here by  $q_{CO_2}$

$$\Delta CO_2/\Delta t = k_T(q_0 - q_{CO_2})_T.$$

Hence

$$k_T = (\Delta CO_2/\Delta t)/(q_0 - q_{CO_2})$$

and with

$$k_T = A \exp(-E/RT),$$

$$\ln(\Delta CO_2/\Delta t)/(q_0 - q_{CO_2}) = -E/RT + \ln A.$$

Activation energies thus calculated were

Compound	$E$ (kcal mole <sup>-1</sup> )
$UO_3$	$7.0 \pm 2.0$
$U_3O_8$	$8.0 \pm 2.0$
$USbO_5$	$11.0 \pm 2.0$

### Adsorption of Butadiene

Figure 4 shows that there are two types of butadiene adsorption on  $USb_3O_{10}$  catalyst, one being weak and dissociative with a total adsorption of  $0.10 \text{ cm}^3 \text{ g}^{-1}$  (similar

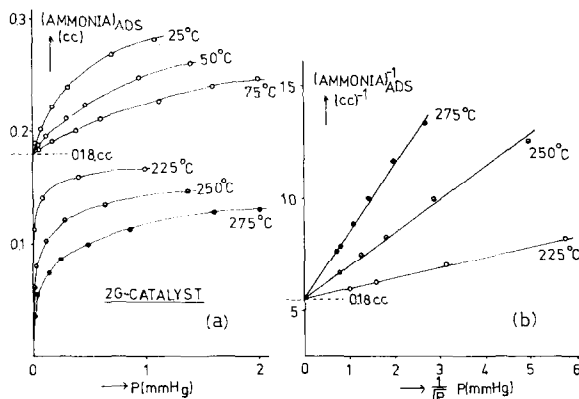


FIG. 5. Adsorption of ammonia on  $USb_3O_{10}$ . (a) Adsorption equilibria; (b) strong and dual-site adsorption isotherm.

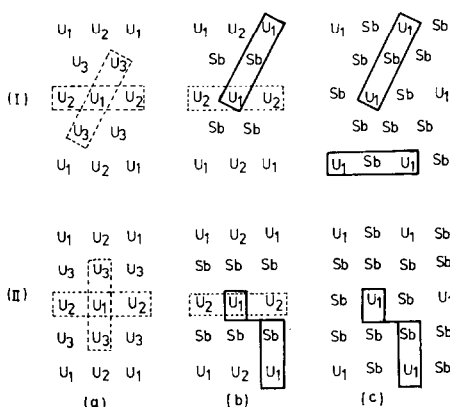


Fig. 6. Metal ion positions of  $UO_3$ - $Sb_2O_3$  catalysts. (a)  $UO_3$ ; (b)  $USbO_5$ ; (c)  $USb_3O_{10}$ .

in amount to the adsorption of butene-1), the other being strong and nondissociative with a total adsorption volume of  $0.045 \text{ cm}^3 \text{ g}^{-1}$ . The ratio between the maximum adsorption volume of the strong and weak adsorption of butadiene is near to  $1/2$ , i.e., the same ratio as found for  $600^\circ\text{C}$ -preheated  $Bi_2MoO_6$  (8). The heats of adsorption calculated are  $14.8 \text{ kcal mole}^{-1}$  for weak adsorption and  $23.3 \text{ kcal mole}^{-1}$  for the strong adsorption.

#### Adsorption of Ammonia

Figure 5 shows that it is possible to distinguish two different types of ammonia adsorption on the  $USb_3O_{10}$  catalyst. One is weak and nondissociative with a heat of adsorption of  $5.6 \text{ kcal mole}^{-1}$ , the other is strong and dissociative and with a heat of adsorption of  $28.8 \text{ kcal mole}^{-1}$ . It is remarkable that the volume of strongly adsorbed ammonia is nearly twice that of the strongly adsorbed butadiene, just as for  $Bi_2MoO_6$  (9). All adsorption data are given in Table 1.

