JOURNAL OF CATALYSIS 58, 1–7 (1979)

The Surface Compounds and the Routes of Formation of the Reaction Products in the Interaction of Propylene with Zinc Oxide

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Received April 19, 1978; revised November 6, 1978

Thermodesorption of propylene, acrolein, allyl bromide, and their conversion products on zinc oxide has been investigated. Infrared spectra of allyl bromide have been studied. On the basis of the results obtained and the literature data a scheme of propylene transformation on zinc oxide has been proposed which explains the presence of dimerization products and the absence of acrolein in the reaction products by difficulty of transformation of an allylic compound to a cationic form on this catalyst. The interaction of allyl bromide, forming an allyl cation, with zinc oxide leads to evolution of acrolein.

INTRODUCTION

Zinc oxide has been a classical subject of the investigations of the interaction of olefins with the surface of oxide catalysts (*1–7*). The surface π-allyl complex, proposed by several workers on the basis of isotopic data to be an intermediate in the formation of acrolein (*8–11*), was first discovered on this catalyst (*1*). Later, a radical form of surface allyl was identified on this oxide by ESR (*5*). Some workers investigated (*2–4, 6, 7*) the interaction of adsorbed olefin with oxygen on zinc oxide and showed the formation of surface oxygen-containing compounds. Nevertheless, in all these studies the formation of acrolein could not be discovered. The formation of acrolein was also not observed in the catalytic oxidation of propylene on zinc oxide (*12*). The reaction proceeded in the direction of oxidative dimerization and aromatization. It should be also noted that the π-allyl complexes found in (*1*) on zinc oxide differ in spectral characteristics from the allylic complexes discovered later on some oxide catalysts (*13–16*). Thus for the latter, $\nu_{as}{}^{ccc}$ lies in the region from 1400 to 1460 cm^{-1}, whereas on zinc oxide this frequency is 1545 cm^{-1}. This difference may be due to the possibility of stabilization on the surface of an oxide catalyst of complexes in various charge states (anionic, radical, cationic), which may lead to different reaction products (*17*).

This work is an attempt to elucidate the routes of transformation of surface complexes and the possibility of acrolein formation from allylic structures on zinc oxide. Toward this end we have studied thermodesorption of propylene and the products of its interaction with oxygen as well as thermodesorption of allyl bromide and its conversion products from this catalyst and their ir spectra.

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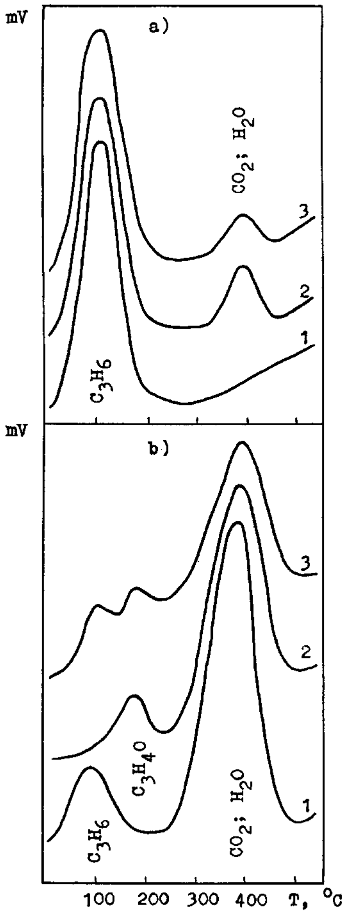


FIG. 1. Thermodesorption from reduced (a) and oxidized (b) zinc oxide (the results of the analysis of thermodesorption spectra are represented in Table 1). (a) 1—C_3H_6; 2—$(O_2^-)_{ads}$ + C_3H_6; 3—$(C_3H_6)_{ads}$ + O_2; (b) 1—C_3H_6; 2—C_3H_4O; 3—C_3H_5Br.

EXPERIMENTAL

In our work we used "specially pure" zinc oxide which had a surface area of 4.7 m^2/g and showed no absorption bands above 1100 cm^{-1}. The experiments were carried out on vacuum-reduced and oxidized samples. The former pretreatment consisted in heating the samples in vacuum at 400°C for 4 hr ($P_{res} = 10^{-5}$ Torr; 1 Torr = 133.3 N m^{-2}). In the latter case, this vacuum treatment was followed by calcining under oxygen (P = 100 Torr) at 400°C for 2 hr, cooling to room temperature, and evacuating to $P_{res} = 10^{-4}$ Torr. The adsorption of the reactants was done at room temperature and at a pressure of 10 Torr. The propylene used was chromatographically pure. The "pure" grade allyl bromide and acrolein were purified by repeatedly freezing out in vacuum. The ir spectra were recorded on a ir-20 spectrometer at room temperature with gas phase compensation. The spectral slit width was 8 cm^{-1} at 1000 cm^{-1}. Thermodesorption measurements were carried out in an installation described in (*18*). The desorption was performed by linear heating of the samples at a rate of about 16°/min. The flow rate of helium was 40 ml/min.

