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Adsorption Equilibria of Acrolein and Ammonia on the Bismuth Molybdate Koechlinite Catalyst

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The adsorption equilibria of acrolein and ammonia were studied on oxidized and partially reduced Bi_2MoO_6. Acrolein was found to be adsorbed according to two modes, one being a strong but slow adsorption of the dual-site type equal in amount to the number of *A-sites.* A similar adsorption exists on pure Bi_2O_3 which appears to support an earlier supposition that it is connected with Bi ions. The other one is a fast but weak adsorption, equal in volume to the number of *B-sites,* and again dual-site in character. For ammonia adsorption there is a strong adsorption (slow and dual-site type) that is double that of the number of *A-sites* and a weak adsorption (fast and single-site type) to the extent of 3/2 the *B-sites.* On the pre-reduced catalyst, the strong adsorption is eliminated and replaced by an equal amount of weak adsorption. Moreover, a new type of adsorption is observed (moderately strong and single-site type) equal to the number of *A-sites.* It is closely similar to the adsorption of water on the reduced catalyst.

It was further observed that above 400°C ammonia is oxidized according to a first order reaction, its rate being independent of the presence or absence of oxygen (activation energy is 37 $kcal/mol^{-1}$). For this reaction we propose a model between two surface fragments of ammonia. The mechanism of the ammoxidation of propene to acrylonitrile is discussed on the basis of this model.

INTRODUCTION

Measurements on the adsorption of butene, butadiene, oxygen and water on the surface of fully oxidized or partly reduced Bi_2MoO_6 (koechlinite) were reported in two earlier papers (*1*, *2*). The results were explained on the basis of the following model. Starting from the crystal structure proposed by Zemann (*3*) for the mineral koechlinite, the catalyst was supposed to consist of layers of Bi_2O_2, similar to those encountered in BiOCl, and layers of MoO_2 consisting of Mo^{6+} in octahedral surroundings, the octahedra sharing corners. The crystal surface was considered to consist entirely of the edges of these layers. Each edge is a regular sequence of O^{2-} and empty anion-sites [Bi^{3+} or Mo^{6+}-*cus* in the terminology of Burwell *et al.* (*4*)]. One in every four of the O^{2-} on the BiO-edge (O_A-site) can be removed by a reduction via an olefin: the resulting anion vacancy forms the site for a reversible adsorption of H_2O or of a dissociative adsorption of O_2. On one of the Bi-cus next to O_A a butadiene molecule can be adsorbed in a strong but slow single site adsorption, it being postulated that the molecule forms a dihydrofuran type of surface complex with O_A. A Mo-cus acts as a site on which olefins such as propene, butene but also butadiene can be adsorbed in a fast, reversible, weak adsorption that is usually dissociative. The reaction of butene to butadiene was supposed to occur on a Bi-cus next to O_A in accordance with the kinetic measurements of Batist, Prette and Schuit (*5*) which showed a strong inhibition of the butene to butadiene catalytic oxidation by the product butadiene. The nearest neighbors of a Bi-cus, apart from the oxygens on the

BiO-edge are two O_B anions from two different *B-sites.* The rate-determining reaction in the butene oxidation was postulated as an activated dissociative adsorption on this Bi-cus whereby one of the O_B's accepts a proton (or H atom), the resulting allylic structure being adsorbed on the Bi-cus. It is immediately followed by a second H-abstraction to the other O_B. The reaction mechanism is thereby in agreement with the results of measurements on the isotope effect by Adams and Jennings (*6*) and with our observations leading to the conclusion that the reactive site consists of *one A-* and *two B-sites.* The H atoms migrate from the O_B's to one O_A and desorb as H_2O. The model appears consistent with the present knowledge of the catalytic butene to butadiene oxidation: our present inability to account for the fact that only one in every four O^{2-} ions is an O_A remains an unsatisfactory detail. Moreover, in the absence of further information regarding the adsorption of compounds such as acrolein and ammonia it remains uncertain whether the mechanism proposed is related to that of the formation of acrolein from propene and of acrylonitrile from propene and ammonia. To obtain this information it was decided to study the adsorption of acrolein and ammonia on Bi_2MoO_6. This paper reports the data obtained in this study.

EXPERIMENTAL PROCEDURES

Catalyst samples. Bi_2MoO_6 was prepared according to the method given by Batist and Lankhuijzen (*7*). Samples were either calcined at 500°C for 4 hr or 4 hr at 500°C followed by 2 hr at 600°C.; the samples are denoted as '500' and '600.' The 500 sample was also investigated in reduced form (reduction by butene at 350°C to a composition of $Bi_2MoO_{5.5}$). MoO_3 was prepared from molybdic acid by 4 hr calcination at 500°C. Bi_2O_3 was prepared from bismuth nitrate by heating in air at 500°C for 4 hr.

Adsorption materials. Propene and butadiene were research grade samples from the Phillips Petroleum Co. Acrolein was a commercial sample purified by repeated distillation. Ammonia (anhydrous) was from J. T. Baker Chemical Co.

Adsorption techniques. See Matsuura and Schuit (*1*).

Adsorption rate and oxidation of NH_3. The oxidation of ammonia was studied in the presence and absence of O_2 in the adsorption apparatus using a static method with a 200 cm^3 vessel and pressures of 20–60 mm Hg. Water formed was removed by condensation in a trap at −40°C. The degree of conversion was obtained from the decrease in pressure.

No corrections were made for absorption of the ammonia in the ice formed in the trap. Since mass spectroscopic analysis of the products of the oxidation of ammonia over Bi_2MoO_6 in continuous flow failed to show other products than N_2 and H_2O (private communication from S. P. Lankhuijzen), it was further assumed that the only products of the reaction were indeed N_2 and H_2O. The rate of adsorption was moreover measured in the same adsorption apparatus at low temperatures (20–75°C).

