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Propylene and Oxygen Chemisorption on Cupric Oxide and Cuprous Oxide Catalysts

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The adsorption behavior of propylene and oxygen on CuO, a catalyst for total oxidation of propylene, and on Cu_2O, a catalyst for partial oxidation, has been investigated. As well as adsorption from pure gases, adsorption from C_3H_6/O_2 mixtures has been measured. These adsorptions accordingly refer to precatalysis conditions, and have been studied both volumetrically and by infrared spectroscopy.

Differences between the catalysts are related to differences in the composition and structure of chemisorbed intermediate surface complexes (ISC). ISC formed from propylene and oxygen on CuO are considered to contain more oxygen than that corresponding to a 1:1 C_3H_6:O_2 ratio and to be chemisorbed as formate-, acetate-, and oxalate-like compounds. On Cu_2O, however, there is mostly reversible chemisorption of propylene and the formation of ISC without excess oxygen. In this case the complexes are weakly bonded to the catalyst, and the strengths of their C═C and C–H (CH_3 group) bonds are weakened as compared to propylene.

INTRODUCTION

Elucidation of the nature of selectivity is one of the most important problems in heterogeneous catalysis. According to the point of view developed in previous work (*1, 2*), selectivity in hydrocarbon oxidation is associated with the structure and the energy differences between the surface intermediate complexes formed by the hydrocarbon and oxygen molecules and the catalyst. Important information about these complexes can be obtained by investigating the chemisorption of the mixed reactants under precatalysis conditions.

This paper contains data for propylene and oxygen chemisorption from propylene–oxygen mixtures on cupric oxide and cuprous oxide catalysts. The catalysts differ in selectivity: CuO is a catalyst for complete oxidation of propylene and Cu_2O is a catalyst for partial oxidation of propylene.

EXPERIMENTAL

Voumetric and infrared spectroscopic studies have been made at temperatures such that there is no release of reaction products to the gas phase (precatalysis) and no change in catalyst phase composition.

To select the appropriate temperature conditions, initial temperature points for oxide reduction (T_r) and for catalysis (T_c) have been determined by monitoring the reaction products in the effluent gas when passing C_3H_6 or a mixture of C_3H_6 and O_2. It was found that for CuO, $T_r = 180°C$ and $T_c = 130°C$ and for Cu_2O, $T_r = 55°C$ and $T_c = 128°C$.

For the volumetric measurements oxides with specific surface areas $S_{CuO} = 0.5$ m^2/g and $S_{Cu_2O} = 1.7$ m^2/g were used. The total surface of the samples under test was 1 m^2. Before measurement took place, CuO was activated in O_2 for 2 hr at 300°C followed by outgassing for 5 hr at 300°C and at a pressure of 10^{-4} Torr. With Cu_2O, a fresh sample outgassed at 100°C for 3 hr was used for each test. The volume of the adsorption apparatus was 55.9 cm^3 for the adsorption of individual gases and 142.2 cm^3 for the adsorption of mixtures. The adsorption was studied in the pressure range 10^{-3}–8 Torr. Pressure was measured by a MacLeod gauge.

For the spectroscopic work, special plates were prepared by dispersing CuO (2.5% by weight) or Cu_2O (6% by weight) with the inactive support material Aerosil (S = 380 m^2/g) and subsequently pressing at $P = 7t/cm^2$. The specific surfaces of CuO and Cu_2O measured in these specimens by chemisorption of C_3H_6 were 16 and 50 m^2/g, respectively. The plates were placed in a vacuum vessel with external heating and were pretreated as described elsewhere (*3*). After evacuation the specimen transmission for CuO was 20–25% and for Cu_2O 30–40%. Spectra were recorded by an IRS-14 spectrometer in the ranges 1300–1800 cm^{-1} (NaCl prism) and 2200–3100 cm^{-1} (LiF prism). The recording rate was 58 cm^{-1}/min for NaCl and 37 cm^{-1}/min for LiF. The spectral width of the slit did not exceed 10 cm^{-1}. In spectroscopic experiments propylene and acrolein were adsorbed at 10 and 5 Torr, respectively, and under conditions similar to those applied in the volumetric investigations (for C_3H_6). When recording spectra the specimen temperature was 35–40°C.

