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Investigation of the Chemisorption of Butenes on CuO and Cu_2O Catalysts by Infrared Spectroscopy

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The adsorption of butene-1, isobutene, methylvinylketone, and methylacrolein on Cu_2O, and that of butene-1 and isobutene on CuO have been investigated by infrared spectroscopy.

It has been shown that the surface compounds formed in the chemisorption of butene-1 and isobutene on Cu_2O are of the same nature. It has been found that under similar experimental conditions the adsorption of the two main products of butene-1 and isobutene partial oxidation, methylvinylketone and methylacrolein, is essentially different. This difference lies in the fact that methylvinylketone adsorbs on the catalyst mainly irreversibly as surface carbonate compounds, while methylacrolein adsorbs largely reversibly. This difference is considered to be one of the reasons which causes the different selectivity of Cu_2O with regard to the oxidation of butenes. On CuO, both butenes are chemisorbed in the form of carbonate-carboxylate compounds of the same composition. Data on the oxidation of C_3–C_5 olefins and those on their chemisorption on copper catalysts have been compared.

This paper is a continuation of our previous publication on propylene and oxygen chemisorption on catalysts for complete (CuO) and partial (Cu_2O) olefin oxidation (*1*). The point of view developed earlier (*2*), according to which the difference in selectivity of these catalysts is considered to be due to the different nature of the surface complexes obtained, was borne out by the data reported in that study (*1*).

As Cu_2O shows different selectivity in the oxidation of butene-1 and isobutene, and as all olefins, butenes included, oxidize only to CO_2 and H_2O on CuO, one would expect different intermediate complexes to be formed in butene-1 and isobutene chemisorptions on Cu_2O, and the surface compounds of nearly the same composition and with similar properties to be formed in chemisorption of various olefins on CuO.

This paper contains butene-1 and isobutene chemisorption data on CuO and Cu_2O obtained by infrared spectroscopy.

PROCEDURE

The catalyst plates employed in the present infrared spectroscopy studies were similar to those used in our previous investigation (*1*). The procedure of the pretreatment of the oxides has already been described (*1, 3*). Spectra were recorded on an IRS-14 instrument in the region 1300–1800 (NaCl prism) and 2200–3100 cm^{-1} (LiF prism) at room temperature. The spectral slit width did not exceed 10 cm^{-1}. The error in measuring the maximum of the absorption band was of the order of ± 1 and ± 3 cm^{-1} for NaCl and LiF prisms, respectively.

INFRARED SPECTRA OF CHEMISORBED MOLECULES

1. *Chemisorption of Butene-1 on Cu_2O–SiO_2*

Infrared spectra of butene-1 and oxygen chemisorbed on Cu_2O–SiO_2 are given in

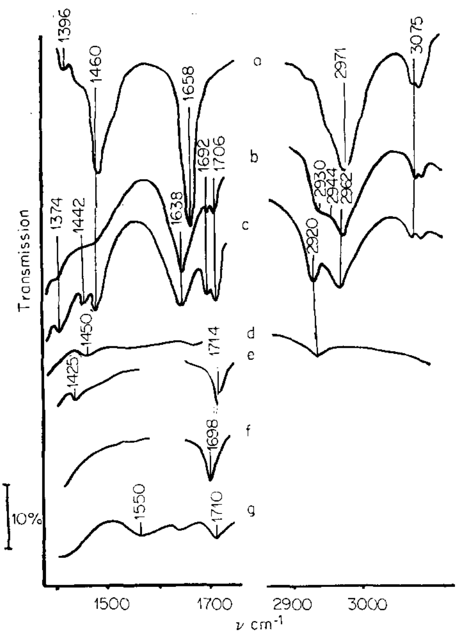


FIG. 1. Infrared spectra of C_4H_8-1 on Cu_2O–SiO_2. (a) Gaseous C_4H_8-1; (b) adsorption of C_4H_8-1 at room temperature; (c) adsorption of a mixture of C_4H_8-1 and O_2 (1:1) at room temperature; (d) pumped for 0.5 hr at room temperature after the adsorption of the mixture; (e) adsorption of acetaldehyde at room temperature; (f) adsorption of acrolein at room temperature; (g) adsorption of a mixture of C_4H_8-1 and O_2 at 300°C, then pumped at 300°C.