EXPERIMENTAL RESULTS

Adsorption of Acrolein

Figure 1a shows that there are two types of acrolein adsorption on the 500 Bi_2MoO_6 catalyst, one being weak and dissociative with a total adsorption volume V_m of 0.125 $cm^3\ g^{-1}$ (see Fig. 1b), the other strong and also dissociative with $V_m = 0.033\ cm^3\ g^{-1}$ (see Fig. 1c). These results are similar to those obtained with butadiene (*1*) where the weak adsorption was supposed to occur on sites named B and the strong adsorption on sites named A. On a reduced bismuth molybdate catalyst with composition $Bi_2MoO_{5.5}$ a very strong irreversible adsorption of acrolein was observed, the volume of which increased with adsorption time: it is actually believed to be a polymerization. The acrolein adsorption on the 600-Bi_2MoO_6 is similar to that on the 500-Bi_2MoO_6 (*2*), the V_m for the weak adsorption being now lower by a factor of 4, and the strong adsorption by a factor of 2. A similar decrease in the number of weak and strong adsorption sites also occurs for

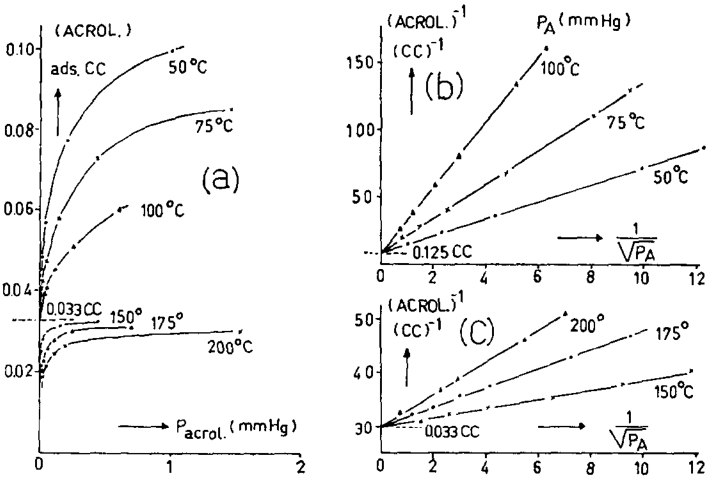


FIG. 1. Adsorption of acrolein on 500-Bi_2MoO_6: (a) adsorption equilibrium, (b) weak and dual-site adsorption isotherm, (c) strong and dual-site adsorption isotherm.

the case of butadiene (see Table 1). Table 1 shows also the result of the acrolein adsorption on Bi_2O_3, again a strong dissociative adsorption, with total adsorption volume (0.09 cm^3 g^{-1}), much higher than on bismuth molybdate, but with a heat of adsorption (21.0 kcal mol^{-1}) equal to that on the bismuth molybdate catalyst. As shown in Table 1, the acrolein adsorption on MoO_3 is weak and dissociative with a heat of adsorption of 11.5 kcal mol^{-1}. This type of adsorption is rather similar to that of butadiene which is also weak and dual site.

Adsorption of Ammonia

Figure 2 shows that on a 500-Bi_2MoO_6 catalyst it is possible to distinguish between

TABLE 1
ADSORPTION EQUILIBRIA OF ACROLEIN AND AMMONIA

Catalyst	Composition	Type of isotherm	V_m (cm^3 g^{-1})	log P_0^0 (mm Hg)	Heat of adsorption Q (kcal mol^{-1})
500-Bi_2MoO_6	C_3H_4O	DS(w)[a]	0.125 ± 0.006	8.6 ± 0.3	11.2 ± 0.5
		DS(s)	0.035 ± 0.004	7.8 ± 0.3	21.2 ± 0.5
	NH_3	SS(w)[b]	0.190 ± 0.006	4.1 ± 0.3	6.2 ± 0.5
	(on oxi.)	DS(s)	0.063 ± 0.004	11.0 ± 0.3	24.0 ± 0.5
	NH_3	SS(w)	0.250 ± 0.010	4.1 ± 0.3	6.1 ± 0.5
	(on red.)	SS(s)	0.033 ± 0.004	7.7 ± 0.3	16.3 ± 0.5
600-Bi_2MoO_6	C_3H_4O	DS(w)	0.028 ± 0.002	9.5 ± 0.5	11.4 ± 0.5
		—(s)	0.014 ± 0.002	Irreversible	
	NH_3	SS(w)	0.028 ± 0.002	3.8 ± 0.3	5.7 ± 0.5
		—(s)	0.028 ± 0.002	Irreversible	
MoO_3	C_3H_4O	DS(w)	0.037 ± 0.004	7.4 ± 0.3	11.5 ± 0.5
	NH_3	SS(w)	0.060 ± 0.004	3.0 ± 0.3	5.1 ± 0.5
		—	0.020 ± 0.002	Irreversible	
Bi_2O_3	C_3H_4O	DS(s)	0.090 ± 0.006	7.7 ± 0.3	21.4 ± 0.5
	NH_3	SS(w)	0.050 ± 0.004	3.4 ± 0.3	4.9 ± 0.5

[a] DS, dual-site adsorption.
[b] SS, single-site adsorption.

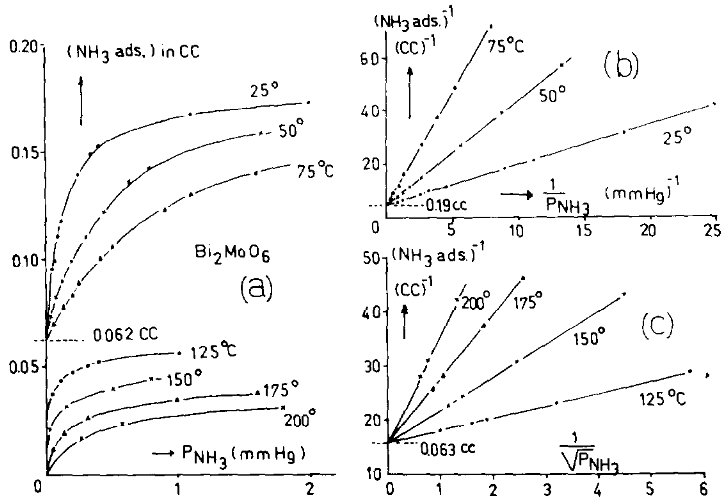


FIG. 2. Adsorption of ammonia on oxidized 500-Bi_2MoO_6: (a) adsorption equilibrium, (b) weak and single-site adsorption isotherm and (c) strong and dual-site adsorption isotherm.

two different types of ammonia adsorption. One is weak and nondissociative with a heat of adsorption of 6.2 kcal mol^{-1} (see Fig. 2b, Table 1) very close to the heat of condensation of ammonia; the other is strong and dissociative, with a heat of adsorption of 24.0 kcal mol^{-1} (see Fig. 2c, Table 1). It is remarkable that the V_m of the strongly adsorbed ammonia (0.063 cm^3 g^{-1}) is nearly twice that of the strong acrolein adsorption.

