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Mechanism of Carbon Monoxide and Hydrocarbon Oxidation on Copper Chromite

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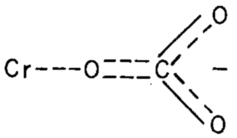
Infrared spectroscopic, gravimetric, and kinetic techniques have been used to study the oxidation of CO and hydrocarbons on a copper chromite catalyst. Carbon monoxide adsorbs concurrently on exposed lattice copper atoms to form Cu—C≡O and on lattice oxygen atoms to form



groups. The source of the oxygen required to form the unidentate carbonate groups is the catalyst, not the gas phase. In the absence of air, the carbonyl group reacts with oxygen from the catalyst to produce CO_2. In the presence of air, the oxidation reaction via the carbonyl group becomes important at temperatures above 80°C and that via the decomposition of the carbonate groups above 200°C. When hydrocarbons adsorb above 130°C they are transformed to unidentate carbonate groups and liberate water vapor. As with CO, above 200°C these carbonate groups decompose to give gaseous CO_2. For the carbonyl decomposition path, the reaction is first order in CO, and pseudo-zero order in O_2. The amount of CO_2 produced by the oxidation reaction does not inhibit the rate.

INTRODUCTION

In 1931, Frazer filed a patent (*1*) for the use of mixtures of copper and chromium oxides for treating internal combustion engine exhaust. This catalyst is a serious contender (*2*) for controlling emissions from automobiles to meet the U.S. Government clean air standards. Lory (*3*) explained conversion of CO to CO_2 with this catalyst by the alternate oxidation–reduction of surface CrO_4^{2-}. Little attention was given to the role of the copper species in his catalytic scheme. Lory suggested a mechanism in which CO reduces the surface CrO_4^{2-}, and gaseous oxygen subsequently reoxidizes the surface to the CrO_4^{2-} state. Later, Frazer and Albert (*4*) studied the adsorption of CO and O_2 on a copper chromite catalyst. However, they preheated the catalyst at 275–300°C in an atmosphere of 400 Torr CO, which reduces the copper and liberates CO_2. They also assumed that CO reduces a surface CrO_4^{2-} species in the catalytic oxidation of carbon monoxide. Since that time several studies have appeared using copper oxide as a catalyst for carbon monoxide oxidation (*5*, *6*), and copper chromite as a catalyst for the water–gas shift (*7*, *8*) reaction and the selective oxidation of propylene (*9*). No attempt to understand the mechanism of the CO–O_2 reaction on copper chromite has appeared in the literature since the early work of Lory (*3*) and Frazier and Albert (*4*).

This study used infrared spectroscopic, gravimetric, and kinetic techniques in order to elucidate the catalytic reaction mechanism of the CO oxidation reactions on copper chromite. The reactive surface intermediates and the specific sites on which they are formed were determined. The reactive intermediates for hydrocarbon oxidation reactions were also identified.

Experimental Methods

Materials

Copper chromite. For the spectroscopic, gravimetric, and some of the kinetic studies, Harshaw copper chromite 1800P catalyst was used. This material has a surface area of 40 m^2/g and contains cupric oxide (overall molar analysis 51% CuO and 47% Cr_2O_3).

Where indicated in the text, an HCl-leached copper chromite was used, either supported or unsupported. The copper chromite is insoluble in hydrochloric acid. X-Ray diffraction measurements showed that the leached copper chromite contained essentially no cupric oxide nor chromic oxide. The supported copper chromite was prepared by pressing ⅛-in. diameter beads containing 10% Al_2O_3 and firing to 800°C for 48 hr.

Ten cubic centimeters of these pellets weighing 12.3 g had a physical surface area of 9.6 m^2/g. To distribute the heat of reaction within the bed, 10 cm^3 of Houdry 100 S Al_2O_3 beads were admixed. Matheson prepurified gases were used throughout.

Spectroscopic Procedure

One-inch diameter self-supporting discs of the catalyst were prepared by pressing the material in a die at about 14000 psi. The disc was mounted in a furnace placed in the sample beam of a Perkin-Elmer Model 421 infrared spectrometer. The furnace was equipped with water-cooled end plates containing infrared-transmitting windows and connected to a conventional vacuum rack. This allowed any desired gas to be admitted to the cell, and spectra were taken of the catalyst disc, including any adsorbed species.

Prior to each experiment, the sample was heated *in situ* in air at 400°C, and evacuated at 300°C.

Gravimetric Procedure

The powdered catalyst was placed in a boat suspended in an Ainsworth vacuum balance which was connected to a vacuum rack and equipped with a furnace. The changes in the weight of the catalyst due to adsorption and desorption were recorded on a strip chart recorder.

Flow Reactors

Two flow reactors were used. Catalyst pellets were supported on a 200-mesh stainless-steel screen sealed into a ¾-in. stainless-steel tube. The catalytic chamber was mounted vertically and heated by a three-zone Norton clam shell furnace with controller. Temperatures both in and above the catalyst bed were recorded to within ±1°C with a chromel–alumel thermocouple.

The composition of the gas stream before and after passing through the reactor was analyzed on a gas chromatograph using a Linde molecular-sieve (5A) column operating at 200°C. The area under each peak was electronically integrated using a Varian aerograph digital integrator. This reactor was operated isothermally as a differential flow reactor; no more than 25% reaction was used.