10% I denotes the scale of absorption band intensity on Figs. 1–6.

Fig. 1. Comparing the spectra of both gaseous and adsorbed butene-1 (Fig. 1a and b), one may notice the following changes in the latter: (a) the $C{=}C$ stretching frequency 1658 cm^{-1} shifts to lower frequencies by 20 cm^{-1}; (b) the stretching frequency of the group CH_3 in the adsorbed molecules does not greatly shift to lower frequencies over that in the gaseous butene-1 spectrum (2962 cm^{-1} vs 2971 cm^{-1}); (c) there is a low intensity shoulder occurring at 2944–2930 cm^{-1}. The corresponding C–H deformation frequencies in the group CH_3 occurred as a broad unresolved band at 1442–1460 cm^{-1} compared to a high frequency band at 1460 cm^{-1} in the gaseous butene-1 spectrum. In the adsorbed butene-1 spectrum there is also a low intensity band at 1706–1692 cm^{-1}. When oxygen is admitted to cuprous oxide surfaces saturated with butene-1, the band at 2944–2930 cm^{-1} shifts to 2920 cm^{-1}. The same shift is observed with an O_2–olefin mixture (1:1) (Fig. 1b). An unresolved band present in the C–H deformation region (1442–1460 cm^{-1}) splits into two bands at 1442 and 1460 cm^{-1} and the intensity of the bands of 1706 and 1692 cm^{-1} increases in the presence of oxygen. The latter are close to the frequencies of $C{=}O$ groups in the spectra of acetaldehyde and acrolein adsorbed on Cu_2O (Fig. 1e and f). The absorption bands at 1710 and 1550 cm^{-1} observed in the spectra of butene-1–oxygen mixture chemisorbed on Cu_2O at 300°C (Fig. 1g), followed by outgassing, are at frequencies close to those observed in the spectrum of irreversibly chemisorbed methylvinylketone (Fig. 3d).

The data obtained in the butene-1 chemisorption on Cu_2O suggest some surface heterogeneity of Cu_2O. On energetically more active sites, even at room temperature, chemisorbed butene-1 reacts with chemisorbed oxygen (the presence of

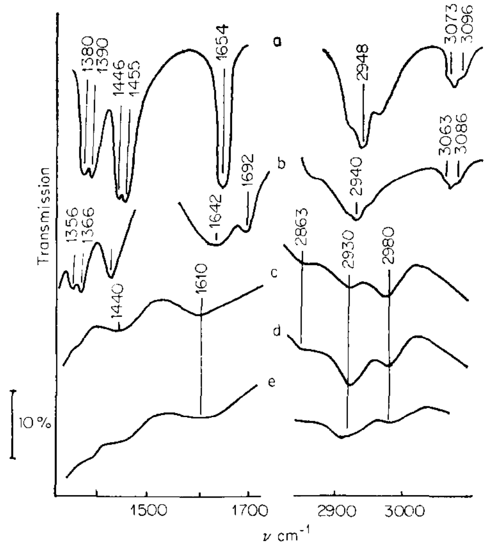


FIG. 2. Infrared spectra of iso-C_4H_8 on Cu_2O–SiO_2. (a) Gaseous iso-C_4H_8; (b) adsorption of iso-C_4H_8 at room temperature; (c) Pumped for 0.5 hr at room temperature after the adsorption of iso-C_4H_8 at the same temperature; (d) pumped for 0.5 hr at 100 and 300°C after the adsorption of iso-C_4H_8 at 100 and 300°C.