Figure 3 shows that on a reduced 500-Bi_2MoO_6 catalyst, also two types of ammonia adsorption can be distinguished. One is weak and nondissociative, with V_m = 0.25 cm^3 g^{-1}, which is twice that of the weak adsorption of acrolein on the oxidized catalyst; the other is moderately strong and nondissociative with V_m = 0.033 cm^3 g^{-1} (see Table 1), and equal to that of the strong acrolein adsorption on a fully oxidized catalyst. On a 600-Bi_2MoO_6 catalyst (see Table 1) the V_m of weak and strong ammonia adsorption are lower by factors

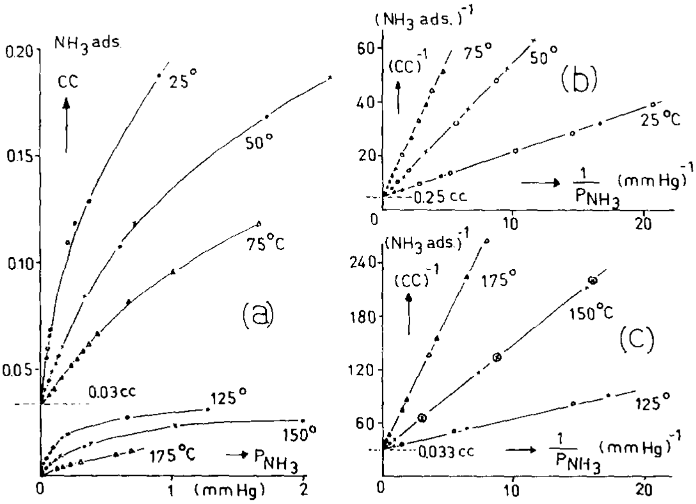


FIG. 3. Adsorption of ammonia on pre-reduced 500-Bi_2MoO_6: (a) adsorption equilibrium, (b) weak and single-site adsorption isotherm and (c) strong and single-site adsorption isotherm.

of 6 and 2, respectively, the V_m for strong adsorption undergoing a similar reduction to that found for the strong acrolein adsorption on the 600-catalyst. The parameters for ammonia adsorption on Bi_2O_3 and MoO_3 are given in Table 1. Measurements of its strong adsorption were made impossible by an early start of the oxidative decomposition.

Adsorption of Propene

Heat of adsorption and total volume V_m of the weak and dissociative adsorption of propene on 500-Bi_2MoO_6 are given in Table 2 where also the accuracy is given: they are closely similar to those reported earlier (*1*) for the weak and dissociative 1-butene adsorption on the same catalyst. Propene adsorption was also measured under conditions where the catalyst was previously contacted with acrolein followed by a short period of evacuation. Only the strongly adsorbed sites remained covered by acrolein. This resulted in a decrease in volume of propene adsorbed from 0.125 to 0.08 $cm^3\ g^{-1}$ (Table 2). A similar effect was found after pretreatment with ammonia (Table 2). On the other hand, pretreatment of the catalyst with butadiene did not reduce the volume of weakly adsorbed propene. The propene adsorption on a 600-catalyst was found to be lower by a factor of 4 compared to the 500-catalyst. The effects of ammonia, of acrolein and butadiene pretreatment on the volume of propene adsorbed are also given in Table 2 and again it is shown that the strongly adsorbed butadiene does not alter the weak propene adsorption. Table 1 gives the parameters for the propene adsorption on MoO_3 which are very similar to the weak propene adsorption on the $BiMoO_6$ catalyst. The propene adsorption on Bi_2O_3 was found to be single site and very weak. It should be noted in this connection that reaction between olefins and Bi_2O_3 starts at much higher temperatures (around 400°C).

Adsorption on the Reduced Bi_2MoO_6 Catalysts

The reduction was carried out at two different temperatures with propene and ammonia, respectively. Reduction carried out at 370°C (see Fig. 6) leaves the number of *B-sites* unaltered independent of the degree of reduction. On the other hand, the number of *A-sites* decreases linearly with increasing reduction of the catalyst. For a reduction carried out at 450°C it is shown that again the number of *A-sites* decreases linearly with reduction, but at this temperature the number of *B-sites* decreases quadratically with the degree of reduction. A similar behavior after reduction at 450°C with 1-butene was reported earlier (*1, 2*). Reduction by ammonia at 450°C, however, has no effect on the number of *B-sites*: that remains constant over a wide range of reduced states. This discrepancy can be explained as follows. The state of reduction was determined after the adsorption measurements simply by measuring the

TABLE 2

ADSORPTION EQUILIBRIA OF PROPENE ON PRETREATED 500-Bi_2MoO_6

	V_m ($cm^3\ g^{-1}$)	log P_0^0 (mm Hg)	Heat of adsorption Q (kcal mol^{-1})
500-Bi_2MoO_6			
Nontreated	0.125 ± 0.006	9.7 ± 0.3	12.1 ± 0.2
NH_3-treated	0.090 ± 0.004	9.1 ± 0.5	9.8 ± 0.5
C_3H_4O-treated	0.080 ± 0.004	9.1 ± 0.5	9.8 ± 0.5
C_4H_6-treated	0.123 ± 0.006	9.6 ± 0.3	10.5 ± 0.2
600-Bi_2MoO_6			
Nontreated	0.028 ± 0.004	10.3 ± 0.3	10.9 ± 0.5
NH_3-treated	0.014 ± 0.004	8.5 ± 0.3	9.6 ± 0.5
C_3H_4O-treated	0.013 ± 0.004	8.8 ± 0.3	9.6 ± 0.5
C_4H_6-treated	0.028 ± 0.004	10.0 ± 0.3	10.2 ± 0.5