#### DISCUSSION

The oxides  $UO_3$ ,  $U_3O_8$ ,  $USbO_5$ , and  $USb_3O_{10}$  present a particularly interesting subject of study since:

(a) Their structures are closely related, as has been shown by Aykan and Sleight (4) and in greater detail by Grasselli and Suresh (5).

(b) Grasselli and Callahan (2) have shown that there is a sudden transition from nonselective to selective oxidation on going from  $USbO_5$  to  $USb_3O_{10}$  (see also Simons *et al.* (3)).

(c) The adsorption properties of  $USb_3O_{10}$  and  $Bi_2MoO_6$  are similar. There are the weak butene adsorption sites (*B-sites*) and strong butadiene adsorption sites (*A-sites*), the ratio A/B being  $1/2$  and finally the ratio of the strong ammonia adsorption to the strong butadiene adsorption being  $1/2$ .

The  $U^{6+}$  ions in  $\alpha$ - $UO_3$  and in  $U_3O_8$  are in an eightfold oxygen surrounding (see Wells (10)). Two oxygens form a linear arrangement O-U-O, and the other six a distorted octahedral surrounding. In  $USbO_5$  one of every two  $U^{5+}$  ions occurs in a similar arrangement, the other being approximately sixfold surrounded, again with two oxygens in the perpendicular position. The  $Sb^{5+}$  ions are octahedrally surrounded. In  $USb_3O_{10}$   $U^{5+}$  ions are eightfold oxygen surrounded as for the  $U^{6+}$  ions in  $\alpha$ - $UO_3$ . There are two different types of  $Sb^{5+}$  ions, all octahedrally surrounded. One type is connected with  $U^{5+}$  and  $Sb^{5+}$  ions, but the other is only surrounded by  $Sb^{5+}$  ions.

Figure 6a(I) presents a simplified diagram of the cationic arrangements in the basic plane for  $\alpha$ - $UO_3$  and Fig. 6a(II) presents the arrangement perpendicular to the basic plane, i.e., parallel to the O-U-O direction. In  $USbO_5$  the cation positions marked 1 and 2 (see Fig. 6b) are occupied by  $U^{5+}$  cations. The  $Sb^{5+}$  cations occur in rows parallel to the U-rows (position 3). In  $USb_3O_{10}$  the 2-positions marked 2 and 3 are occupied by  $Sb^{5+}$  cations (see Fig. 6c).

Now, the number of sites on which one molecule of butene is adsorbed initially is evidently much lower than either the number of cations or anions on the surface. The surface area per molecule adsorbed (including weak adsorption) turns out to be

Compound	Surface area/ adsorbed molecule
$UO_3$	$230 \text{ \AA}^2$
$U_3O_8$	220
$USbO_5$	400
$USb_3O_{10}$	880

which appears to indicate that initial adsorption occurs on U ions and not on Sb ions. We therefore assume that the adsorption occurs at an anion vacancy connected to a U ion. After butene adsorption, the numbers of oxygen ions removed from the surface are

UO <sub>3</sub>	$5.3 \times 10^{18}/\text{m}^2 = \text{one } \text{O}^{2-} \text{ per } 19 \text{ \AA}^2$
U <sub>3</sub> O <sub>8</sub>	$4.7 \times 10^{18}/\text{m}^2 = \text{one } \text{O}^{2-} \text{ per } 19 \text{ \AA}^2$
USbO <sub>5</sub>	$2.4 \times 10^{18}/\text{m}^2 = \text{one } \text{O}^{2-} \text{ per } 41 \text{ \AA}^2$

Assuming that an oxide surface consists of O<sup>2-</sup> ions and oxygen vacancies in the ratio 1:1, all surface oxygens apparently are removed for UO<sub>3</sub> and U<sub>3</sub>O<sub>8</sub> (surface area per O<sup>2-</sup> ion is 10 Å<sup>2</sup>). On USbO<sub>5</sub> half of these surface oxygens are removed. It might be assumed that the oxygens removed are bonded to pairs of U ions because such removable oxygens do not exist on USb<sub>3</sub>O<sub>10</sub>. From these assumptions, the nonselective oxidation sites might be ...U<sub>2</sub>...O...U<sub>1</sub>...O...U<sub>2</sub>... or ...U<sub>3</sub>...O...U<sub>1</sub>...O...U<sub>3</sub>... with an oxygen vacancy on U<sub>1</sub> and a surface oxygen either on U<sub>2</sub> or U<sub>3</sub> (see Fig. 6a and b).