RESULTS AND DISCUSSION

1. *Thermodesorption of Propylene and Acrolein*

The thermodesorption of propylene from a reduced surface of zinc oxide was accompanied by observation in the spectrum of an intense low-temperature maximum (~100°C) representing a reversible form of the adsorbed propylene (Fig. 1a, Curve 1). The same temperature region was reported for the desorption spectrum of the reversible form of propylene adsorption on copper oxide catalysts (*13*) where this form of adsorption was shown to be surface species of allylic type. Comparison with ir-spectroscopic data (*1*) shows that the reversible form of adsorption observed on zinc oxide can also be regarded as surface π-allyl complexes. The amount of propylene desorbed reversibly from a reduced sample was 6×10^{17} molecules/m^2. This value is close to the amount of π-allyl complexes estimated in (*4*, *6*).

Thermodesorption of propylene from an oxidized zinc oxide leads to appearance of two maxima in the spectrum: a low-temperature (~90°C) and a high-temperature (~400°C) (Fig. 1b, Curve 1). Chro-

TABLE 1

Results of the Analysis of Thermodesorption Spectra Given in Fig. 1

Adsorbent	Adsorbates	Desorption products (molecules/m^2)			
		C_3H_6	CO_2	C_3H_4O	C_3H_5Br
Reduced ZnO	C_3H_6	6×10^{17}	—	—	—
	$(O_2^-)_{ads} + C_3H_6$	5×10^{17}	5×10^{15}	—	—
	$(C_3H_6)_{ads} + O_2$	5×10^{17}	1×10^{14}	—	—
Oxidized ZnO	C_3H_6	1×10^{17}	9×10^{16}	—	—
	C_3H_4O	—	6×10^{16}	7×10^{16}	—
	C_3H_5Br	1.8×10^{16}	3.2×10^{16}	1.4×10^{16}	3×10^{16}

matographical analysis of the desorption products showed that, as in the case of a reduced surface, the low-temperature peak corresponds to reversibly chemisorbed propylene and the high-temperature one, to the products of complete oxidation (CO_2 and H_2O). The same spectrum was observed for the desorption of propylene from the oxidized surface of a copper oxide catalyst (*13*). As established in this work, the irreversible form of adsorption corresponding to the high-temperature peak represents oxidized surface species of carbonate–carboxylate type. It can be expected that the form of adsorption characterized by high-temperature desorption peak is represented by species of the same type on zinc oxide, too. The formation of surface formates and carboxylates in the interaction of adsorbed propylene with oxygen on zinc oxide was reported in (*7*). In Fig. 1a (Curve 3) is given a thermodesorption spectrum obtained after the interaction of propylene, adsorbed on a reduced sample, with oxygen ($P_{O_2} = 2$ Torr, $T = 25°C$). As is seen from the figure, the spectrum shows a similar high-temperature peak corresponding to complete oxidation products. As in the previous experiments, the formation of acrolein was not observed.

In (*4*, *5*) the interaction of propylene with a radical-ion form of oxygen, O_2^-, was studied. It was found that the interaction of adsorbed propylene with the radical-ion O_2^- leads to the formation of a surface compound (denoted by the authors as X) which is considered by the authors to be an intermediate in the formation of acrolein. The latter is concluded from the fact that a similar spectrum was observed in the formation of acrolein, too.

To verify the possibility of acrolein formation in the interaction of adsorbed forms of propylene with the radical-ion O_2^-, a special experiment was carried out. First, oxygen was adsorbed on a reduced zinc oxide surface at room temperature ($P_{O_2} = 2$ Torr). This led to formation of radical-ions O_2^- with parameters corresponding to those given in (*19*). The amount of radical-ions was 5×10^{15} molecules/m^2. Then propylene was adsorbed and the thermodesorption was carried out. As in the previous case, the spectrum showed two peaks (Fig. 1a, Curve 2). One peak with a maximum at 100°C represents reversibly adsorbed propylene, another peak corresponds to the products of complete oxidation. The formation of acrolein was again not observed. It can be expected that in this case too, the interaction of propylene with oxygen produces only oxidized carbonate–carboxylate species on the catalyst surface.