oxygen uptake during reoxidation of the catalyst. In the case of a reduction with propene, the catalyst after reduction was heat-treated *in vacuo* for 3 hr at 450°C to remove possible strongly adsorbed reaction products. However, for a reduction with ammonia this special treatment did not appear necessary, the reduced catalysts being supposedly clean enough to proceed with the determination of *B*- and *A-sites*. As found later, the difference in catalyst properties after reduction by the olefins or ammonia was not due to differences in the behavior of the two compounds but to the presence or absence of the subsequent high temperature evacuation. This observation lends support to the hypothesis that the actual removal of the *B-sites* is due to a slow solid state reaction that occurs during the high temperature evacuation, the reaction being too slow to be observed if this evacuation was effected at 400°C [see Batist, Prette and Schuit (*5*)]. However, as shown in Fig. 4 removal of B-sites also affects the reaction rate leading to a more pronounced decrease. The former proposal, i.e., that the catalyst is actually bifunctional, therefore remains valid.

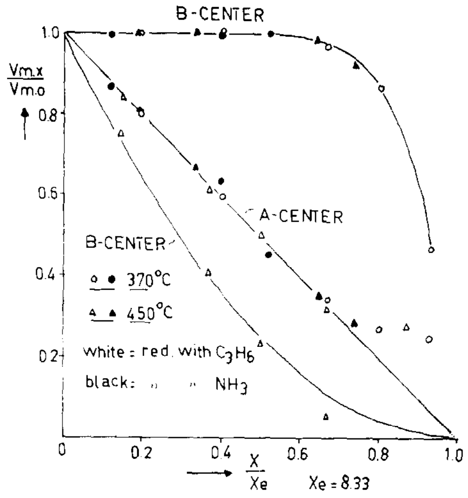


FIG. 4. Dependence of the maximum volume of adsorption (V_m) on the degree of reduction (X).

Oxidation of Ammonia

Figure 5 shows the oxidation of ammonia on the Bi_2MoO_6 catalyst in the absence and in the presence of oxygen, the reaction being carried out at three different temperatures between 350 and 400°C. The parallel lines obtained for reactions in the absence or presence of O_2 show the rate to be only dependent on the ammonia pressure; i.e., $-dP_{NH_3}/dt = kP_{NH_3}$. The activation energy was 37 kcal mol^{-1} and the frequency factor $10^{8.6}$ min^{-1}.

Rate of Ammonia Adsorption

Figure 6 shows the rate of adsorption of ammonia. One observes an initial, very fast, process (weak adsorption), followed

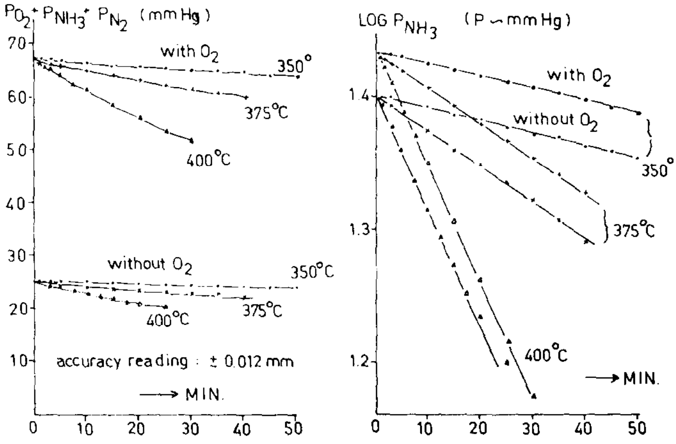


FIG. 5. Oxidation of ammonia on 500-Bi_2MoO_6 as a function of time and temperature. Rate is first order in the ammonia pressure.

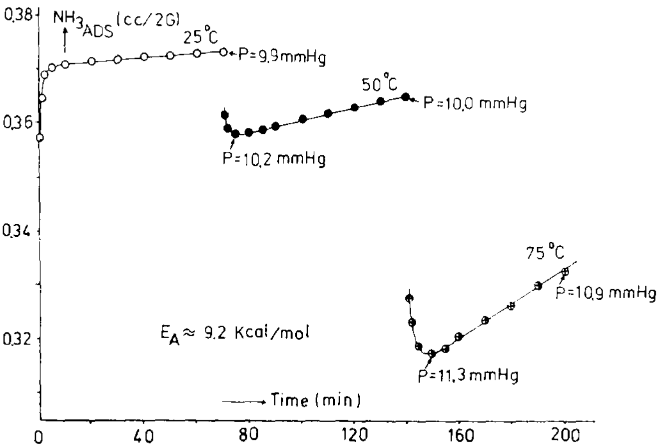


FIG. 6. Strong adsorption of ammonia on 500-Bi_2MoO_6 as a function of time.

by a slower process (strong adsorption). Subsequent measurements at higher temperatures show a fast partial desorption of the weakly adsorbed species but an increase in rate of the adsorption of the slow process. Under the conditions applied (P_{NH_3} = 10 mm Hg, temperature 25–75°C), the strong adsorption should finally lead to full coverage. Since the amount taken up is still far from this value, the rate of adsorption at different temperatures can still be applied for a calculation of the activation energy for strong adsorption. This was found to be of the order of 9 kcal mol^{-1}.

DISCUSSION

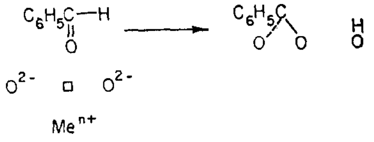
The results of this investigation can be arranged under two headings. The first is formed by the data concerned with maximum volumes of adsorption. Together with those earlier reported for butadiene and butene they form a basis for models aimed at a description of the surface in general and the reactive site in particular. Another set of results, the heats of adsorption and the P_0^0 values, can give us more insight into the characteristics of the adsorption proper and moreover are of importance in discussing the nature of the surface. We shall first discuss the former set and return later to the latter set. A summary of the results is given in Table 3.