It is noteworthy that the ratio of sites that adsorb butadiene strongly (*A-sites*) to those that adsorb butene weakly (*B-sites*) is equal to 1:2, just as for the 600°C-preheated Bi<sub>2</sub>MoO<sub>6</sub>. In an earlier paper, Matsuura and Schuit (8) proposed that the *A-site* is the active site provided it is connected to two *B-sites*. An *A-site* was postulated to be a set of two anion vacancies on Bi<sup>3+</sup> ions (Bi<sup>3+</sup>-cus) with an oxygen (O<sub>A</sub>) in the center also connected to a Bi<sup>3+</sup> (or Bi<sup>5+</sup>) ion belonging to a Bi<sub>2</sub>O<sub>2</sub> edge. This oxygen ion is selectively removed by partial reduction of the catalyst. A *B-site* is a combination of two O<sup>2-</sup> ions and one vacancy connected to a Mo<sup>6+</sup> ion: this combination of sites adsorbs olefins, either as π-bonded complexes at the vacancy or as a σ-bonded allyl-intermediate with one of the two O<sup>2-</sup> ions, the other being occupied by the H atom dissociated. If we are allowed to assume a similar configuration for the *A-site* on USb<sub>3</sub>O<sub>10</sub>, i.e., vacancy on Sb<sup>3+</sup> or Sb<sup>5+</sup> . . . oxygen on Sb<sup>5+</sup> . . . vacancy on Sb<sup>3+</sup> or Sb<sup>5+</sup> and for the *B-site*, i.e., a combination of two O<sup>2-</sup> ions and one vacancy con-

nected to a U<sup>6+</sup> or U<sup>5+</sup> ion, the following arrangement represents the active site viz.

<i>B-site</i>	<i>A-site</i>	<i>B-site</i>
vacancy on U <sup>6+</sup> or U <sup>5+</sup>	O <sub>A</sub> on Sb <sup>5+</sup>	vacancy on U <sup>6+</sup> or U <sup>5+</sup>

On the selective catalyst USb<sub>3</sub>O<sub>10</sub> there are actually two possibilities to represent this arrangement: one is in the basal plane (Fig. 6c(I)) which is similar to the model given by Grasselli and Suresh (5), and the other is in a perpendicular direction (Fig. 6c(II)) more alike to that suggested earlier for Bi<sub>2</sub>MoO<sub>6</sub> (7). A similar situation for the active sites is present on the planes of the less selective USbO<sub>5</sub> catalyst (Fig. 6b). There is, however, a difference with USb<sub>3</sub>O<sub>10</sub> where the eightfold coordinated U<sup>5+</sup> ion is connected with 8 Sb<sup>5+</sup> ions: in USbO<sub>5</sub> a correspondingly coordinated U<sup>5+</sup> ion is connected with six Sb<sup>5+</sup> ions and two U<sup>5+</sup> ions. Differences in environment of the active sites might affect the adsorption properties leading to a strong difference in the selectivities of USb<sub>3</sub>O<sub>10</sub> and