Results and Discussion

Adsorption of C_3H_6 and O_2 Mixtures on CuO and Cu_2O

Adsorption was investigated for three mixture compositions ($C_3H_6:O_2$ = 3:1, 1:1, 1:3) at 50 and 125°C on CuO, at 50°C on Cu_2O and also at 20°C on Cu_2O for mixture 1:1. The results are given in Table 1.

It is evident that the total adsorption from the mixture is more than additive both for CuO and Cu_2O at all the temperatures studied and for the different proportions of C_3H_6 and O_2; the adsorption capacity for oxygen from the mixture is greater and that of propylene is less than in the case of the separate gas adsorption. On increasing the temperature from 50 to 125°C with CuO, the adsorption of C_3H_6 from the mixture, regardless of composition, is reduced (approximately twofold with the 1:1 mixture and that of O_2 is increased 1.2 times), while without oxygen present the adsorption of C_3H_6 on CuO is increased. No desorption of gas was observed.

Propylene adsorption from the mixture on Cu_2O is increased (14 times for the 1:1

TABLE 1

C_3H_6 AND O_2 ADSORPTION FROM MIXTURES AND SEPARATELY ON CuO AND Cu_2O

		Adsorption of C_3H_6 (cm^3/m^2)					Adsorption of O_2 (cm^3/m^2)			
From mixture ($C_3H_6:O_2$)	$P_{C_3H_6}$ (Torr)	CuO		Cu_2O		P_{O_2} (Torr)	CuO		Cu_2O	
		50°C	125°C	20°C	50°C		50°C	125°C	20°C	50°C
3:1	5.7	0.030	0.013		0.090	1.6	0.040	0.065		0.083
1:1	3.4	0.019	0.010	0.006	0.084	3.7	0.050	0.062	0.028	0.096
1:3	1.6	0.017	0.002		0.055	5.7	0.052	0.060		0.125
Separately										
	5.9	0.038	0.039		0.135	1.8	0.012	0.019		0.018
	3.9	0.025	0.032	0.010	0.120	4.0	0.012	0.020	0.019	0.040
	1.7	0.022	0.030		0.100	6.0	0.013	0.021		0.072

mixture) on raising the temperature from 20 to 50°C. In this case oxygen adsorption is also increased, but to a considerably lesser degree (3 times) than with C_3H_6.

Adsorption rates W for C_3H_6 and O_2 on CuO and Cu_2O were calculated from kinetic curves of the uptake, the times used being those required to produce equal volumes of adsorbed gases (W_{mix} for O_2, C_3H_6 in the case of the separate adsorption mixture, and W_{sep} for O_2, C_3H_6 in the case of separate adsorption). Results are given in Table 2.

The data show that at 50°C W_{sep} for both C_3H_6 and O_2 on Cu_2O is higher than on CuO. At 50°C W_{sep} for C_3H_6 is higher than W_{sep} for O_2 on both oxides. In the case where both gases are present, W_{mix} for C_3H_6 is reduced, but W_{mix} for O_2 is increased. However, the rate of C_3H_6 adsorption from the mixture on Cu_2O is higher than on CuO, but for oxygen it is the reverse.

W_{sep} for C_3H_6 and O_2 on both oxides is increased with temperature, but in the case of the mixture the two oxides behave differently. The rate of C_3H_6 adsorption from the mixture on CuO is somewhat reduced when the temperature increases from 50 to 125°C, but on Cu_2O it increases by a factor of 10^2 in the range 20–50°. The rate of oxygen adsorption from the mixture on Cu_2O is likewise increased when temperature is raised from 20 to 50°C.

The data for the C_3H_6 and O_2 adsorption capacities and adsorption rates when the gases are present together imply that an increase in the amount and in the rate of O_2 adsorption is caused by irreversibly chemisorbed C_3H_6.