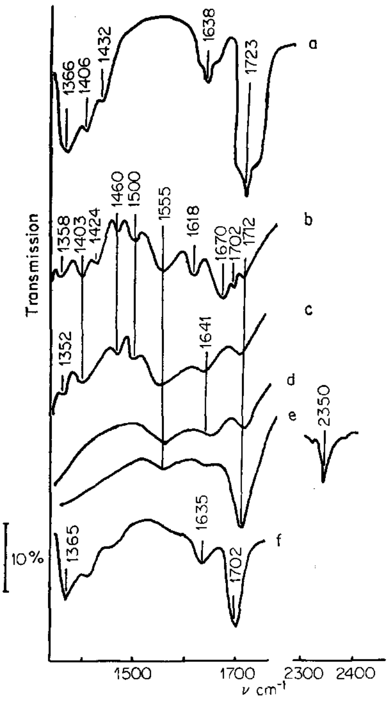
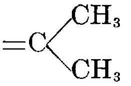
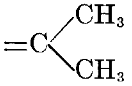


FIG. 3. Infrared spectra of methylvinylketone on Cu_2O-SiO_2. (a) Gaseous methylvinylketone; (b) adsorption at room temperature; (c) pumped for 0.5 hr at room temperature after the adsorption; (d) pumped for 0.5 hr at 300°C after the adsorption of methylvinylketone at 300°C; (e) adsorption of a mixture of methylvinylketone and O_2 at 100 and 300°C, then pumped for 0.5 hr at the same temperatures; (f) adsorption of methylvinylketone on SiO_2 at room temperature.

which on the surface of Cu_2O is very likely as outgassing was performed at 100°C) to form acetaldehyde and acrolein. On less active sites butene-1 chemisorbs reversibly; the C=C bond strength decreases, and under oxygen influence the C–H bond strengths in the methylene groups decrease. This is confirmed by the appearance of a weak band at 2944–2930 cm^{-1} which may be ascribed to asymmetric stretching frequencies of the CH_2 groups (*4*, *5*) by its shift to 2920 cm^{-1}, and the occurrence of the frequency 1442 cm^{-1} in the region of the C–H deformation vibrations in the presence of oxygen [a corresponding frequency in the gaseous butene-1 spectrum is 1470 cm^{-1} (*4*)]. It is worth mentioning that no marked effect of oxygen on the band positions of C=C, CH_3, and CH_2 groups was observed in the experiments performed. The low intensity bands observed in the spectrum of irreversibly chemisorbed butene-1 at 2920 and 1450 cm^{-1} (Fig. 1d), which do not disappear when the outgassing temperature is raised as high as 350–400°C, may be attributed to vibration frequencies of hydrocarbon fragments involving mainly $-CH_2$ groups on the surface of Cu_2O (*5*).

2. *Chemisorption of Isobutene on Cu_2O-SiO_2*

Infrared spectra of isobutene chemisorbed on Cu_2O are given in Fig. 2. Comparing spectra of gaseous isobutene with those of adsorbed isobutene at 20°C (Fig. 2b), one may notice the following changes in the latter. The maximum of the C=C band at 1654 cm^{-1} shifts to lower frequencies by 12 cm^{-1}. The frequencies of ν_{as} CH_3 (2948 cm^{-1}), $\nu_{as}{=}CH_2$ (3073–3096 cm^{-1}), δ_{as} (1446, 1455 cm^{-1}), and δ_s (1380, 1390 cm^{-1}) of CH_3 groups, as well as the deformation frequency defining a change in the  $=C{<}\begin{matrix}CH_3\\ CH_3\end{matrix}$ angle (1380 cm^{-1}) (*6*), are smaller in adsorbed molecules than the corresponding frequencies in gaseous molecules by 8, 10, 18, and 24 cm^{-1}, respectively. This suggests a decrease in the strengths of the C=C and C–H bonds and in the  $=C{<}\begin{matrix}CH_3\\ CH_3\end{matrix}$ bond angle as a result of adsorption. The absorption band at 1692 cm^{-1} present in the spectrum of adsorbed isobutene occurs at a frequency close to that observed in the spectrum of acrolein adsorbed on Cu_2O (1698 cm^{-1}) (Fig. 1f). An identical band also arises in the spectrum of methylacrolein adsorbed on Cu_2O (Fig. 4b). Therefore, this band may be supposed to correspond to one of these compounds formed in the adsorption of isobutene on Cu_2O at room temperature. In the spectrum of irreversibly chemisorbed isobutene (Fig. 2c), the frequencies 2980, 2930, and 2963 cm^{-1} are observed, while in the deformation vibration