Acrolein is adsorbed on the Bi_2MoO_6 catalyst according to two different types of process apparently related to those of butadiene. There is a fast but weak adsorption of the dual site type with a V_m (maximum adsorption) closely similar to that for butene and for the weak butadiene adsorption. Therefore it is presumably connected with the *B-sites* (for the nomenclature of the various sites, see Matsuura and Schuit (*1*). The second type is a slow process with, however, a greater heat of adsorption and with a V_m equal to that of the strong adsorption of butadiene: it therefore presumably takes place on the *A-sites*. Its heat of adsorption on the 600-Bi_2MoO_6 catalyst appears so high that desorption occurs only by decomposition. The weak adsorption is also seen to occur on MoO_3 while an adsorption with similar characteristics to the strong adsorption is observed on Bi_2O_3. This represents an additional argument to support an earlier assumption, viz, that the *B-sites* occur on the edges of the MoO_2-layers and the *A-sites* on the edges of the Bi_2O_2-layers. The difference in site characteristics (dual instead of single) for the strong acrolein adsorption as compared to that of butadiene is an interesting detail. Sachtler *et al.* (*8*) proposed a model for the adsorption of benzaldehyde on V_2O_5–SnO_2 catalysts in which the infrared data are explained by assuming the hydrogen from the –COH group to be dissociated and donated to a

TABLE 3
SUMMARY OF ADSORPTION DATA

Composition	Catalyst state	MoO_3			Bi_2O_3			500-Bi_2MoO_6			600-Bi_2MoO_6			Remarks
		log	P_0^0	Q	log	P_0^0	Q	log	P_0^0	Q	log	P_0^0	Q	
C_3H_6	Oxid.	DS	9.6	10.8	SS	4.7	5.0	DS	9.7	12.1	DS	10.3	10.9	Fast, weak adsorption similar for MoO_3 and Bi_2MoO_6 *B-site*
C_4H_8		DS	9.3	12.0	SS	4.7	5.0	DS	9.5	11.8	DS	10.3	12.1	
C_4H_6		DS	6.7	9.2	SS	4.6	5.8	DS	6.7	9.6	DS	8.5	9.6	
C_4H_6								SS	6.8	18.6	Irreversible			Strong, slow *A-site*
C_3H_4O		DS	7.4	11.5				DS	8.6	11.2	DS	9.0	11.4	*B-site*
C_3H_4O					DS	7.7	21.4	DS	7.8	21.2	Irreversible			Strong, slow *A-site* similar on Bi_2O_3
NH_3		SS	3.0	5.7	SS	3.4	5.5	SS	4.1	6.2	SS	3.8	5.7	Occurs on all sites
NH_3		Irreversible						DS	11.0	24.0	Irreversible			Connected with *A-site*
NH_3	Red.							SS	8.3	16.4				Extra on NH_3 but replaces strong NH_3 adsorption
H_2O								SS	7.7	16.3				Replaces *A-site* adsorption

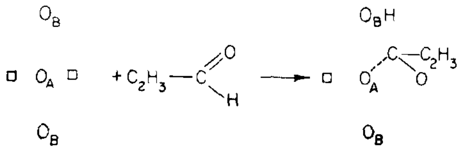
surface O atom while the residual carbonyl group occupies a surface anion vacancy with its oxygen atom, thereby becoming bonded to a neighboring surface oxygen.



This model would also fit our data.

Experiments to measure the V_m of the weak adsorption of propene on a surface covered with strongly adsorbed acrolein shows it to become lower. The strong adsorption of acrolein decreases the number of *B-sites* by an amount equal to 0.045 $cm^3 g^{-1}$ on the 500-catalyst which is of the order of the number of *A-sites* (butadiene, strongly adsorbed, does not influence the weak propene adsorption).

This indicates that the associated H atom occupies one of the surface O atoms belonging to a *B-site*. Since we postulated these O atoms as belonging to the O-layers linking the Bi_2O_2- and MoO_2-layers and therefore to be near a Bi ion (see Matsuura and Schuit (*2*), Fig. 8) this is well feasible and moreover even necessary if we assume with Sachtler *et al.* (*8*) that the residual carbonyl group becomes bonded to a neighboring O atom, i.e. and O_A. The adsorption can therefore be visualized as follows:



A similar picture is obtained for the 600-Bi_2MoO_6 catalyst where the difference between propene adsorption before and after the acrolein adsorption is exactly equal to the number of *A-sites*. Moreover, these results appear to give some additional information concerning the manner in which an olefin is adsorbed. The *B-site* has been postulated by us to consist of two O atoms next to an anion vacancy on a Mo cation. It remained somewhat difficult how to visualize the position of the residual allylic system, i.e., σ-bonded to an O atom or π-bonded to a cation. In the latter case adsorption of a H atom from acrolein would still be possible without interfering with the olefin adsorption. Since this is not in agreement with the experimental results the allyl is in all probability σ-bonded to the O atom. The weak acrolein adsorption can be visualized in a similar manner to the butadiene weak adsorption, the double bond now occupying an anion vacancy situated directly above Mo ions. It is noteworthy but not well understood that the strong acrolein adsorption does not seem to diminish its own weak adsorption.

The adsorption of ammonia is more complicated than that of acrolein. Again we find two different types on an oxidized surface, a weak single-site process and a strong dual-site process. The strong adsorption has a V_m that is either double that of the *A-sites* or half that of the *B-sites*. The latter possibility can be discarded on the argument that it should diminish the olefin adsorption by the amount of the ammonia volume adsorbed. The olefin adsorption was found to be decreased, but this occurs only to the extent of half the volume of strongly adsorbed ammonia. Therefore this ammonia adsorption is connected with the *A-sites*. That it is equal to double the volume of butadiene adsorbed can be explained by letting it occupy the two Bi-cus next to the O_A. These therefore appear to be identical for the reaction. The dissociative character of the adsorption suggests a process such as $NH_2 + H$. Since the adsorption of propene is only decreased to an extent of half the volume ammonia adsorbed, one of the two NH_3 molecules adsorbed donates its H to an O_B. The second NH_3 may donate its H to another O and this is probably the O_A. The NH_2 groups then go to the Bi-cus next to this O_A. An alternative model is that both H atoms go to one and same *B-site*. This would indicate that some *B-sites* are more active in accepting H atoms than others, which does not seem entirely impossible considering the special position of the O_A.

