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Interactions of Acetone with MoO_3

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Interactions of acetone and acetone/oxygen mixtures with MoO_3 were studied at 215–300°C by pulse method. It has been shown that acetone is deoxygenated to propylene or oxidized to acetic acid, CO, and CO_2. Moreover a part of acetone is reversibly adsorbed and several minutes are necessary for acetone to be removed with a flow of carrier gas. As the surface is endowed with deoxygenating and oxidizing sites the desorbing acetone leaves the reactor mainly in the form of CO. These results agree with theoretical predictions based on the bond-strength model of active sites, according to which the sites of the first type (conversion of acetone) are localized on (100) face of MoO_3 and those of the second type (adsorption) on (001) and (101) planes. Both types of sites consist of surface anion vacancies and differ in the strength of bonding of oxygen. On the (100) face the bond strength is sufficiently large to break C=O bond in acetone. On the other faces the interactions between acetone and surface are much weaker. In this context the application of acetone as poison of other reactions (e.g., conversion of methanol) is discussed.

INTRODUCTION

Tatibouët and Germain (*1*) have determined the initial selectivities (*S*) to all products formed at 291°C in conversion of methanol over a series of MoO_3 samples of different grain morphology. Percentage (*P*) of various crystallographic planes in the external surface of MoO_3 grains was determined by statistical study of microphotographs. On the basis of *S–P* correlations the quoted authors have univocally ascribed the selective formation of formaldehyde, methylal, and dimethyl ether to (010), (100), and (001) + (101) planes, respectively. Let us focus our attention on the formation of methylal and dimethyl ether, both reactions involving dehydration. As pointed out in (*1, 2*) active centers for dehydration can be identified with surface anion vacancies, which in terms of acid–base mechanism are equivalent to Lewis acid centers. The presence of two types of such centers of different strength on MoO_3 surface has been demonstrated in (*3*) by ir studies of adsorbed piridine, ammonia, and acetone. In particular it has been observed that acetone is adsorbed on MoO_3 in a nondissociative way. The quoted bases added by pulses to the flow of the reaction mixture (at 215°C) were also used as poisons blocking the Lewis acidic sites. It has been found that admixture of piridine or ammonia (strong bases) results in complete and irreversible inhibition of the formation of both methylal and dimethyl ether, while acetone (weak base) hinders selectively the formation of ether. Poisoning with acetone has been found to be reversible and the yield of dimethyl ether reached its initial level in about 15 min after injecting a pulse of acetone. The authors (*3*) concluded thus that dimethyl ether is formed on the stronger of Lewis acidic centers present on the surface of MoO_3 and methylal on the weaker ones.

The structure of dehydration sites on MoO_3 has been recently discussed also in terms of the bond-strength model of active sites (BSMAS) (*4*). In this model geometric and energetic correspondence between adsorbed reactant and the neighborhood of adsorption site is regarded. Structural con-

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siderations concerning various planes of catalysts are based on crystallographic data and on available shapes and dimensions of molecules. Bond strength calculated according to the modern bond-length–bond-strength concept (*5, 6*) is taken as a measure of binding energy. Elementary steps consisting in the exchange of oxygen atom between the organic species and catalyst surface are thought to proceed on the condition that the bond strength of oxygen with presumed step product is higher (or comparable) than that with the substrate. To evaluate the probability of a given presumed reaction we have thus to compare the strength of oxygen bonding with organic species (s_{C-O}) and the sum of strengths of its bonds with the catalyst surface (Σs_{Me-O}). Condition for exchange of hydrogen is entirely analogous. Detailed data concerning BSMAS and its applications are given in (*4, 7–9*).

In particular, dehydration of methanol to dimethyl ether is thought to commence with dissociative adsorption of two molecules of alcohol resulting in their dehydrogenation and location of methoxyls on two adjacent anion vacancies. One of these methoxyls should be firmly bonded to the surface with $\Sigma s_{Me-O} > s_{C-O}$, so that deoxygenation could occur. The liberated methyl group reacts with the other more loosely

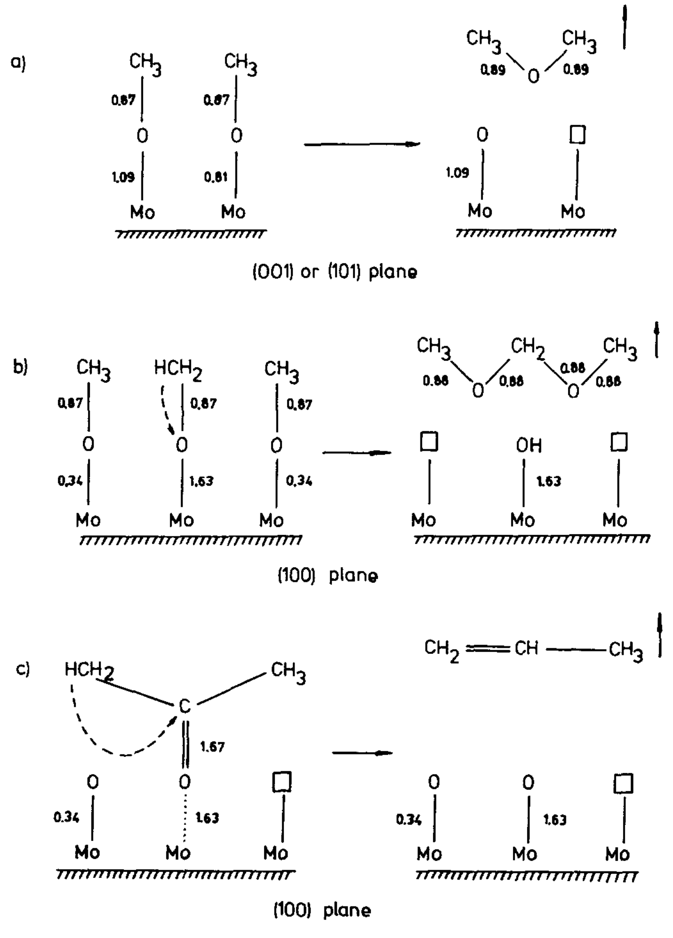

FIG. 1. Bond-strength schemes for the reactions: methanol → dimethyl ether (a), methanol → methylal (b), and acetone → propylene (c) on various morphological planes of MoO_3. Numbers indicate the bond strength in valence units.

bonded methoxyl (for which $\Sigma s_{Me\text{-}O} < s_{C\text{-}O}$) to form dimethyl ether. Active sites fulfilling the above-mentioned geometric and energetic conditions have been identified on (001) and (101) planes of MoO_3 and the respective energetic scheme is recalled in Fig. 1a.

The mechanism of methylal formation (Fig. 1b) is highly analogous. It requires three adjacent anion vacancies of which only the central one can act as deoxygenation center. Moreover, one hydrogen must be abstracted from central carbon atom as marked in Fig. 1b. As it has been indicated in (*4*), (100) plane is unique among the morphological planes of MoO_3 on which three methoxyls may be adsorbed in a configuration convenient to form methylal directly.

Both reactions discussed above involve dehydrogenation and evolution of water. Detailed data concerning these steps are given in (*4*), where argumentation for the selective formation of formaldehyde on (010) plane of MoO_3 is also provided.

As can be seen, the theoretical analysis performed in terms of BSMAS provides the geometric and energetic argumentation for precise location of various active sites on various faces of MoO_3, the conclusions remaining in complete agreement with experimental facts given in (*1*). However, if we consequently assume that the bond strength may be taken as a measure of the strength of Lewis acidic sites we must conclude that methylal is formed on stronger sites ($\Sigma s_{Mo\text{-}O} = 1.63$) as compared to those yielding dimethyl ether ($\Sigma s_{Mo\text{-}O} = 1.09$). This conclusion is precisely opposite to that of paper (*3*).

The following explanation of the above mentioned contradiction may be offered. The $s_{C\text{-}O}$ in acetone is equal to 1.67 (*4*). In the conditions of catalytic reaction (conversion of methanol) acetone can be adsorbed on both types of Lewis acidic sites: stronger on (100) plane (yielding methylal) and weaker on (001) and (101) planes (yielding dimethyl ether). The latter sites become empoisoned with acetone and formation of dimethyl ether is hindered. On the contrary, $\Sigma s_{Mo\text{-}O}$ of the former sites is comparable with $s_{C\text{-}O}$ in acetone and thus its deoxygenation appears possible. The simplest reaction pathway yielding propylene is shown in Fig. 1c. The hydrogen transfer from the lateral to central carbon is probably accomplished with intermediation of surface OH group. An alternative reaction pathway could consist in degradation of highly activated $CH_3{—}\underset{\|}{C}{—}CH_3$ species and its deep oxidation to C_2 and C_1 products with simultaneous formation of water. In this process oxygen atoms originally abstracted from molecules of acetone are expected to be consumed. The latter mentioned oxygens can also be used in formation of water with hydrogens abstracted from methanol in the main reaction (conversion of methanol to formaldehyde and to methylal). In such a way the self-cleaning of Lewis acidic sites on (100) plane can take place, the sites remaining vacant and able to take part in formation of methylal.

The aim of the present work is to check experimentally the above hypothesis.

EXPERIMENTAL

$MoO_3 \cdot xH_2O$ was precipitated from 20% aqueous solution of ammonium paramolybdate with HNO_3 (1 : 1) at pH $\approx$ 2. The precipitate was filtered, washed out, dried at 120°C for 5 h and annealed successively at 300°C for 24 h, 350°C for 2 h, and 400°C for 2 h. The BET (krypton) surface area of the obtained MoO_3 preparation was 3.50 m^2/g. Its X-ray pattern (Dron-2 diffractometer, Cu$K\alpha$) agreed with literature data (*10*). X-Ray reflections were narrow, indicating that the preparation was well crystallized. Relative intensities of the main reflections (020), (110), (040), (021) were 62, 40, 52, 100, respectively, proving that orientation effects were insignificant and thus that participation of various morphological planes in the external grain surface was comparable. The conclusions from X-ray analysis were confirmed with scanning electron mi-

FIG. 2. Typical grain shapes of MoO_3 as observed with scanning electron microscopy (20,000×).

croscopy (JXA-50A JEOL, 20,000×). The typical grain shapes are shown in Fig. 2. They are the same found and discussed in detail in (*1, 11*).

Reactions of acetone were studied at 215, 250, and 300°C by pulse method. Pulses (0.3 μl) of liquid acetone (Ac) (which immediately evaporated inside a warm tube) were introduced into a stream of helium by means of a syringe and those of 0.3 μl of liquid acetone + 0.6 ml of gaseous oxygen (Ac/O_2) with the help of six-port valve. The carrier gas passed at the rate of 30 ml/min over 1.1 g (1 ml) sample of MoO_3 placed in stainless-steel microreactor of 8.5 mm i.d. Before the catalytic testing fresh sample of MoO_3 was heated for 30 min at reaction temperature in the stream of carrier gas. After 5–15 pulses of Ac or Ac/O_2 a "stationary state" was reached as described in detail in the next paragraph. Results obtained in this state are considered and discussed. As it may be easily estimated, one pulse of acetone could cover about 6% of the surface of MoO_3. Taking into account experimental values of conversion (20–50%, cf. Figs. 3 and 4) and existence of dynamic "equilibrium" between the gas phase and surface we may conclude that real coverage was much smaller. It may be also worth noting that the number of O_2 molecules introduced in one pulse of Ac/O_2 exceeded three times that required for total combustion of simultaneously pulsed acetone.

The reactor was connected with the system of gas chromatographs. FID part (path 1, separation of liquids) consisted of a 3-m column filled with 20% Carbowax 20 M and 4% terephtalic acid on Chromosorb W, working at programmed temperature 60–140°C. To distinguish between acetone and acrolein (which could be one of the reaction products) additional analyses were performed using 2-m column with $\beta\beta'$ODPN, and these experiments excluded the presence of acrolein among the reaction products. TCD part (separation of gaseous products) consisted of 1-m column with molecular sieve 13× (path 2, analysis of CO) and of a 4-m column filled with 15% DMS on Chromosorb W (path 3, analysis of CO_2), working at room temperature. The entire analysis of the reaction products required thus three pulses directed alternatively into analytical paths 1, 2, and 3. Such procedure is justified for catalyst working in a "stationary state."

Results of experiments are expressed in the following terms: conversion, C = (acetone consumed/acetone introduced), yield of i-product, Y_i = (acetone transformed to i/acetone introduced). Total yield ΣY_i is also given in each case as it is always distinctly smaller than C.

RESULTS AND DISCUSSION

Preliminary studies of interactions of pure Ac or Ac/O_2 mixtures with MoO_3 have shown that

1. Four products are formed in various proportions. These are propylene (P), acetic acid (AA), CO, and CO_2 (with the exception of experiments done at 215°C, where AA is absent).

2. If Ac or Ac/O_2 are pulsed over fresh sample of MoO_3, conversion and distribu-

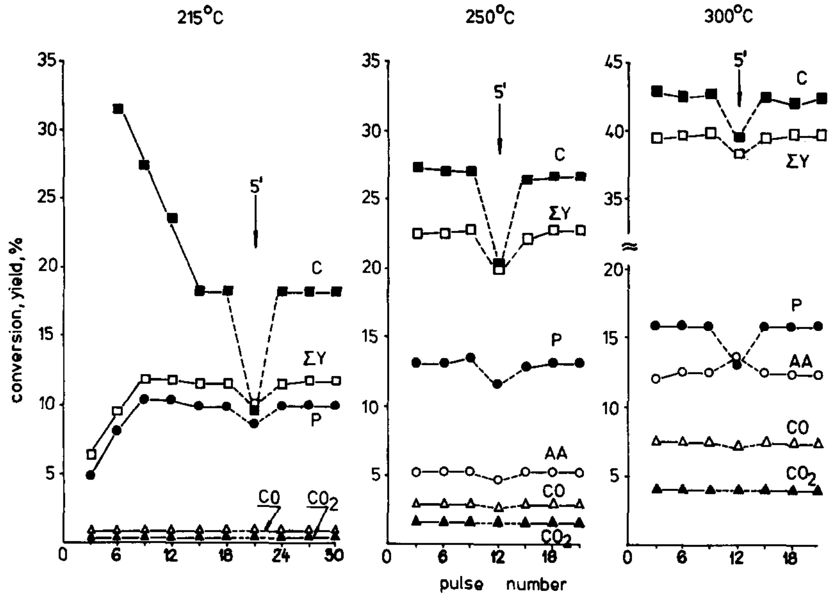

FIG. 3. Conversion of acetone, C = (acetone consumed/acetone introduced), yields to various products, Y_i = (acetone transformed to i/acetone introduced), and total yield ΣY_i as function of a number of Ac pulses and of temperature. P, propylene; AA, acetic acid. The period of time between subsequent pulses was 10 min with exception of those marked 5′.

tion of products for the first 5–15 pulses are nonreproducible, irrespectively of reaction temperature. However, once "stationary state" is reached, reproducibility of successive pulses becomes excellent, provided that additional condition explained in point No. 3 is fulfilled. The above-mentioned initial effect does not appear again either after prolonged isothermal heating of the sample in a stream of helium or after changing reaction temperature.

3. If the period of time Δt between subsequent pulses is equal at least 10 min, conversion and distribution of products in the "stationary state" are the same for each pulse. If Δt is shorter (e.g., 5 min), remarkable decrease of C and minor decrease of ΣY is observed. A Δt = 10 min was thus chosen as standard.

Figures 3 and 4 show the representative sets of experimental data for Ac and Ac/O$_2$ pulses, respectively. As an example initial effect is included in Fig. 1, 215°C and Fig. 2, 215°C. Effect of Δt = 5 min is demonstrated in each set of data.

As already mentioned, P, AA, CO, and CO$_2$ are identified as reaction products. This means that in agreement with the hypothesis offered in the Introduction acetone is partly deoxygenated to propylene and partly oxidized.

Propylene is usually the main reaction product. With increasing temperature and on passing from Ac to Ac/O$_2$ pulses, ΣY increases and selectivity to propylene decreases in favor of those to the products of oxidation. This is considered to be the expected trend.

ΣY is always markedly smaller as compared to C, calculated from the amount of consumed acetone. The difference between them, diminishing with temperature increase, is ascribed to the reversible adsorption of acetone on MoO$_3$ surface (*3*). If $\Delta t \geq$ 10 min adsorbed acetone is entirely removed with carrier gas during that time. If $\Delta t <$ 10 min, both C and ($C - \Sigma Y$) are markedly reduced as adsorption sites are still partly occupied. This effect also diminishes with temperature increase. Shorten-

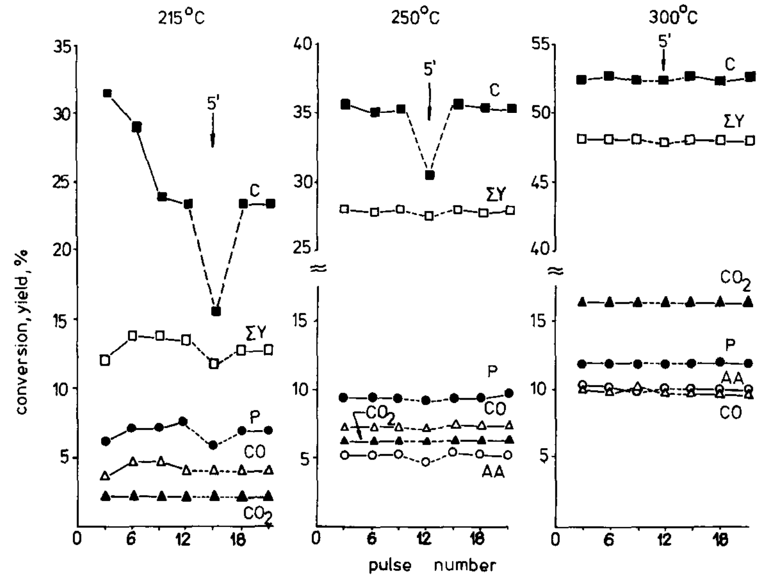

FIG. 4. Conversion of acetone, yields to various products and ΣY_i as function of a number of Ac/O_2 pulses and of temperature (cf. Fig. 3).

ing of Δt strongly influences C, but only slightly the yields to all reaction products and their sum ΣY. This means that in agreement with theoretical prediction (cf. Introduction) two types of sites exist on MoO_3 surface. On the first of them acetone is only reversibly adsorbed (5–10 min are necessary for acetone to be removed with carrier gas), on the other sites acetone is converted to various products.

To study the destiny of acetone reversibly adsorbed on MoO_3 surface the following four experiments were performed at 215°C, i.e., at temperature at which adsorption was the most efficient.

(i) U-shape trap of stainless steel, plunged in liquid nitrogen was mounted after the reactor and after the four-port valve. At the beginning of the experiment the valve directed the stream to the analytical part of the aparatus. The reactor contained a fresh sample of MoO_3. Fifteen pulses of acetone (0.3 μl) were introduced each 10 min to reach a "stationary state" of the catalyst. The catalyst was left for 30 min in a stream of helium at 215°C. Then one 0.3-μl pulse of Ac was introduced and 30 s later (30 s were sufficient to remove the reaction products) the stream was directed to the trap for 15 min. After this time the trap was closed, heated up in boiling water, and its content was analyzed with gas chromatography. Only a trace of propylene was detected. This result allows us to conclude that adsorbed acetone either remained accumulated on the catalyst surface in an unknown form or it desorbed during the experiment in form of CO which could not be trapped in the above mentioned way.

(ii) Fresh MoO_3 sample was pretreated in the reactor in the same way as described above (15 pulses of Ac + 30 min in the stream of carrier gas at 215°C). Then one pulse of Ac (0.3 μl) was introduced, the stream being directed to the atmosphere. Thirty seconds later the stream was joined to the analytical part and 1 ml of O_2 was pulsed over the catalyst. O_2 pulses were repeated each 2 min. Analysis by gas chromatography proved that O_2 pulses result in removing CO_2 from the catalyst. The first pulse produced 0.35 μmole of CO_2, the second 0.15 μmole, the third 0.05 μmole, and the fourth only traces. The entire amount of

CO_2 produced in this way corresponded to about 70% of adsorbed acetone, i.e., to about 70% of $(C - \Sigma Y)$. It was observed moreover in a separate experiments that if the first pulse of O_2 is introduced 10–15 min after the last pulse of Ac no CO_2 is produced. Combining the results of experiments (i) and (ii) and taking into account that acetone is indeed adsorbed on MoO_3 in a nondissociative form (ir studies reported in (*3*)) one may conclude that acetone is first adsorbed in acetone-like form and it poisons the respective sites. About 5–10 min are necessary for acetone to be removed with carrier gas. As the MoO_3 surface is endowed with deoxygenating and oxidizing sites the slowly desorbing acetone leaves the reactor mainly in form of CO (however, desorption of acetone may be accelerated by O_2 pulses converting it to CO_2). This conclusion was verified in experiment (iii).

(iii) Fresh MoO_3 sample was pretreated in the reactor in the same way as in (i) and (ii). Thirty seconds after the last pulse of Ac the stream of carrier gas was directed for 15 min to the standard I_2O_5-containing tube for colorimetric detection of CO (sensitivity of about 0.2 μmole). The experiment was repeated 10 times. It has been found that CO indeed slowly leaves the reactor and its entire amount is comparable with that corresponding to the adsorbed acetone. As the I_2O_5-tube is sensitive also to hydrocarbons U-shape trap plunged in liquid nitrogen was used in the last-mentioned experiment, placed between the reactor and the I_2O_5-tube. Efficiency of this protection was verified experimentally.

(iv) It could seem that this is not acetone but one of the reaction products (e.g., CO) which is adsorbed on the catalyst surface. If so, however, each next pulse of Ac introduced before much of the accumulated material is desorbed (Δt = 5 min), should result in increasing the yield of the product which is adsorbed. Such effect was not observed. To be entirely sure the last experiment was performed in the following way. Fresh sample of MoO_3 was pretreated in the reactor in the same way as in (i), (ii), and (iii) and several pulses of CO (18 μl), CO_2 (18 μl), and propylene (6 μl) were introduced at 215°C and analyzed with gas chromatography. The size of pulses corresponded to the amount of adsorbed acetone. Neither adsorption nor conversion of these three reactants was observed.

CONCLUSIONS

Two types of interactions of acetone with MoO_3 have been predicted theoretically on the basis of BSMAS. This prediction has been confirmed experimentally which speaks in favor of possible applications of the model.

A part of acetone pulsed over MoO_3 at 215–300°C is adsorbed on its surface. As results from (*3*) this is nondissociative adsorption. The adsorption is reversible and several minutes are necessary for acetone to be removed from MoO_3 surface and to be carried away with a flow of carrier gas. Desorbed acetone, moving slowly along the catalyst bed is oxidized to CO on the sites mentioned below. In the meantime the adsorption sites are blocked with acetone. Acetone can be thus used as a poison of catalytic reaction (e.g., conversion of methanol) which proceeds on the same sites on which it is adsorbed.

There are, however, other sites on the surface of MoO_3, on which the most part of pulsed acetone is deoxygenated to propylene or oxidized to acetic acid, CO, and CO_2. These reactions are very rapid and thus quick self-cleaning of the sites of the second type takes place. Thus acetone cannot be an efficient poison of the reactions developing on the latter mentioned sites.

According to the theoretical, BSMAS-based, considerations presented in Introduction the sites of the first type can be localized on the (001) and (101) planes of MoO_3, while the sites of the second type on the (100) plane.

It seems that the obtained results can have more general significance. Various molecules are frequently used as catalytic poisons in works aiming at identification of active sites. In each case interactions of a given molecule with a given catalyst should be carefully examined in advance. In particular, if the studied reactions proceed at elevated temperatures, data concerning room temperature should be used with caution.

It seems also noteworthy that conversion of isopropanol is sometimes used as a test for the presence of dehydrating and dehydrogenating sites on catalyst surface. In this case the yield ratio of propylene and acetone is taken as a measure of population of the two above-mentioned sites. This would be true if both reactions were independent (parallel). The present studies prove that propylene may be consecutively formed of acetone. In such a case Y_P/Y_{Ac} ratio depends not only on the nature of the catalyst surface but also on various external reaction conditions (contact time, temperature). Kinetic studies are thus necessary before using Y_P/Y_{Ac} ratio as a measure of site population.

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