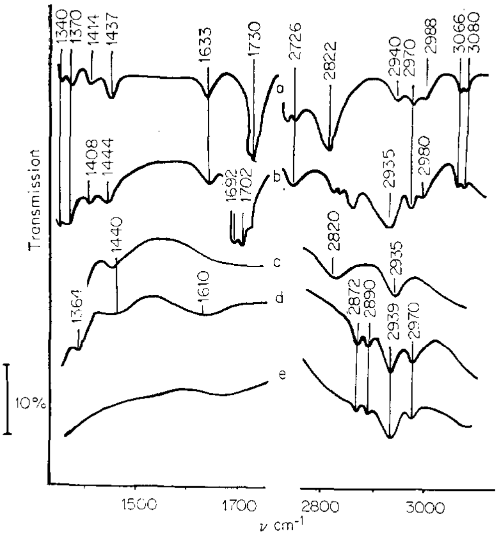
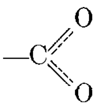


FIG. 4. Infrared spectra of methylacrolein on Cu_2O–SiO_2. (a) Gaseous methylacrolein; (b) adsorption of methylacrolein at room temperature; (c) pumped for 0.5 hr at room temperature after the adsorption; (d) pumped for 0.5 hr at 300°C after the adsorption at 300°C; (e) treated by O_2 for 10 min at 300°C.

region unresolved bands with maxima at 1610 and 1440 cm^{-1} are present. An increase in adsorption temperature as high as 100 and 300°C does not affect the band intensity at 1610 and 1440 cm^{-1}. The band intensity increases at 2930 cm^{-1} and decreases at 2980 cm^{-1} (Fig. 2). The bands at 2930 cm^{-1} and 2980 cm^{-1}, like those obtained in the spectrum of butene-1 adsorbed on Cu_2O, may be assigned to the C–H stretching vibrations (*4*, *5*). The band at 1610 cm^{-1} may be attributed to the



vibrations of the carboxylate ion, while the unresolved band at 1440 cm^{-1} obviously corresponds to the overlapped deformation frequencies in alkyl groups and symmetric stretching frequencies of the carboxylate ion.

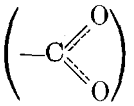
Infrared spectra of adsorbed butenes suggest an identical character for butene-1 and isobutene adsorptions on cuprous oxide involving a decrease in the C=C and C–H bond strengths in reversibly adsorbed molecules under precatalysis conditions, the formation of irreversibly adsorbed surface hydrocarbon compounds and the carboxylate ion. It follows that the lower selectivity in butene-1 oxidation cannot be interpreted by different compositions and structures of the intermediate complexes formed.

3. *Chemisorption of Methylvinylketone and Methylacrolein on Cu_2O–SiO_2*

The chemisorption of the two main products, methylvinylketone and methylacrolein resulting from partial oxidation of butene has also been studied. Their spectra are shown in Figs. 3 and 4.