The weak adsorption of ammonia presents a more subtle problem. At first sight it may be described to a physisorption, but there are some objections to this suggestion. Firstly, the quantity adsorbed is such that each ammonia molecule occupies an area in the order of 50 Å^2, which does not seem particularly probable for physiosorption. Secondly, it seems to occur in volumes that are related to those encountered in the chemisorption processes discussed. If we assume that all the cus ions, except those already covered by strong ammonia, bind a molecule via σ-bonding to the cation, the 500-catalyst would adsorb $0.25 - 0.06 = 0.19$ cm^3 g^{-1}, precisely the observed value. If this happens to be correct it presents valuable information since it is the sole evidence so far for the reality of an inactive Bi-cus.

The ammonia adsorption on a fully reduced catalyst ($Bi_2MoO_{5.5}$) is readily accounted for in terms of the model proposed since it is obviously the counterpart of the H_2O adsorption on reduced catalysts. It is equal in quantity to the *A-sites* and therefore occurs on the anion vacancies left by O_A after removal by reduction. It is a moderately strong adsorption that moreover occurs rapidly. An interesting detail in the experiments on reduced catalysts is that the weak adsorption increases compared to that on the oxidized catalyst with just the amount of the strong adsorption; the latter is absent on the reduced system, which is another point in favor of a description of the weak adsorption as a chemisorption.

Surveying the new adsorption data we notice that they are in excellent agreement with the model set up to explain the previous measurements on olefin and diene adsorption. In particular they have strengthened the assumption as to the assignment of the strong adsorption to the Bi_2O_2-edge and the conclusion that only a fraction of the available sites on this edge can be *A-sites*. Moreover, they have given information on the interrelation of A- and B-sites in that these seem to share O^{2-} ions.

Having established the nature of the adsorption of ammonia, we shall now proceed to discuss its *reaction* with Bi_2MoO_6 catalyst. In the temperature range of 350–400°C the rate is strictly first order in the partial NH_3 pressure and completely independent of the absence or presence of oxygen. The activation energy is 37 kcal mol^{-1} and the frequency factor is $10^{8.6}$ min^{-1} g^{-1}. The observation that the rate is independent of the presence of oxygen in the gas phase proves that the oxidation involves the oxygen ions of the solid. In the 400°C experiment about $\frac{1}{3}$ of the ammonia was consumed, necessitating about $1\text{–}2 \times 10^{19}$ atom O. Assuming a surface area of 3.6 m^2 g^{-1}, a surface area per oxygen ion of 10 $Å^2$ and one in every two sites being an oxygen, this is about equal to the total number of O^{2-} ions at the surface. If only O_A are counted as potentially available for oxidation it surpasses this number by at least a factor of 10. There must hence be a supply of oxygen from the interior that is very fast. In fact it must be much faster than the reduction proper since otherwise the first-order dependence on NH_3 could not exist. Moreover, since we know that oxygen is adsorbed rapidly, this particular adsorption has to occur at a different site or a different surface plane than that where the reduction occurs. These observations are in excellent agreement with those reported by Keulks (*9*) on the lack of incorporation of ^{18}O from gaseous isotopic oxygen, only ^{16}O from the solid being present in the products of the oxidation of propene.

A first-order decomposition of NH_3 to N_2 and H_2O, a reaction in which two ammonia molecules must take part, can occur only when the reaction is not determined in its rate by the adsorption of ammonia. From the rate of the adsorption its activation energy was found to be 9 kcal mol^{-1}, hence much lower than the activation energy for ammonia decomposition, viz. 37 kcal mol^{-1}. Therefore ammonia adsorption will be fast relative to the decomposition and equilibrium will be established at oxidation temperature (350–400°C). The rate determining process in the ammonia decomposition should therefore be a reaction between two fragments already adsorbed on the surface. Strongly adsorbed ammonia appears an appropriate starting point: it occurs dissociatively and according to what has been established as regards to the adsorption equilibrium, the coverage at the temperature of the reaction is low and of the order of 0.1. Hence, rate $= k\ \theta^2$, and $\theta = (P/P_0)^{1/2}$, so rate $= k\ P/P_0$.

A mechanism for ammonia oxidation was proposed by Zawadzki (*10*) that is valid for several oxides. Zawadzki put forward the following elementary processes:

N_2O formation: $NHO + NHO \rightarrow N_2O + H_2O$
N_2 formation: $NH + NH \rightarrow N_2 + H_2$
or $NH + NHO \rightarrow N_2 + H_2O$.

Recently Otto, Shelef and Kummer (*11*) studied the reaction of a mixture of isotopically labeled $^{15}NH_3$ and NO on promoted catalysts containing Pt or CuO. They observed the reaction product N_2 to contain one isotopic nitrogen atom ($^{15}N^{14}N$). Therefore they concluded that N_2 is produced by a reaction between NH_3 and NO according to

$$NO + {}^{15}NH_2 \rightarrow N^{15}N + H_2O.$$

We now suggest that the decomposition of ammonia follows a related mechanism. It is assumed that the first process in the reaction network is the formation of a $(NH)^{2-}$ species on a Bi^{3+}-cus according to the following reactions:

$$\mathrm{NH_3 + Bi^{3+} + O_B^{2-} \rightleftarrows (NH_2)^{-}Bi^{3+} + (O_BH)^{-}},$$
$$\mathrm{(NH_2)^{-}Bi^{3+} + O_B^{2-} \rightarrow (NH)^{2-}Bi^{3+} + (O_BH)^{-}}.$$

If both Bi^{3+}-cus next to O_A are occupied in this manner we arrive at a situation

$$\begin{array}{ccccccccccc} (\mathrm{NH})^{2-} & & \mathrm{O_A}^{2-} & & (\mathrm{NH})^{2-} & & \mathrm{NH} & & \mathrm{O} & & \mathrm{NH} \\ & & & & & & \| & & \| & & \| \\ \mathrm{Bi^{3+}} & \mathrm{O^{2-}} & \mathrm{Bi^{3+}} & \mathrm{O^{2-}} & \mathrm{Bi^{3+}} & \text{or} & \mathrm{Bi^{1+}} & \mathrm{O^{2-}} & \mathrm{Bi^{1+}} & \mathrm{O^{2-}} & \mathrm{Bi^{1+}}, \end{array} \quad \text{(Ia)}$$

in which the two representations are equivalent and only differ in the ways of describing the bonds, i.e., ionic or covalent.