Apparently one reason for complete oxidation of C_3H_6 on CuO lies in its irreversi-

TABLE 2

RATES OF PROPYLENE AND OXYGEN ADSORPTION ON CuO AND Cu_2O[a]

Mixture (C_3H_6:O_2)	C_3H_6 adsorption (cm³/m²)	$10^3 \times W_{sep}$ C_3H_6 (cm³/m² per min)	$10^3 \times W_{mix}$ C_3H_6 (cm³/m² per min)	O_2 adsorption (cm²/m²)	$10^3 \times W_{sep}$ O_2 (cm³/m² per min)	$10^3 \times W_{mix}$ O_2 (cm³/m² per min)
			Cu_2O, 20°C			
1:1				0.01	10.0	2.8
1:1	0.005	2.2	0.9	0.005	10.0	2.8
			Cu_2O, 50°C			
3:1	0.01	∞	5.6	0.01	0.9	136.0
1:1	0.01	∞	5.3	0.01	13.0	250.0
1:1	0.005	∞	12.0	0.005	20.0	280.0
1:3	0.01	∞	1.4	0.005	∞	∞
			CuO, 50°C			
3:1	0.01	11.5	1.6	0.005	1.0	∞
1:1	0.01	10.3	0.8	0.005	2.0	∞
1:1	0.005	21.1	2.0			
1:3	0.01	8.5	0.6	0.005	5.1	∞
			CuO, 125°C			
3:1	0.01	∞	1.2	0.005	7.0	∞
1:1	0.01	∞	0.0	0.005	20.2	∞
1:1	0.005	∞	1.1			
1:1	0.005	∞	0.7	0.005	30.1	∞

[a] ∞ indicates that quantitative comparison of rates for equal amounts of adsorption was not possible, because of the high rates for $W_{sep}(C_3H_6)$ and $W_{mix}(O_2)$ in the initial adsorption period.

ble adsorption, which is 100% on CuO and only 25% on Cu_2O (*3*, *4*). Knowing the way the nature of the adsorption changes with temperature (in the precatalysis region) one can extrapolate these data to catalytic conditions with a certain degree of confidence. Such an extrapolation for C_3H_6 and O_2 adsorption leads to the conclusion that under real conditions of catalysis the surface of CuO is mostly covered with oxygen and in this case the propylene adsorption capacity is comparatively low, while on the contrary the surface of Cu_2O is mostly covered with C_3H_6 in comparison with which O_2 adsorption is lower.

Infra-red Spectra of Chemisorbed Molecules

The results of the spectroscopic study of C_3H_6 and O_2 chemisorption on CuO/SiO_2 are shown in Table 3 and in Fig. 1.

Figure 1c shows that the spectrum of irreversibly chemisorbed C_3H_6 at 125°C on CuO is characterized by absorption bands at 2980, 2940, 2860, 1575, 1440, 1410 and 1390 cm^{-1}, and at 175°C (Fig. 1d) by bands at 2980, 2940, 2860, 2329, 1550, 1440 and 1410 cm^{-1}.

At 175°C the absorption band intensity at 2980 cm^{-1} is reduced and at 2940 cm^{-1}

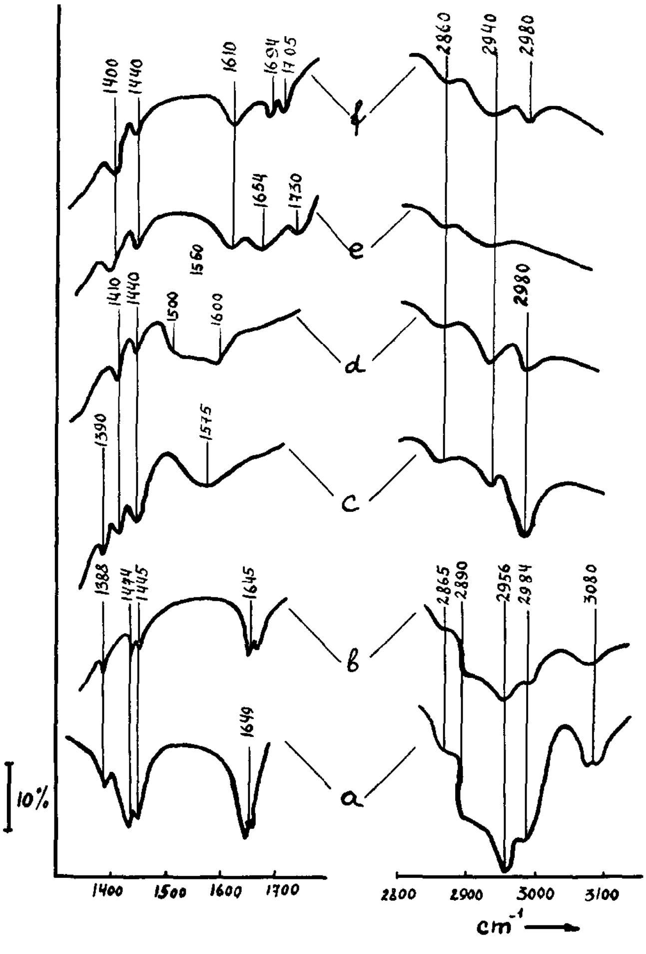
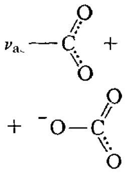
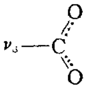


