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STEADY STATE OF A BISMUTH-TIN CATALYST IN THE OXIDATIVE DEHYDRODIMERIZATION OF PROPYLENE

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The effect of the extent of reduction of a bismuth-tin oxide catalyst on the rate of oxidative dehydrodimerization and total oxidation of propylene and on the oxygen binding energy has been studied by pulse and calorimetric techniques. It is shown that the steady state surface is reduced by 80% and is characterized by the presence of one type of oxygen with a binding energy of 90 kcal/mol.

Импульсным и калориметрическим методами изучены зависимости скоростей окислительной дегидродимеризации и полного окисления пропилена и энергии связи кислорода от степени восстановления висмутоловянного окисного катализатора. Показано, что в стационарном состоянии поверхность образца восстановлена на 80% и характеризуется наличием однородного кислорода с прочностью связи 90 ккал/моль.

Study of the simultaneous and separate interaction of mixture components with a catalyst provides valuable information on the steady state of the catalyst /1-4/. With this aim the rates of reduction of a bismuth-tin catalyst with propylene have been measured and compared with the binding energies of surface oxygen.

EXPERIMENTAL

An oxide catalyst with Bi/Sn = 1 was prepared by precipitating bismuth hydroxide on dispersed tin dioxide obtained by dissolving the metals in nitric acid. After calcination at 600 °C, $Bi_2Sn_2O_7$ (S = 2.5 m^2/g) with small amounts of individual oxides was obtained /5/.

The interaction of a propylene-oxygen mixture (0.7% C_3H_6 + 0.4% O_2 + 98.9% He) and propylene (0.7% C_3H_6 + 99.3% He) with the catalyst was examined in a pulse installation with a vibrofluidized bed and by chromatographic analysis of the reaction mixture.

Prior to the experiments on catalysis and reduction, the sample was heated in an oxygen stream at 450 °C for 2 hrs and then flushed with helium to remove oxygen from the reactor. Then pulses of the mixture were passed through the catalyst at 15 min intervals.

The amount of oxygen removed from the catalyst was determined from the quantities of the products, taking into account the stoichiometric equations. To calculate the extent of surface reduction, we assumed the area occupied by an oxygen atom to be 7.84 $Å^2$.

The propylene conversion in the pulses did not exceed 15%. Under these conditions diallyl and carbon dioxide were the main products. Benzene (the product of subsequent transformation of diallyl) was practically not formed.

The binding energy of surface oxygen was determined calorimetrically at 445 °C from the heat of catalyst reduction with carbon monoxide and the heat of oxygen adsorption on the reduced surface /6/. Similar results were obtained in both cases.

RESULTS AND DISCUSSION

Data on the interaction between propylene-oxygen mixtures and the oxidized catalyst surface at 450 °C are given in Fig. 1. In the first pulses, the olefin is oxidized primarily by the catalyst oxygen. In this case CO_2 is the main reaction product. With surface reduction, consumption of the catalyst oxygen decreases, while the contribution of gaseous oxygen becomes appreciable. Simultaneously, a decrease in the rate of total oxidation and a slight increase in the rate of diallyl formation are observed. Finally, there comes a point when only gaseous oxygen

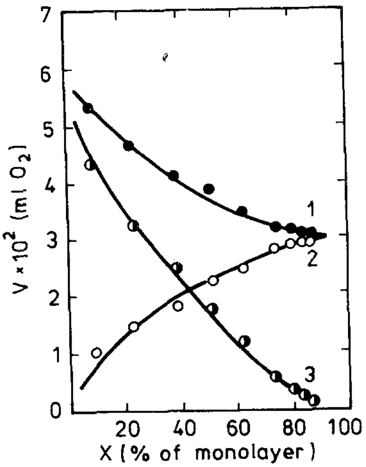

Fig. 1. Oxygen consumption vs. the extent of catalyst reduction in the catalytic oxidation of propylene (1 - total consumption, 2 - from the gas phase, and 3 - from the catalyst surface)

participates in the formation of products. This corresponds to the steady state of the catalyst which is characterized by a constant activity and a certain extent (0.8 monolayer, Fig. 1) of surface reduction.

The interaction of a pulse of a propylene-helium mixture with the catalyst of steady-state composition yields mainly diallyl and carbon dioxide. Their formation rates are 0.80×10^{16} and 0.67×10^{16} molecules C_3H_6/m^2 sec, respectively. The catalyst state remains almost unchanged as proved by subsequent injection of a pulse of the propylene-oxygen-helium mixture.

The extent of surface reduction corresponding to the steady state may also be achieved by consecutive treatment of the catalyst with the propylene-helium mixture. Figure 2 shows the results of these experiments carried out at 450 °C and the oxygen binding energies as a function of its amount removed from the surface.

The completely oxidized catalyst is characterized by the presence of surface oxygen with a rather low binding energy (about 50 kcal/mol). At extents of

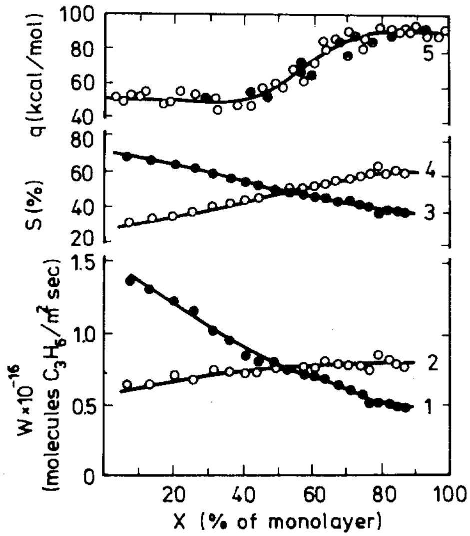

Fig. 2. Rates and selectivity of formation of CO_2 (1, 3) and diallyl (2, 4) during catalyst reduction with propylene, and the binding energy of surface oxygen (5) vs. the extent of catalyst reduction

surface reduction below 80%, the binding strength of oxygen increases to 90 kcal/mol. Further it remains constant up to the reduction extent of 140%.

The rate of CO_2 formation falls most drastically on the part of the surface covered with inhomogeneous oxygen (i.e. the extent of reduction is less than 75-80%). At the same time, the rate of diallyl formation even increases slightly with proper changes in the selectivity. The dependences obtained indicate that the weakly bonded oxygen participates mainly in the total oxidation and inhibits the process of propylene oxydehydrodimerization. This is proved by a small increase in the reaction rate in the range of reduction extents studied. Apparently, this is due to the fact that both reactions proceed partly through the same propylene intermediate, viz. a π-allyl complex. The latter transforms primarily to the products of total oxidation on the oxidized surface in the presence of weakly bonded oxygen.

With the consumption of weakly bonded oxygen during catalyst reduction the proportion of dimerizing complexes increases.

At surface reductions from 75 to 85% the rates of diallyl and CO_2 formation remain unchanged and equal to 0.77×10^{16} and 0.56×10^{16} molecules C_3H_6/m^2 sec, respectively. Their coincidence with the values obtained for the interaction of propylene with the catalyst of steady-state composition shows that this surface state is close to a steady-state one under the conditions of catalysis.

Thus, during the reduction of a bismuth-tin catalyst with propylene, an increase in both the binding energy of surface oxygen and the selectivity with respect to diallyl is observed. The steady-state catalyst is characterized by high selectivity, about 80% surface reduction and the presence of strongly bonded oxygen with a binding energy of 90-92 kcal/mol. Similar results were reported earlier for the partial oxidation of olefins on other oxide catalysts /2-4/.

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