This situation is closely similar to that proposed by Zawadzki (*10*): connecting O_A to one of the NH groups would lead directly to his model. For the case of Otto, Shelef and Kummer (*11*), i.e., the reaction of NH_3 + NO, the intermediate situation would be arrived at by an initial adsorption of NO on a metal ion, followed by acceptance of a H and donation of O to another metal. This way of describing the reactions of NH_3 during decomposition therefore appears more generally applicable.

Decomposition of intermediate state (Ia) occurs as follows

$$\mathrm{2(NH)^{2-}Bi^{3+} + O_A^{2-}Bi^{3+} \rightarrow N_2 + H_2O_A + 3Bi^{+}}. \quad \text{(Ib)}$$

Recently Matsuura and Schuit (*2*) proposed that the oxidation of propene to acrolein proceeded via the intermediate reaction

$$\mathrm{(C_3H_4)^{2-}Bi^{3+} + O_A^{2-}Bi^{3+} \rightarrow C_3H_4O_A + 2Bi^{+}}, \quad \text{(II)}$$

which involves an intermediate situation (II) where one of the Bi^{3+}-cus was left unoccupied.

We now propose that the ammoxidation of propene to acrylonitrile proceeds via a combination of intermediate states (Ia) and II),

$$\mathrm{(C_3H_4)^{2-}Bi^{3+} + O_A^{2-}Bi^{3+} + (NH)^{2-}Bi^{3+} \rightarrow H_2O_A + C_3H_3N + 3Bi^{+}}, \quad \text{(III)}$$

in which the intermediate activated complex contains one $(C_3H_4)^{2-}$ and one $(NH)^{2-}$ next to O_A^{2-}. This mechanism is closely similar although somewhat more detailed to that proposed by Grasselli and Suresh (*12*) for the oxidation of propene to acrolein and the ammoxidation of propene to acrylonitrile on U–Sb oxide catalysts. In particular it follows their concept of a direct reaction to acrylonitrile without an intermediate formation of acrolein but also incorporates the importance of the $(NH)^{2-}$ intermediate introduced by them.

Before leaving this subject we would like to discuss two related aspects. The first is a point raised by Haber and Grzybowska (*13*). Of primary importance in our concept is the donation of two H atoms in successive steps to O_B ions that actually belong to Mo, while according to Haber and Grzybowska the first H abstraction is entirely connected with Bi and only the second with Mo. This is a subtle difference since we also considered the passage of the allyl system to Bi^{3+} as the rate determining step even when Mo is present.

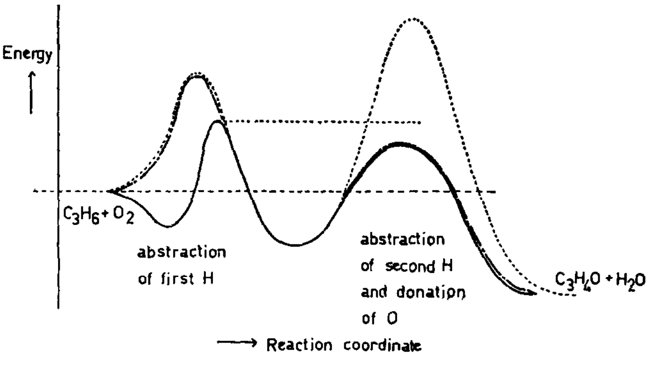


FIG. 7. Energy as function of the reaction coordinate. I (- - -) theoretical situation for Bi_2O_3; II (—) situation according to Haber and Grzybowska (*13*) for Bi-molybdates; III (—) situation for Bi-molybdates according to Matsuura and Schuit (*2*).

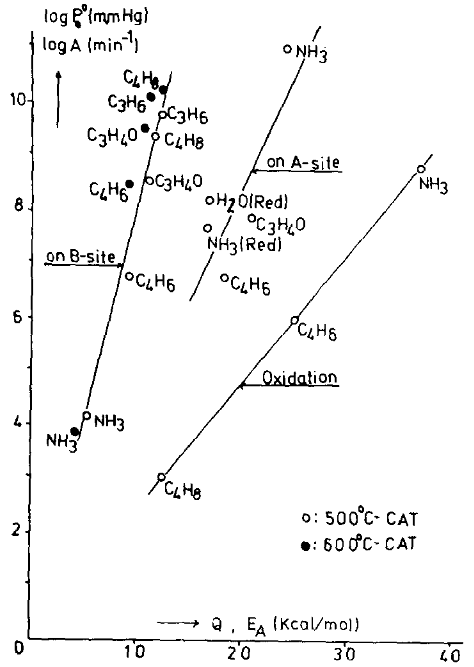


FIG. 8. Relation of log $P_0{}^0$ versus heat adsorption and log A versus activation energy.

However, we still prefer our mechanism, since it is internally more consistent. The problem can be elucidated with help of Fig. 7 where the energy is given as a function of the reaction coordinate. For Bi_2O_3 the abstraction of the H atoms lead to two energy maxima of which the first is the lowest, hence dimers are formed. Haber and Grzybowska's scheme leads to a lowering of the second maximum in the presence of Mo while we assume both maxima to be lowered by Mo, but the first one to a lesser degree than the second; hence this is a less extreme assumption. Of course, the second step involves also a donation of oxygen and is therefore intrinsically different from the first but in view of the parallelism between the butene to butadiene oxidation (not involving O transfer) and the propene to acrolein oxidation we do not believe this an essential feature.