Comparing spectra of gaseous methylvinylketone (Fig. 3a) with those of adsorbed methylvinylketone on Cu_2O at 20°C (Fig. 3b and c), one can see that the latter is chemisorbed mainly in the form of stable carbonate and carboxylate surface compounds. The absorption bands at 1712, 1641, 1555, 1500, 1460, 1403, and 1358 cm^{-1} remain in the spectrum when outgassing was performed at room temperature, and the bands at 1712, 1641, and 1555 are still present with outgassing at 300°C (Fig. 3d). After a short contact of the sample with oxygen at 100–300°C, the band intensity at 1712 cm^{-1} increases, while the intensity of the rest of bands decreases. Furthermore, the frequency corresponding to gaseous CO_2 (2350 cm^{-1}) appears in the gas phase spectrum (Fig. 3e). All the bands disappear from the spectrum when the sample was treated with oxygen for two or three hours at 350°C.

In the spectrum of methylacrolein chemisorbed at 20°C (Fig. 4b and c), absorption bands are not observed at 1500–1700 cm^{-1}. Consequently, unlike methylvinylketone, stable chemisorbed surface compounds of carbonate and carboxylate types are not formed from acrolein at low temperatures. The bands present in the spectrum at 2935, 2820, and 1440 cm^{-1} (Fig. 4c) seem to correspond to irreversibly chemisorbed compounds of the polymeric type (*5*). In the spectrum of irreversibly chemisorbed methylacrolein at 300°C (Fig. 4d), the bands at 2872–2930 cm^{-1} correspond to the C–H stretching frequencies in methyl and methylene groups, and the low intensity frequencies 1610 cm^{-1}



1440–1400 cm^{-1} (δ_{as} $-CH_3$) and 1364 cm^{-1} (δ_s $-CH_3$) correspond to irreversibly chemisorbed compounds of carboxylate and polymeric types. The bands at 1610 and 1400 cm^{-1} disappear from the spectrum when a short treatment of the sample with oxygen was carried out at 100–300°C, while the remaining bands which may be ascribed to polymer compounds disappear only when outgassing was performed for two to three hours at 300°C. Therefore, one may suppose that they only block a part of surface, while on the rest of it catalysis occurs via formation and oxidation of carbonate structures. As in methylvinylketone adsorption these structures are formed at lower temperatures and in greater quantities than with methylacrolein adsorption, one can think that methylacrolein is affected by further oxidation to CO_2 to a lesser extent than methylvinylketone. It is possible that this fact stipulates greater selectivity in isobutene oxidation compared to that of butene-1.

4. *Chemisorption of C_4H_8-1 on CuO–SiO_2*

Infrared spectra of butene-1 chemisorbed on CuO are presented in Fig. 5. A number of bands are observed after adsorption at 20°C and outgassing. The bands at 1540–1710 cm^{-1} may be ascribed to different firmly chemisorbed carbonate and carboxylate surface compounds, and the bands at 2854, 2926, and 2968 cm^{-1} to the C–H stretching vibrations in irreversibly chemisorbed hydrocarbon compounds. It is impossible to make an unambiguous assignment of the frequencies in the region down to 1540 cm^{-1}, as the frequencies observed can be attributed to both types of the identified surface compounds.

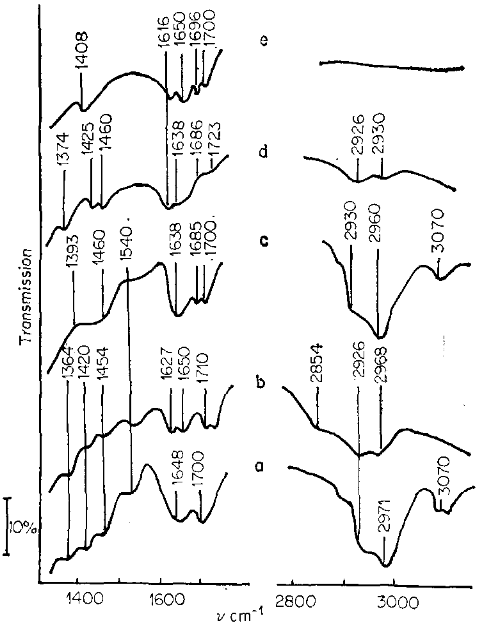


FIG. 5. Infrared spectra of C_4H_8-1 on CuO–SiO_2. (a) Adsorption of C_4H_8-1 at room temperatue; (b) pumped for 0.5 hr at room temperature and 100°C after the adsorption at the same temperature; (c) adsorption of C_4H_8-1 at 100°C; (d) pumped for 0.5 hr at 300°C after the adsorption of C_4H_8-1 at 300°C; (e) adsorption of a mixture of C_4H_8-1 and O_2 at 300°C, then pumped for 0.5 hr at the same temperature.