The second reactor consisted of a 7.5-mm glass tube with a depression for holding the catalyst powder. This was mounted within a stainless-steel tube furnace. The gas compositions were measured on an MSA combustible gas detector.

Results and Conclusions

The infrared spectroscopic experiments consisted of exposing the catalyst to CO, propylene, hexane or methane at various temperatures, both in vacuum and with added air. The appearance or disappearance of the various bands indicated which surface species were formed or had decomposed. The infrared bands were observed, and the identification of the species (*10, 11*) which gave rise to these bands are listed in Table 1. In Fig. 1 are given some typical spectra of the copper chromite before and after the addition of carbon monoxide. Note that many of the bands are rather broad and irregular, suggesting that the surface sites are not perfectly homogeneous.

At 80°C or below, carbon monoxide adsorbs immediately on a previously evacu-

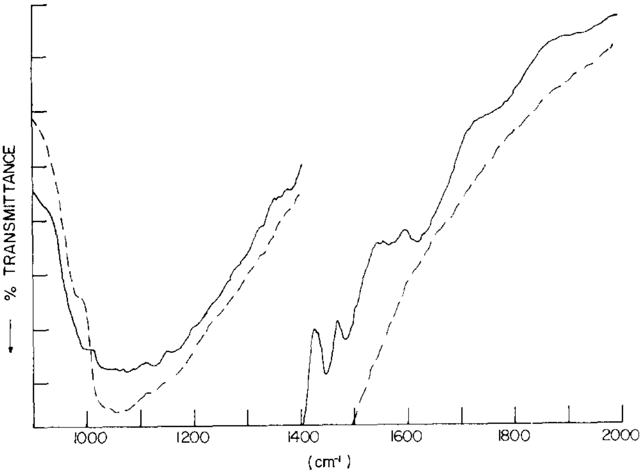
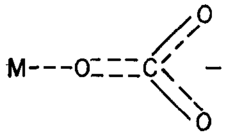
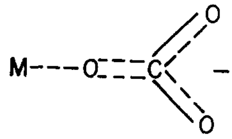
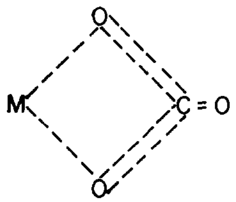


FIG. 1. Spectra of copper chromite. (— —) At 80°C, (—) at 80°C after CO had been added and the sample heated to 250°C in vacuum. The (— —) base line has been displaced downward for clarity, since the addition of oxygen abstracting gases causes an increase in the background transmittance.

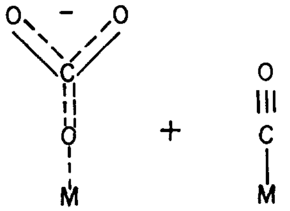
TABLE 1

OBSERVED INFRARED ABSORPTION BANDS USED TO IDENTIFY ADSORBED SPECIES[a]

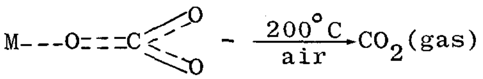
Species	Infrared bands (cm⁻¹)				
	1540	1340 1305	1090		Unidentate carbonate
	1475	1340 1305	1030		Unidentate carbonate
	1430	1470	1110		Uncoordinated carbonate ion
	1600	1150	1030		Bdentatecarbonate
M—C≡O		2110			Terminal carbonyl
$[CO_2]_{ADS}$		2285			Weakly adsoibed CO_2
SO_2/SO_3	1370	1300	1150	1060	

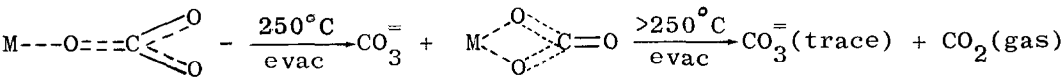
[a] Where the same band is listed for more than one species, it is not possible to determine to which species it belongs. All frequencies are ±25 cm⁻¹.

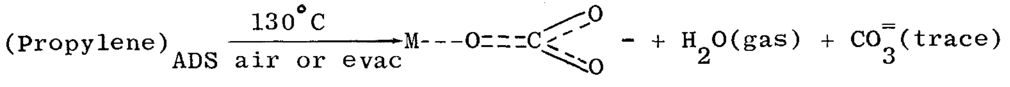
ated CuO–$CuCr_2O_4$ mixture to give carbonate and carbonyl species. Bands due to



at least two discrete unidentate carbonates are observed (cf. Table 1). Since these two discernible carbonates behave similarly under the conditions used here, they will be referred to simply as the unidentate carbonates. The specific surface sites on which the various species are adsorbed and the behavior of the terminal carbonyl group M—C≡O are considered below. The species observed on the catalyst surface and in the gas phase can be most easily summarized in the flow diagrams below. The temperatures are given where significant changes were observed. At low temperatures propylene adsorbs readily on the catalyst and at 130°C is transformed to a unidendate carbonate species. Hexane also adsorbs readily, but a significant amount desorbs reversibly as hexane at temperatures be 130°; however, enough remains adsorbed near 130°C to form a carbonate group and water. