INTERACTION BETWEEN THE COMPONENTS OF THE REACTION
MIXTURE AND THE SURFACE OF CATALYSTS FOR THE OXIDATIVE
AMMONOLYSIS OF PROPYLENE

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A study was made of the change in the properties of tin-antimony and bismuth-molybdenum oxide catalysts during the partial reduction of their surfaces with propylene and a propylene-ammonia mixture. Different characteristics of the interaction of ammonia with the surface of the catalysts studied were established.

Исследовано изменение свойств оловосурьмяного и висмутмолибденовых катализаторов при частичном восстановлении их поверхности пропиленом и смесью пропилена с аммиаком. Установлен различный характер взаимодействия аммиака с поверхностью исследованных катализаторов.

INTRODUCTION

Bismuth-molybdenum and tin-antimony oxide catalysts have a high selectivity in the oxidative ammonolysis of propylene but differ with regard to kinetic law of this reaction /1, 2/. When reducing with butylene /3/, the oxygen on the bismuth-molybdenum oxide catalysts was found to be uniform with respect to binding energy. Fot the tin-antimony oxide catalyst, the binding energy of oxygen varies depending on the degree of surface reduction. According to kinetic data /1/, on the bismuth-molybdenum oxide catalyst acrylonitrile is formed via consecutive

formation of acrolein, whereas with the tin-antimony oxide catalyst the direct reaction prevails.

The purpose of the present study is to compare the properties of tin-antimony and bismuth-molybdenum oxide catalysts during the reduction with propylene and a propylene-ammonia mixture. Such an approach permits us to reveal characteristics of the interaction of the reaction mixture components with the catalyst surface and their influence on the oxidation process.

EXPERIMENTAL

The investigations were carried out using a pulse-microcatalytic method with a vibrofluidized catalyst bed /4/. A complete chromatographic analysis of the reaction products was made for each pulse. Reduction was performed with helium-diluted mixtures of the following compositions: 0.3% C_3H_6 + 99.7% He; 0.3% C_3H_6 + + 0.4% NH_3 + 99.3% He. Below, by propylene and a propylene-ammonia mixture, diluted mixtures will be meant. The amount of oxygen removed from the catalyst surface was calculated using the corresponding stoichiometric equations /5/. Catalysts used: tin-antimony oxide catalyst with a Sn : Sb ratio of 2 : 1 and a specific surface area of 29.7 m^2/g, bismuth molybdates $Bi_2O_3 \cdot 3MoO_3$ (α-phase) and $Bi_2O_3 \cdot MoO_3$ (γ-phase) prepared according to the method described in Ref. /6/, with specific surface areas of 2.0 and 3.4 m^2/g, respectively.[*] Prior to the experiment the samples were subjected to standard pretreatment in oxygen /7/.
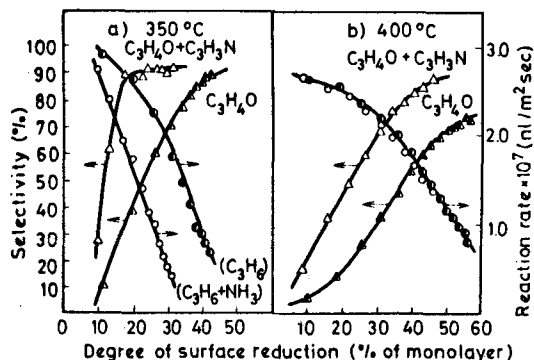
Fig. 1.   Reduction of tin-antimony oxide catalyst (catalyst 0.27 g, helium flow
40 ml/min)
○, △ – rate of overall conversion of propylene and overall selectivity to
acrolein and acrylonitrile, reduction with C_3H_6 + NH_3 mixture
◐, ▲ – rate of overall conversion of propylene and selectivity to acrolein,
reduction with C_3H_6

RESULTS AND DISCUSSION

The data on the reduction of the tin-antimony oxide catalyst are given in Fig. 1.
With the increasing degree of reduction of the catalyst surface, a sharp decrease in
the rate of the overall conversion of propylene is observed. Simultaneously, the
selectivity to the partial oxidation products increases. During the reduction of the
catalyst with a C_3H_6 + NH_3 mixture, acrolein is formed among the reaction prod-
ucts together with acrylonitrile. The selectivity to acrylonitrile is 7 to 10 times
higher that to acrolein. This ratio remains unchanged as the reduction proceeds from
the first pulse on. The characteristics of the change in the rate of the overall con-
version of propylene and the selectivity may be explained by nonuniformity of the
surface oxygen which was established during the reduction of this catalyst with but-
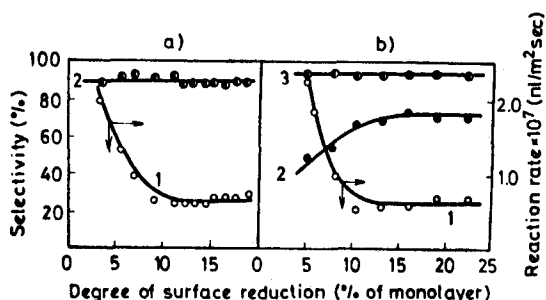ylene /7/.