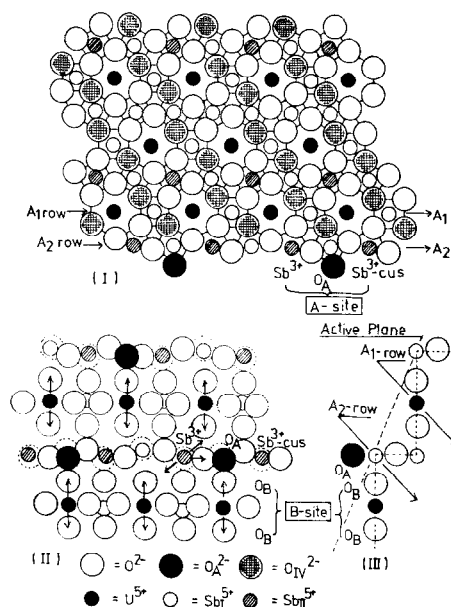


Fig. 7. Surface model of USb<sub>3</sub>O<sub>10</sub>. (I) Basal plane: Active surface according to Grasselli and Suresh (5); (II) active surface according to Matsuura (9); (III) active plane.

USbO<sub>5</sub>. Moreover on USbO<sub>5</sub> there is present a similar presumably nonselective oxidation site for the configuration U<sub>2</sub>···O···U<sub>1</sub>···O···U<sub>3</sub> on UO<sub>3</sub> as shown in Fig. 6a and b.

In Fig. 7(I) a more detailed picture of the situation is given for the basal plane of USb<sub>3</sub>O<sub>10</sub>. Let us assume that this plane represents the surface. Half of all the cations are covered by an oxygen anion, and for the other half the oxygen position is vacant. The surface anions presumed to be active by Grasselli and Suresh (5) are the O<sub>IV</sub> ions; the oxygens covering the cations in the mixed rows (U–Sb–U–Sb) belong to this category. In these rows there are *B-sites* and *A-sites*: although the site arrangement is precisely that proposed by Grasselli and Suresh (5), the *B/A*-ratio being 1 in this surface, it is not in accordance with our measurements. Although this surface plane corresponds to Grasselli and Suresh's site arrangement, it apparently is not an acceptable proportion.

Another and more realistic surface plane is given by Fig. 7(II). It represents a cut through the unit cell as indicated by Fig. 7(III). It fits both demands, that of Grasselli and Suresh as to the site arrangement and that of our ratio *B/A* being 2. In this plane there is alternately a row of *A*<sub>1</sub> (U and Sb cations alternately arranged) and *A*<sub>2</sub> (only Sb cations arranged), connected by inner rows of oxygen anions. There are four crystallographically different types of oxygen ions, viz. O<sub>I</sub> and O<sub>IV</sub> in the *A*<sub>1</sub> and *A*<sub>2</sub>-rows and O<sub>II</sub> and O<sub>III</sub> in the interconnecting oxygen rows with *A*<sub>1</sub>-rows (for the nomenclature of oxygen, see Grasselli and Suresh (5)). Therefore the *B-site* will be present as the combination of a vacancy on a U<sup>6+</sup>-ion in the *A*<sub>1</sub>-row with two O<sub>III</sub>'s, the model being similar to the *B-site* of Bi<sub>2</sub>MoO<sub>6</sub>. The *A-site* is an O<sup>2-</sup> ion on a Sb<sup>5+</sup> ion with two anion vacancies on Sb<sup>3+</sup> ions (Sb<sup>3+</sup>-cus) in the *A*<sub>2</sub>-row edge comparable to the two anion vacancies on Bi<sup>3+</sup> ions with center of an O<sup>2-</sup> ion on Bi<sup>3+</sup> (or Bi<sup>5+</sup>) ion in the Bi<sub>2</sub>O<sub>2</sub> layer edge of Bi<sub>2</sub>MoO<sub>6</sub> (see Matsuura and Schuit (8), Fig. 10). According to this model the ratio of *B/A* is 2 in good agreement with the

experimental value and also a similar type of reaction site for Bi<sub>2</sub>MoO<sub>6</sub>.