FIG. 1. Infrared spectra of C_3H_6 on CuO/SiO_2: a: C_3H_6 gas; b: C_3H_6 at SiO_2; c: [C_3H_6], 125°C; d: [C_3H_6], 175°C; e: [C_3H_6], 125°C, O_2: 300°C; f: [C_3H_6 + O_2], 125°C. A [ ] indicates gas irreversibly chemisorbed. The 10% line indicates 10% transmission.

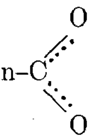
TABLE 3

Frequency Values (cm^{-1}) and Band Assignments in Spectra of C_3H_6 Chemisorbed on CuO/SiO_2[a]

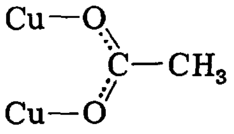
C_3H_6 gas (cm^{-1})	SiO_2 + C_3H_6	CuO + [C_3H_6] 125°C	CuO + [C_3H_6] 175°C	CuO + [C_3H_6] + O_2; 300°C	CuO + [C_3H_6 + O_2]; 125°C	Cu(Ac)	Cu(Fo)	Assignment
3080	3080							$\nu_{as}{=}CH_2$
2984	2984							$\nu_s{=}CH_2$
2956	2956	2980	2980		2980			$\nu_{as}{-}CH_3$
		2940	2940	2940	2940			$\nu_{as}{-}CH_2{-}$
2890	2890							$\nu_s{-}CH_3$
2865	2865							
		2860	2860	2860	2860			$\nu_s{-}CH_2$
			2329		2329			CO_2
				1730	1705			
				1654	1694			ν_{as} C=O
				1610	1610			
1649	1645							ν C=C
						1596		
		1575					1570	
			1550					
1474	1474							
1445	1445	1440	1440	1440	1440	1440		$\delta_{as}{-}CH_3$
		1410	1410	1400	1400	1400		
		1390					1388	
1388	1388					1346		$\delta_s{-}CH_3$

[a] [ ] indicates gases irreversibly chemisorbed.

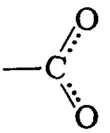
is increased as compared to the intensities after propylene chemisorption at 125°.

There are absorption bands at 1596 and 1410 cm^{-1}, and 1510 and 1388 cm^{-1} in the spectra of copper acetate [Cu(Ac)] and copper formate [Cu(Fo)] respectively, which are typical for valence asymmetric ν_{as} and symmetric ν_s ion-  vibrations in these compounds; there are also bands at 1440 and 1346 cm^{-1} corresponding to deformational antisymmetric δ_{as} and symmetric δ_s vibrations of the methyl radical in Cu(Ac). Using these data the absorption band with a maximum at 1575 cm^{-1} in the spectrum of irreversibly chemisorbed propylene at 125° (Fig. 1c) can be considered as ν_{as} of the two carboxylate radicals overlapped upon one another, the frequencies at 1410 and 1390 cm^{-1} as ν_s of this ion in Cu(Ac) and Cu(Fo) correspondingly, while the absorption band at 1440 cm^{-1} can be considered as δ_{as} methyl radical in Cu(Ac).