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Fig. 2. Reduction of bismuth-molybdenum oxide catalyst (α-phase, catalyst 1.0 g, helium flow 30 ml/min)
a) reduction with C_3H_6; 1 – rate of overall conversion of propylene, 2 – selectivity to acrolein
b) reduction with $C_3H_6 + NH_3$ mixture; 1 – rate of overall conversion of propylene, 2 – selectivity to acrylonitrile, 3 – overall selectivity to acrylonitrile and acrolein

During the reduction of the tin-antimony oxide catalyst with the propylene-ammonia mixture, ammonia blocks a part of the surface area, which results in a decrease in the rate of the surface reduction. A sharper increase in the selectivity to the partial oxidation products with the propylene-ammonia mixture indicates that ammonia blocks mainly the weakly bound surface oxygen. The surface of the tin-antimony oxide catalyst is capable of retaining rather strongly the absorbed ammonia at the experimental temperatures (350, 400 $^\circ$C). The oxidation of ammonia to molecular nitrogen proceeds at a low rate. Treatment with a helium flow does not remove the absorbed ammonia, so it may participate in the formation of acrylonitrile upon passing C_3H_6 pulses to the catalyst sample.

During the reduction of the bismuth-molybdenum oxide catalysts with propylene and the propylene-ammonia mixture, the rate of the overall conversion of propylene falls with the onset of oxidation and then remains constant (Fig. 2). How-

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ever, the selectivity to the partial oxidation products is independent of the degree

of surface reduction. The observed decrease in the rate of reaction cannot be explained

by consumption of a portion of the surface oxygen for the following reasons. According to the calorimetric measurements /3/, the surface oxygen of bismuth molybdate

is uniform. This is also indicated by the constancy of the selectivity to the partial

oxidation products. During the interaction of α-butylene with the surface of the

bismuth-molybdenum oxide catalyst at the same temperatures, the reaction rate is

independent of the degree of reduction /3/. The decrease in the reaction rate

during the first pulses appears to be due to an irreversible adsorption of small amounts

of acrolein on the surface of bismuth molybdate. Poisoning does not occur if oxygen

is present in the reaction mixture. Here, the rate of the steady reactions of oxidation or oxidative ammonolysis of propylene approximates the rate of reduction in

the first pulse. When keeping the sample in a helium atmosphere at the experimental temperature (350, 400 $^{\circ}$C) after a series of the reduction pulses, the absorbed

acrolein is oxidized to CO_2 owing to the high mobility of the bulk oxygen in bismuth

molybdate, which is supported by the chromatographic data. Therefore, the activity of the catalyst attains the initial value after the pause (Fig. 3). The nature of

the dependence of the reaction rate on the degree of reduction is not changed by

the repeated reduction. It was shown by special experiments that the introduction

of acrolein to the catalyst in an amount equal to that formed in the first pulse reduces the reaction rate to a constant value upon subsequent reduction with propylene

(Fig. 3). Addition of a further portion of acrolein does not change the rate. The

introduction of a large amount of acrolein to the fresh catalyst immediately reduces

the reaction rate to a constant level. The interaction of bismuth molybdate with a

propylene-ammonia mixture at 350 and 400 $^{\circ}$C is accompanied by oxidation of a
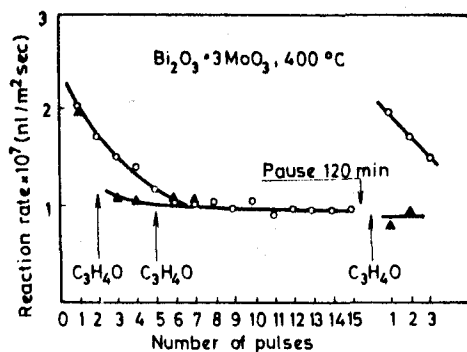
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Fig. 3. Influence of acrolein on the rate of reduction of bismuth-molybdenum oxide catalyst with propylene (α-phase, catalyst 2.0 g, helium flow 40 ml/min)

○ — reduction without introduction of acrolein

▲ — reduction with introduction of acrolein

Arrows indicate the introduction of pulses of acrolein.

portion of ammonia to nitrogen. Therefore, the propylene-ammonia mixture, un-like the tin-antimony catalyst, reduces the surface of the bismuth-molybdenum cat-alysts at a higher rate than propylene only.

The regularities observed during the reduction of bismuth molybdates of dif-ferent compositions are the same. The difference is that the γ-phase is somewhat more active, and with the α-phase, the selectivity to the partial oxidation products is higher.

Thus, the investigations have shown that the correlation between the selec-tivity and the bond strength of the surface oxygen found earlier /3/ holds for the tin-antimony oxide catalyst in the reactions of oxidation and oxidative ammono-lysis of propylene. The surface oxygen of bismuth-molybdenum oxide catalysts is uniform, but unlike the reduction with butylene, the reduction with propylene is inhibited by the product acrolein. The differences in the nature of the interaction

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of ammonia with the surface of the catalysts studied have been established. The

presence of large amounts of absorbed ammonia on the surface supports the assump-

tion /1/ that the direct formation of acrylonitrile prevails on this catalyst.

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