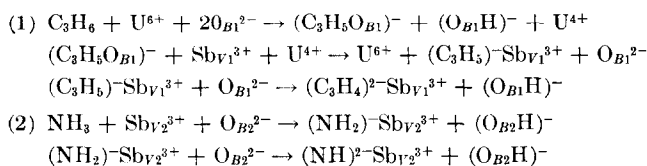
There is another interesting aspect if one compares the two models (I) and (II); it is connected with the position of the weakly bonded oxygen ions of the type O<sub>IV</sub>. According to Grasselli and Suresh (5) they are located in the *A*<sub>1</sub> rows of the basal plane (I) marked by O<sub>IV</sub>, and considered by them as the selective oxygen ions. In the new model (II) the same oxygen ions O<sub>IV</sub> in the *A*<sub>2</sub>-row edge are chosen as the selective oxygen ions. Moreover, this selective oxygen in the *A*<sub>2</sub>-row edge O<sub>A</sub> is connected with weakly bonded oxygen ions O<sub>IV</sub> in the bulk (see Fig. 7, I and II) that form an important aspect of the selective olefin oxidation site as mentioned Grasselli and Suresh (5), the model being now also similar to that for Bi<sub>2</sub>MoO<sub>6</sub>.

The comparison of the adsorption properties for both selective catalysts USb<sub>3</sub>O<sub>10</sub> and Bi<sub>2</sub>MoO<sub>6</sub> shows stronger adsorptions on the former compound. This can be related to the observed catalytic activities, the activation energies for butene oxidation being 8 kcal mole<sup>-1</sup> on USb<sub>3</sub>O<sub>10</sub> (3), and 12 kcal mole<sup>-1</sup> on Bi<sub>2</sub>MoO<sub>6</sub> (6), as measured with pulse experiments. In a previous report (8) we suggested that the butene oxidation mechanism could proceed as follows: dissociative adsorption of butene on *B-site* → activated complex in which an allyl is bonded to a Bi<sup>3+</sup> (Sb<sup>3+</sup>)-cus next to the O<sub>A</sub> → dissociation of the second H atom to an oxygen belonging to the *B-site* → desorption of butadiene. The final process, i.e., the desorption of H<sub>2</sub>O, occurs after migration of two H atoms to an O<sub>A</sub>. In this reaction mechanism the rate determining step is the formation of the activated complex. Therefore it is possible that the stronger adsorption on USb<sub>3</sub>O<sub>10</sub> as compared with Bi<sub>2</sub>MoO<sub>6</sub> will lead to a more easy formation of the activated complex and since this step is rate determining the activation energy becomes lower.

The strong adsorption of ammonia has a *V<sub>m</sub>* (maximum adsorption) which is double that of the O<sub>A</sub> as found on Bi<sub>2</sub>MoO<sub>6</sub> (9). Therefore this ammonia adsorption has to occur on the two Sb<sup>3+</sup>-cus next to the O<sub>A</sub>.

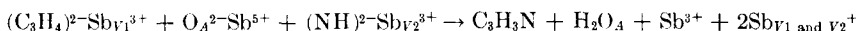
Grasselli and Suresh's mechanism (5) for the ammoxidation of propene to acrylonitrile on  $USb_3O_{10}$  catalyst suggested that the reaction between a  $C_3H_4$  complex on  $Sb^{5+}$  and a NH intermediate is important, as was proposed by us in a closely similar reaction mechanism based on adsorption measurements on  $Bi_2MoO_6$  (9).

This mechanism can be modified for  $USb_3O_{10}$  as follows:



where  $O_{B1}^{2-}$  and  $O_{B2}^{2-}$  are oxygen ions belonging respectively to *B-site* number 1 and 2, and  $Sb_{V1}^{3+}$  and  $Sb_{V2}^{3+}$  are the  $Sb^{3+}$ -cus on both sides of  $O_A^{2-}$ .

Acrylonitrile is formed directly from  $(C_3H_4)$  and  $(NH)$  complexes next to  $O_A^{2-}$ :



In particular it follows that the direct reaction to acrylonitrile from ammonia and propene needs three oxygen ions that have to be supplied simultaneously from the catalyst. It is important for selective olefin oxidation that the special mobile bulk oxygen in the rows are connected with the  $O_A$  on the surface.

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