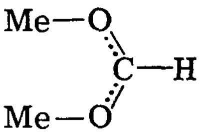
The absence of a band at 1346 cm^{-1} in the chemisorbed propylene spectrum probably results from its low intensity and from a high degree of absorption by Aerosil in this region. Absorption bands in the region of 2800–3000 cm^{-1} correspond to ν_{C-H} of hydrocarbons (see below). Van Niekerk and Schoening (*5*) showed experimentally and by means of calculation that the acetate anion in Cu(Ac) was coordinated to metal ions in the following way:



with ν_{as} and ν_s values for the

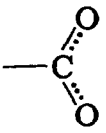


radical being 1600 and 1420 cm^{-1}. The structure

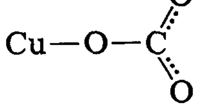


for formate anions has been found by Hirota *et al.* (*6*).

The absorption band at 1550 cm^{-1} obtained after propylene chemisorption at 175°C (Fig. 1d) can be attributed to ν_{as} overlap of the carboxylate ion

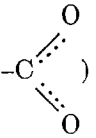


in Cu(Ac) (1597 cm^{-1}) and carbonate ion in the monodentate surface compound

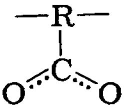


the vibration frequencies of which are 1529 and 1326 cm^{-1} according to Gatehouse *et al.* (*7*).

The same frequencies as those obtained by propylene chemisorption at 175°C were found in the spectrum of CuO with propylene irreversibly chemisorbed at the surface at 125°C when the specimen was subsequently heated *in vacuo* to 175°C.

The experimental results show that of the two surface compounds 1 and 2 the latter is the more reactive, and at temperatures above 125°C it is converted into a compound of type 3 which at T_r and above is apparently a source of CO_2 generation. This fact is indicated (Fig. 1) by the absence of an absorption band at 1390 cm^{-1} (ν_s- ) in Cu(Fo) and by the appearance even at 175°C of a low intensity peak at 2329 cm^{-1} (not shown in Fig. 1) corresponding to adsorbed CO_2, the intensity of which increases with temperature. This band completely disappears from the spectrum in the course of 20-min evacuation.

Absorption bands present in the region of 2800–3000 cm^{-1} (Fig. 1c,d) can be attributed to valence variation of CH_3 (2980 cm^{-1}) and CH_2 radicals (2940, 2860 cm^{-1}). The two latter bands appearing in the spectrum of irreversibly chemisorbed propylene at 125°C and the increase of their intensity with temperature point to interaction of methyl radicals in surface compound 1 and to formation of methylene radicals–CH_2–. The nature of this process has not been investigated in detail but data obtained by Little (*8*) confirm its reality. The structure of the hydrocarbon residuum in the molecule cannot be explained unequivocally, so we represent it conventionally as:

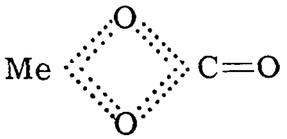


It should be noted that the surface OH radicals of Aerosil do not take part in this process. This is evident from the data of propylene absorption spectra obtained at different temperatures and different times of contact with Aerosil (Fig. 1b).

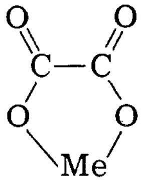
A series of spectrum changes results

when irreversibly chemisorbed propylene is treated with oxygen at 300°C (Fig. 1e): absorption bands in the region 1500–1590 and 2980 cm^{-1} disappear, new frequencies at 1730, 1654, and 1610 cm^{-1} appear and the intensities of the bands at 2940 and 2860 cm^{-1} are reduced. The band intensity in the region of 1610–1654 cm^{-1} is somewhat reduced on evacuating the sample during 2 hr, but all the remaining bands are conserved. Note that bands in the region of 1600–1700 cm^{-1} also appear in the case of oxygen and propylene mixture chemisorption, but without an absorption band in the region of 1500–1590 cm^{-1}. Moreover, in contrast to experiments involving subsequent treatment in oxygen (Fig. 1e), in this case an absorption band at 2980 cm^{-1} (νCH_3) is observed and in contrast to separate propylene chemisorption at 125°C a weak absorption band corresponding to adsorbed CO_2 (2329 cm^{-1}) appears.