Such species may be formed also in the interaction of acrolein with the surface of

TABLE 2

Frequencies Observed in the ir-Spectra upon Adsorption of C_3H_5Br on ZnO and Their Interpretation[a]

Frequency, cm^{-1}	Assignment	After desorption at 200°C	After desorption at 300°C
1370	$\nu_s COO^-$	1370↓	—
1430	$\nu_s COO^-$	1430↑	1430↓
1470	$\nu_{as} CCC$	—	—
1550	$\nu_{as} COO^-$	1550↑	1550↓
1580	$\nu_{as} COO^-$	1580↓	—
1680	$\nu C{=}O$	—	—
2870	νCH	2870↓	—
2950		2950↓	—
2985		2985↓	2985↓
3050	$\nu CH{=}$	—	—
3090		—	—

[a] ↓—decrease, ↑—increase.

zinc oxide containing oxygen (*7*). The study of acrolein thermodesorption from an oxidized surface of zinc oxide showed two peaks in the spectrum (Fig. 1b, Curve 2). One peak with the maximum at 180°C corresponds to reversibly adsorbed acrolein. Another peak with the maximum at 400°C corresponds, as in the thermodesorption of propylene, to the irreversible form of adsorption that decomposes to form only the products of complete oxidation.

Thus, in all cases, the interaction of propylene with oxygen does not lead to the formation of acrolein. According to the data of the present work and the results in (*7*) such an interaction can be expected to result only in the formation of surface oxydized species which decompose to form the products of complete oxidation. As shown in (*12*) higher pressures and temperatures may lead to formation of demerization products. The π-allyspecies observed in the adsorption of propylene on zinc oxide (*1*) does not appear to be able to undergo direct transformation to acrolein.

2. Thermodesorption of Allyl Bromide

According to (*20*), the allylic complex formed in the adsorption of propylene on zinc oxide is of a carbanionic nature. The same conclusion about the nature of primary allylic complexes was made in (*5*), where the authors observed the formation of a π-allyl radical resulting, as they proposed, from the interaction of allylic complexes with a hole center. If this type of allylic complexes is not able to undergo direct transformation to acrolein it is possible to try to obtain a cationic form of the allylic fragment and to test the possibility of transformation of this form to the product of selective oxidation. The cationic form may be formed in the interaction of the catalyst with an allyl halide. Therefore, we studied thermodesorption of allyl bromide from the surface of an oxidized zinc oxide.

The thermodesorption spectra showed three maxima: 100°C, 180°C, 400°C (Fig. 1b, Curve 3).

The high-temperature maximum corresponds to the formation of complete oxidation products. Among the thermodesorption products corresponding to the low-temperature maxima are allyl bromide, propylene, and acrolein. The formation of propylene in the desorption of allyl bromide indicates a dissociative adsorption of the latter. Since no other halide-containing products were observed it can be expected that the halide ions, formed as a result of dissociative adsorption of allyl bromide, are stabilized on the surface cations. It should be noted that a repeated desorption of propylene carried out after the desorption of allyl bromide does not change the original thermodesorption spectrum, i.e., a single desorption of allyl bromide does not produce an essential promotion of the surface.

Thus, unlike the experiments on the adsorption of propylene, in the present case acrolein does actually form and evolve. It is natural to relate this to different types of allylic complexes formed in the interaction of zinc oxide with propylene and allyl bromide. To reveal this dif-

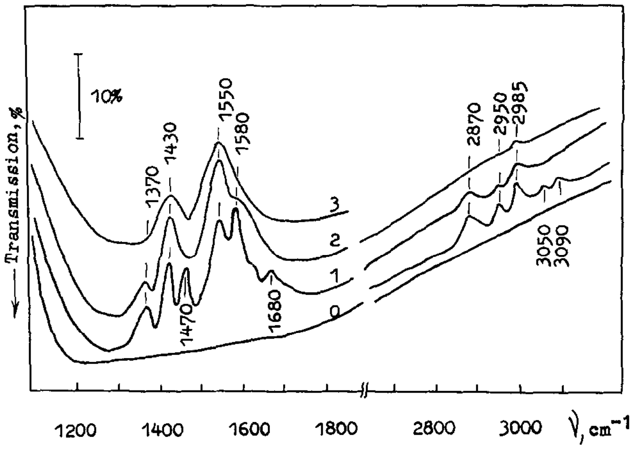


FIG. 2. Infrared spectra after adsorption of allyl bromide on zinc oxide: 0—the spectrum of the initial sample of zinc oxide; 1—adsorption at 20°C; 2—desorption at 200°C; 3—desorption at 300°C.

ference the ir spectra of allyl bromide were compared with the spectra obtained in the adsorption of propylene.

3. Infrared Spectroscopic Studies of the Adsorption of Allyl Bromide

The adsorption of allyl bromide on an oxidized surface of zinc oxide at 20°C with subsequent removal of the gas phase leads to the appearance of several absorption bands in the spectrum. The results of the experiments are represented in Fig. 2 and Table 2. The absorption bands at 1470, 1680, 3050, and 3090 cm^{-1} disappear after desorption at 200°C. The rest of the bands at 1370, 1430, 1550, 1580, 2870, 2950, 2985 cm^{-1} do not disappear from the spectra at this temperature.