It is necessary to give consideration to essential differences in the spectra of butene-1 adsorbed on CuO–SiO_2 (Fig. 5b) and on Cu_2O–SiO_2 (Fig. 1d), at 20°C. As can be seen in Fig. 1d, there are no characteristic frequencies in the region 1540–1700 cm^{-1} corresponding to carbonate and carboxylate compounds. The intensity of the C–H stretching frequencies is well below that of Fig. 5b. This is evidence for a greater degree of butene-1 irreversible chemisorption at low temperature on CuO against that on Cu_2O.

It should be noted that under given conditions one cannot judge from the results obtained about the irreversible chemisorption of butene-1, as the absorption bands of the C=C stretching vibration and CH_3 deformation vibration are overlapped by the absorption bands of irreversibly chemisorbed compounds (Fig. 5a). The absence of a shift in the C–H stretching frequency (2971 cm^{-1}) may be accounted for either by insufficient adsorption for spectral detection or by complete interaction of adsorbed butene-1 and CuO to form the above-mentioned surface compounds at room temperature.

The presence of absorption bands in the region 1510–1700 cm^{-1} in spectra of butene-1 adsorbed at higher temperature (100–300°C) suggests the formation of irreversibly chemisorbed surface compounds of the carbonate and carboxylate types. Cupric oxide appears to be partially reduced. This can be seen from the spectra given in Figs. 5b and c, and 1b. The C=C and CH_3 stretching frequencies shift to lower frequencies in the spectrum of butene-1 adsorbed at 100°C (Fig. 5c) compared to those in the gaseous butene-1 spectrum (Fig. 1a) and in the spectra of butene-1 adsorbed at 20°C (Fig. 1b) and coincide with corresponding frequencies in the spectrum of olefin adsorbed on Cu_2O.

5. *Chemisorption of Isobutene on $CuO–SiO_2$*

As one can see in Fig. 6 in the irreversibly chemisorbed isobutene spectra obtained in isobutene adsorption at 20°C and higher temperatures, the same bands are present as in the spectra of butene-1 irreversibly chemisorbed on CuO. These bands correspond to characteristic vibration frequencies of carbonate and carboxylate compounds (about 1520–1700 cm^{-1}) and the C–H stretching frequencies (2965, 2930 cm^{-1}). Therefore, the qualitative composition of the surface compounds formed in the irreversible chemisorption of the two butenes on CuO may be supposed to be identical.

However, the CH_3 and $=CH_2$ stretching frequencies of isobutene in the gas phase spectrum shift by 8 and 10 cm^{-1}, while this is not observed with butene-1 (Fig. 6a). This fact enables us, to some extent, to think that the amount of irreversibly chemisorbed isobutene on CuO is greater compared to that of butene-1.