A mathematical analysis of vibrations observed in the region of 1600–1700 cm^{-1} in different oxygen–carbon complexes was carried out by Nakamoto *et al.* (*9*) for the purpose of theoretically characterizing the frequencies. They found that bidentate carbonate complexes having the structure:



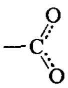
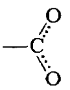
absorb at 1630–1590 and 1270 cm^{-1} and oxalate complexes Me(Ox):



at 1640–1720 and 1240–1490 cm^{-1}. In particular for Cu(Ox) the following values of

TABLE 4

FREQUENCY VALUES (cm^{-1}) AND BAND ASSIGNMENTS IN SPECTRA OF C_3H_6 CHEMISORBED ON Cu_2O/SiO_2[a]

Cu_2O + C_3H_6, 20 and 50°C	Cu_2O + $[C_3H_6]$[b]	Cu_2O + C_3H_6 + O_2	Cu_2O + $[C_3H_6 + O_2]$	Cu_2O + C_3H_4O (300°C)	Cu_2O + $[C_3H_4O]$	CuO + C_3H_4O (300°C)	CuO + $[C_3H_4O]$	Assignment
3080		3080						$\nu_{as}{=}CH_2$
2956	2980	2980 2956	2980					$\nu_{as}—CH_3$
2934	2934	2934	2934					$\nu_{as}—CH_2—$
2865		2865						$\nu_s—CH_3$
	2860		2860					$\nu_s—CH_2—$
1702		1702		1698		1698		$\nu C{=}O$
1626		1626						$\nu C{=}C$
			1610	1610	1610	1610	1610	ν_{as} 
1430		1430	1440		1440	1440	1440	$\delta_{as}—CH_3$
			1400	1406	1406	1406	1406	ν_s 
1364		1364		1360	1360	1360	1360	$\nu_s—CH_3$

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[a] Frequencies of C_3H_4O chemisorbed on Cu_2O/SiO_2 and CuO/SiO_2 are included in the table.

[b] [ ] indicates gases irreversibly chemisorbed.

frequencies have been found: 1720, 1672, and 1645 cm^{-1} for ν_{as} of free C=O and 1411 cm^{-1} for ν_s (C–O) + (C–C). We have obtained frequencies similar to these values with irreversibly chemisorbed propylene treated with oxygen (Fig. 1e), propylene, and oxygen-mixture chemisorption (Fig. 1f), and after heating *in vacuo* gases irreversibly chemisorbed from the mixture.

These data imply that surface compounds of type 1 or type 4 are also sources of CO_2 generation. Our volumetric results on oxygen chemisorption in the presence of propylene show that this process is realized through hydrogen atoms separated by chemisorbed oxygen being located at the surface in sufficient quantity and in an active form. In this case surface compounds of type 5 or 6 are first formed, and then they decompose yielding CO_2: this is indicated by the reduction with evacuation of absorption band intensity in the region of 1610–1654 cm^{-1} (Fig. 1e) where the frequency of the water deformation vibration is also situated (1630 cm^{-1}).

However, it should be noted that the surface compound of type 4 is not removed from the surface even after a 3-hr treatment in oxygen at 300°C; only a longer period of heating and evacuation can remove it from the surface. On the one hand this points to an energetic nonuniformity of the CuO surface and on the other it shows that a surface compound of type 4 partially contaminates the catalyst under normal catalytic conditions.

Table 4 and Fig. 2 show frequencies of absorption bands observed in the spectrum of propylene chemisorbed on Cu_2O/SiO_2 at 20 and 50°. Comparison of the gaseous propylene spectrum (Fig. 1a) with that of propylene chemisorbed on Cu_2O/SiO_2 (Fig. 2a) in the region of 1700–1300 cm^{-1} shows that the latter contains a series of bands which disappear during a short evacuation at room temperature (Fig. 2b), their frequencies being similar to those of gaseous propylene but displaced to lower frequencies.