Our second problem is connected with the transfer of electrons and protons during the oxidation process. For reasons of convenience we have written the electron transfer simply as $Bi^{3+} \rightarrow Bi^{+}$. Actually, we tend to the belief that the actual electron transfer during the oxidation is preceded by another one such as $Bi^{3+} + 2Mo^{6+} \rightarrow Bi^{5+} + 2Mo^{5+}$ or $Bi^{3+} + Mo^{6+} \rightarrow Bi^{5+} + Mo^{4+}$ so that the final state after reduction is $Bi^{3+} + 2Mo^{5+}$ or $Bi^{3+} + Mo^{4+}$. It is then noteworthy that a process such as the decomposition of NH_3 or the ammoxidation formally necessitates the transfer of six protons and six electrons. If considered to occur on a site-complex that is limited in size, Zemann's koechlinite structure does not present a combination of six O_B's and three Bi, let alone six Mo. Either, therefore, electron and proton migration occur very readily over large distances or there are defects in the solid structure (such as shear structures) in which the cations are moved from their original position to closer distances. We intend to discuss both aspects, i.e., initial transfer of electrons from one cation to another and the occurrence of defect structures, possibly related processes, in a later paper.

We now discuss the characteristics of the various types of adsorption as given by heats of adsorption and the $P_0{}^0$ values. In Fig. 8 log $P_0{}^0$ versus the heat of adsorption on the one hand and log A (preexponential constant) versus activation energy on the other hand are plotted. For the adsorption we observed two different groups, one belonging to weak adsorption on *B-sites* and another to strong adsorption on *A-sites* demonstrating the different properties of the two adsorptions. For the reactions we find a compensation effect between the preexponential constant and the activation energy, perhaps indicating a close similarity between the oxidation of butene, butadiene and ammonia as to their mechanism.

From the heat of adsorption and the equilibrium pressure for half coverage, experimental values of the differential adsorption entropy (ΔS_{ads}), are calculated by means of the well-known thermodynamic relation

$$\Delta S = (\Delta H - \Delta G)/T \text{ and } -\Delta G = RT \ln K_p,$$

whence

$$\frac{\Delta S_{ads}}{R} = \frac{\Delta H}{RT} + \ln K_p,$$

TABLE 4
EXPERIMENTAL DIFFERENTIAL ADSORPTION ENTROPY AND CALCULATED TRANSLATIONAL ENTROPY (IN ENTROPY UNITS)

	500-Bi_2MoO_6	$-\Delta S_{\mathrm{ads}}$ (strong ads)	600-Bi_2MoO_6				
Composition	$-\Delta S_{\mathrm{ads}}$ (weak ads)		$-\Delta S_{\mathrm{ads}}$ (weak ads)	${}_3S_{\mathrm{tr}}$	${}_2S_{\mathrm{tr}}$	$-\Delta S_{\mathrm{calc}}$	ΔS_{vap}
C_3H_6	31.4 ± 2		30.7	37.3	18.0	19.3	19.9
C_4H_8	28.6		35.2	38.2	19.3	18.9	22.2
C_4H_6	17.6	18.1	25.8	38.1	19.2	18.9	20.2
C_3H_4O	23.9	22.7	30.4	37.3	18.0	19.3	23.1
NH_3	5.9	37.6	4.0	34.5	14.2	20.3	20.7
NH_3 (on red.)		22.4					
H_2O (on red.)		23.8		34.8	14.3	20.5	27.0

where K_p the equilibrium constant, is defined by the relation $K_p = \theta/(1-\theta)\,P$ and is actually the reciprocal $P_0{}^0$-value. In Table 4 the differential adsorption entropies ΔS_{ads} at 25°C are recorded. In the same table the translational entropy of a perfect three-dimensional gas (${}_3S_{\mathrm{tr}}$) and of a perfect two-dimensional gas (${}_2S_{\mathrm{tr}}$) are shown, as calculated following the equations *(14)*

$$
\begin{aligned}
{}_3S_{\mathrm{tr}} &= R \ln M^{3/2}T^{5/2} - 2.3, \\
{}_2S_{\mathrm{tr}} &= R \ln MTa + 65.80, \\
\Delta S_{\mathrm{calc}} &= {}_2S_{\mathrm{tr}} - {}^3S_{\mathrm{tr}}.
\end{aligned}
$$

where M is the molecular weight of the gas and a the area available per molecule. The area available per molecule is assumed to be C_3H_6 = 34 Å², C_4H_8 = 46 Å², C_4H_6 = 45 Å², C_3H_4O = 39 Å², NH_3 = 13 Å² and H_2O = 12 Å². Moreover, we also give ΔS_{vap}, i.e., the entropy increase accompanying the vaporizing of a liquid under 1 atm pressure, as calculated from ΔH_{vap} at 25°C by means of the following relation

$$\Delta S_{\mathrm{vap}} = \Delta H_{\mathrm{vap}}/T + R \ln P_s,$$

where p_s is the ratio between the actual vapor pressure and 1 atm pressure. The experimental data for ΔS_{ads} have been given in Table 4 and for comparison also the values of ${}_3S_{\mathrm{tr}}$, ${}_2S_{\mathrm{tr}}$, ΔS_{calc} as the difference between ${}_2S_{\mathrm{tr}}$ and ${}_3S_{\mathrm{tr}}$ and finally the entropy of vaporization (T = 25°C). It is seen that the entropy loss of most weak adsorptions is situated between a loss of three and two translational degrees of freedom. The values for the adsorption on reduced catalysts are more near to the loss of two translational degrees of freedom. Weakly adsorbed ammonia on an oxidized catalyst is however almost "free" in its translational freedom while the strong adsorption of ammonia is almost entirely immobile. A rather interesting case is given by strongly adsorbed butadiene and acrolein. These are apparently similar to the liquid states, an observation somewhat difficult to explain. The present data are in need of a more extensive theoretical analysis which we shall not give here. However, a most relevant feature is the observation that all adsorption on *B-sites* belongs to one group and all adsorption on *A-sites* to another group, which we believe strengthens our hypothesis of a different origin for the two sites. It is quite interesting in this connection that we find a similar relation between the frequency factor A and the activation energy (compensation law) but again with a different slope. Proceeding from the considerations above there is an indication that the *R-site* (the site on which the activated complex occurs) is different from either *A-* or *B-sites*. We intend to return to this point in a latter publication.

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