The thermodesorption data show that at temperatures above 200°C only the products of complete oxidation evolve. With regard to this data the bands at 1580 and 1370 cm^{-1} disappearing upon desorption at 250 and 300°C can be assigned to surface formates and the bands at 1550 and 1430 cm^{-1} disappearing at 350 to 400°C, to surface acetate (*7, 21*). Apparently, it is these structures that correspond to the high-temperature desorption peak containing the products of complete oxidation. As already mentioned, similar results were obtained on copper oxide catalysts (*13*).

At temperatures below 200°C, propylene, acrolein, and allyl bromide are desorbed from the surface of zinc oxide. Therefore, the absorption bands disappearing at temperatures below 200°C can be related to the vibrations of the molecules or fragments which had no destruction at C–C bonds. The band at 1680 cm^{-1} can be assigned to the vibrations of the carbonyl group in the adsorbed acrolein (*13*). The maxima at 1470, 3050, and 3090 cm^{-1} can be assigned to the surface allylic species removed as allyl bromide or propylene as a result of desorption. The bands at 3050 and 3090 cm^{-1} characterize the stretching vibrations of C–H at the double bond, which unambiguously indicates an unsaturated nature of the fragment. The maximum at 1470 cm^{-1} can be assigned either to deformation vibrations (δ) of C–H or to $\nu_{\mathrm{as}}^{\mathrm{ccc}}$ in the allyl fragment.

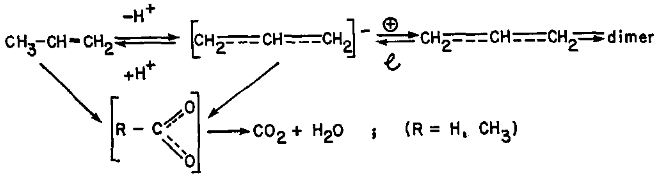
It should be noted that the assignment of the intense absorption band at 1470 cm^{-1} to δCH vibration in the fragment C_3H_5 is unlikely for the following reasons: (i) in the adsorption of propylene the absorption band at 1470 cm^{-1} was not observed,

(ii) according to (*1*) the absorption bands at 1300 to 1500 cm^{-1} characterizing δCH vibrations in the fragment C_3H_5 are of low intensity (less than that of νCH stretching vibrations). On the basis of these data and the lower surface area of the zinc oxide samples studied by us (and accordingly lower intensity of the absorption bands δCH) it can be concluded that in our case δCH either won't be observed at all or they will have a very low intensity. At the same time, the extinction coefficient of the stretching vibrations νC=C is significantly larger (about an order) than that of the deformation vibrations δCH in the allylic structures.

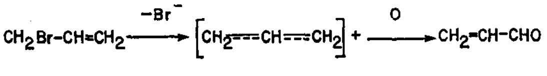
Taking into consideration the things said above, the absorption band at 1470 cm^{-1} cannot be assigned to deformation vibrations. Apparently, it characterizes ν_{as}^{ccc} in the allylic fragment. The change in the frequency of the allylic fragment when going from propylene to allyl bromide (1545 and 1470 cm^{-1}) appears to be due to the fact that unlike propylene adsorption, where an anionlike species is probably formed, the allyl is stabilized as a cation in the latter case. It is noteworthy that the absorption band at 1470 cm^{-1} falls into the region of frequencies observed in the adsorption of propylene on partial oxidation catalysts (*13–15*).

CONCLUSION

On the basis of the results of the present work as well as from literature data cited above, the transformation of propylene on zinc oxide can be represented as follows:



The formation of acrolein in this sequence of transformations does not take place. According to (*17*), for acrolein to be formed it is necessary that an electron be transferred from the allylic species to form a carbcation which then react with an oxygen ion of the catalyst surface. On zinc oxide, a semiconductor of *n* type with a high concentration of carriers, such a transfer is hindered and the reaction proceeds mainly in the direction of dimerization. The hindered stage of recharging of the surface allyl can be avoided by using instead of propylene allyl bromide which forms directly a carbcation. In this case the formation of acrolein by the route



$$CH_2Br-CH=CH_2 \xrightarrow{-Br^-} [CH_2\text{---}CH\text{---}CH_2]^+ \xrightarrow{O} CH_2=CH-CHO$$

does indeed take place. As pointed out in (*17*) the use of a semiconductor of *p* type (for example, Cu_2O) as an allylic oxidation catalyst promotes the formation of an allyl cation. In this case direct transformation of propylene to acrolein is observed.

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