These bands can be assigned to $\nu_{C=C}$ (1626 cm^{-1}) and to the deformation vibration of CH_3 (1430, 1364 cm^{-1}) in the spectrum of reversibly chemisorbed propylene; the nature of the frequency displacements allows us to conclude that the strength of the C=C and C–H bands is reduced in the chemisorbed form. The absorption band at 1702 cm^{-1} can result from molecules containing a carbonyl group which appear at the surface. This fact is indicated by the spectrum of acrolein chemisorbed on this catalyst (Fig. 2e) with a value of the C=O vibration frequency of 1698 cm^{-1}.

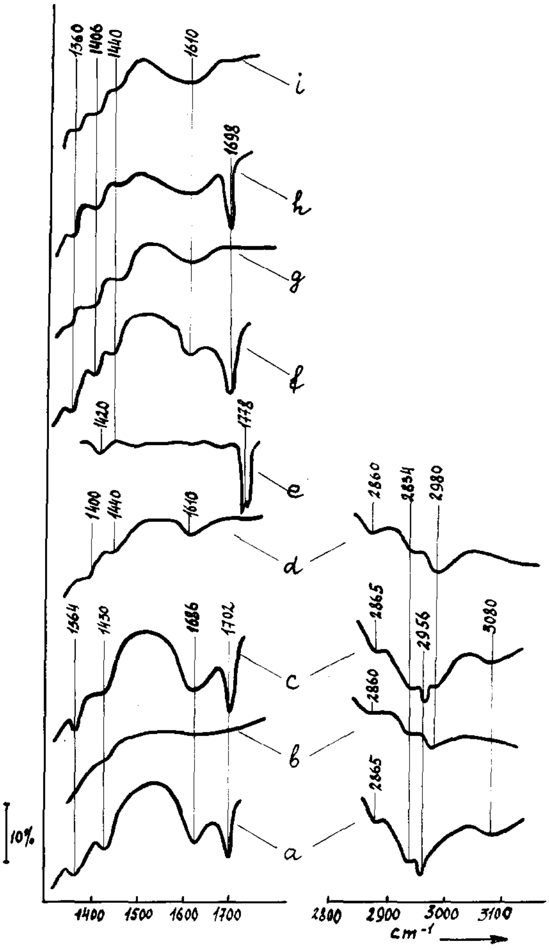
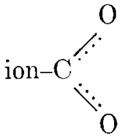


FIG. 2. Infrared spectra of C_3H_6 on Cu_2O/SiO_2: a: C_3H_6 on Cu_2O/SiO_2, 20 and 50°C; b: $[C_3H_6]$, 20 and 50°C; c: $C_3H_6 + O_2$, 50°C; d: $[C_3H_6 + O_2]$; e: Acrolein, C_3H_4O, P = 5 Torr, gas; f: C_3H_4O on Cu_2O/SiO_2, 300°C; g: $[C_3H_4O]$, 300°C; h: C_3H_4O on CuO/SiO_2, 300°C; i: $[C_3H_4O]$, 300°C. A [ ] indicates gas irreversibly chemisorbed. The 10% line indicates 10% transmission.

This band is also lost from the spectrum in the case of acrolein evacuation (Fig. 2f).

Absorption bands occurring in the Cu_2O/SiO_2 spectrum at 2980, 2934, and 2860 cm^{-1} after gas phase evacuation (Fig. 2b) belong to irreversibly chemisorbed propylene. These values agree with the data for propylene irreversible chemisorption on Cu_2O/SiO_2 in Fig. 1c. One may suppose, therefore, that the compositions of the surface compounds formed by propylene irreversible chemisorption on CuO and Cu_2O are analogous. Apparently the absence of the corresponding absorption bands in the region of CH and  $\text{ion–C}\begin{smallmatrix}O\\O\end{smallmatrix}$ deformation vibration is explained by their low concentration making them insufficient for detection. In the case of the propylene and oxygen mixture chemisorption at 20°C (Fig. 2c), these bands are observed in the spectrum after gas phase evacuation, and as with CuO they are removed only by high temperature treatment in oxygen. One may presume that these bands appear as a result of a concentration increase due to oxygen adsorption in the neighborhood of propylene irreversible chemisorption leading to formation of surface compounds of type 1 or 4. The absence of any other visible change in the Cu_2O spectrum by mixture absorption indicates either a negligible effect of chemisorbed oxygen on irreversibly chemisorbed propylene or its absence.