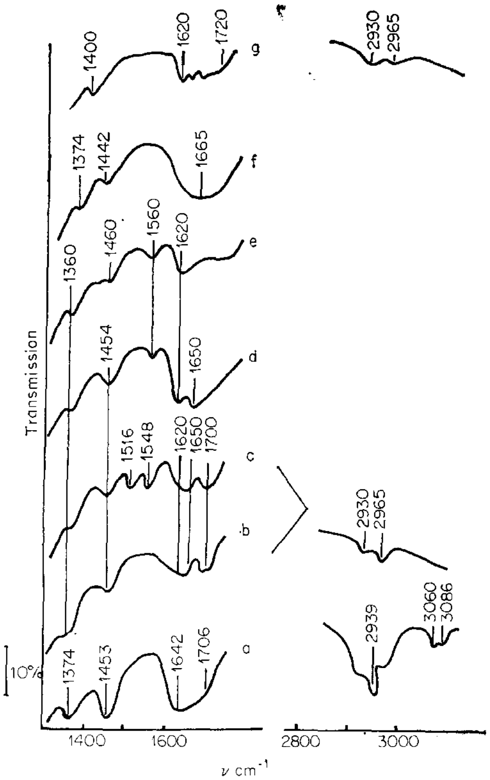


FIG. 6. Infrared spectra of iso-C_4H_8 on $CuO–SiO_2$. (a) Adsorption of iso-C_4H_8 on $CuO–SiO_2$ at room temperature; (b) pumped for 0.5 hr at room temperature after the adsorption of iso-C_4H_8; (c) adsorption of a mixture of iso-C_4H_8 and O_2 at room temperature, then pumped for 0.5 hr at the same temperature; (d) the same procedure as in "c," at 100°C; (e) adsorption of a mixture of iso-C_4H_8 and O_2 (1:1) at 300°C; (f) pumped for 0.5 hr at 300°C after the adsorption of the mixture at 300°C.

DISCUSSION

The spectroscopic data on butene-1 and isobutene chemisorptions on Cu_2O suggest that the reversible chemisorption mechanisms of both butenes are identical. They also allow us to assume the identity of their oxidation mechanism on Cu_2O via the conversion of olefin chemisorbed in the form of the π-complex on Cu^+ ions into the π-allyl surface compound followed by further oxidation of the latter. Therefore, the different selectivity of Cu_2O in isobutene and n-butene oxidations, as mentioned above, cannot be attributed to differences in adsorption of these olefins. It may be a consequence of different chemisorptions of the two main products of the partial oxidation of these butenes on Cu_2O, methylvinylketone and methacrolein. The results obtained suggest an increased chemisorptive capacity of methylvinylketone resulting in the formation of intermediate compounds of the carbonate and carboxylate type which oxidize to CO_2 at 100–300°C. Methylacrolein adsorption on Cu_2O is far weaker than that of methylvinylketone and as a result it hardly undergoes further oxidation: this stipulates greater selectivity of Cu_2O in the oxidation of isobutene to methylacrolein. One can see a complete analogy in adsorptions of acrolein and methylacrolein on Cu_2O and in the end results of the oxidations of C_3H_6 and iso-C_4H_8 on this catalyst. These conclusions drawn on the basis of the spectroscopic data are well consistent with kinetic data on butene (*7*) and pentene (*8*) oxidations on cuprous oxide. The selectivity of Cu_2O in the oxidation of branched pentenes is also higher than in the oxidation of n-C_5H_{10} (*9*). This fact is evidently due to further oxidation of the partial oxidation products of n-C_5H_{10} as compared to the oxidation products of isopentenes.

On CuO both butenes are chemisorbed mostly irreversibly involving double bond breaking and the formation of carbonate, carboxylate, and hydrocarbon compounds of similar composition. These intermediate compounds are formed both in the presence of oxygen and in the adsorption of olefin alone. It shows that oxygen in the lattice of oxide catalysts for complete oxidation is active enough to react with the olefin and break bonds in the molecule which are rather strong (about 80–150 kcal/mole).

The facts given above suggest that the different selectivity of cuprous and cupric oxides displayed in the oxidation of all olefins is due to differences in their adsorption on these catalysts to form the intermediate surface complexes different in structure and strength involving olefin, oxygen, and catalyst. The different selectivity of the same catalyst, Cu_2O, in the oxidation of olefins of different structure is due to differences in the adsorption (and, accordingly, in stability) of the partial oxidation products. This fact is of primary importance both in the choice of catalysts and conditions for catalysis.

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