The data quoted in the literature show that during propylene oxidation on Cu_2O at temperatures over 320°C (*1*) the acrolein formed is partially oxidized to CO_2. Hence, investigation of its chemisorption on the copper oxides was of interest.

Figure 2 (f–i) and Table 4 show that absorption bands at 1698, 1610, 1440, 1406, and 1360 cm^{-1} are present in the spectra of Cu_2O/SiO_2 and CuO/SiO_2 samples after heating in acrolein at 300°C. Of these, only the band at 1698 cm^{-1} disappears upon sample evacuation, and all the rest corresponding to a surface compound of type 1 or 4 disappear only upon high temperature treatment in oxygen. From these results we conclude that there is some reversible adsorption of acrolein on Cu_2O and CuO. However, we also conclude that there is a strongly chemisorbed surface compound such that a splitting off of the carbonyl group (in the form of CO and CO_2) occurs in the process of chemisorption and the rest of the molecule combines with oxygen atoms of the lattice.

CONCLUSIONS

The volumetric and spectroscopic investigation of C_3H_6 and O_2 chemisorption on CuO and Cu_2O has shown that the important difference in selectivity of these catalysts results from a substantial difference in the nature of the surface complexes formed at the oxide surfaces.

Firstly, the adsorption data at different temperatures have shown that under precatalysis conditions surface complexes on CuO, unlike those on Cu_2O, apparently contain more oxygen than propylene. The same conclusion has been reached by the authors (*10*, *11*) in regard to the composition of complexes on SnO_2 on the one hand and on MoO_3, antimonous–stannic, and molybdenum–stannic oxide (catalysts for partial oxidation of propylene) on the other hand. Thus, surface complexes on catalysts for partial and total oxidation differ in their composition. One of the reasons for total hydrocarbon oxidation on catalysts such as CuO, SnO_2, Co_2O_3, Fe_2O_3, etc., is their greater adsorbability towards oxygen as compared to hydrocarbons, and hence the formation of surface complexes enriched with oxygen.

Secondly, these complexes differ substantially in their energetics, i.e., in adsorption strength, as indicated by different degrees of reversibility. Thus, propylene is adsorbed mainly irreversibly on CuO, while C_3H_6 chemisorption on Cu_2O is mainly reversible.

Finally, the surface complexes on CuO and Cu_2O differ in the orientation of the olefin molecules at the surface, i.e., they have different structures. According to the ir data, propylene adsorption on CuO is accompanied by breaking of the double bond and formation of formate-like and acetate-like compounds. Subsequently these residues of propylene molecules, which are quite strongly bonded to the surface, interact with oxygen prevalent at the surface to result in complete oxidation of propylene. On Cu_2O, the C=C double bond, though somewhat perturbed (cf., the 1649–1626 cm^{-1} frequency displacement), is preserved. Bands typical of the C–H bond in the methyl radical are displaced, too. Apparently propylene is adsorbed on Cu_2O with the double bond directed to univalent copper, a π-complex weakly bonded to the surface being formed. At the same time the methyl radical interacts with oxygen, resulting in the displacement of the frequencies typical of the methyl radical. This interaction increases with temperature and at the catalysis temperature we proposed that an H atom is separated from the methyl radical of the surface π-complex and a surface intermediate allyl radical is formed:

$$\mathrm{CH_2\underset{\downarrow}{=}CH\text{-}CH_3 \xrightarrow{-H} CH_2\underset{\cdots}{-}CH\underset{\cdots}{-}CH_2.}$$

We could not detect this radical in the present work, for at the temperatures of our investigation it was either not yet formed at all or its concentration at the surface was negligible. We consider that this radical subsequently unites with oxygen at the surface without desorption to the gas phase and with the formation of acrolein.

Such a mechanism of propylene adsorption on Cu_2O and subsequent transformation of the adsorbed molecule completely agrees with the data on allyl radical formation obtained by the method of labeled atoms (*12*).

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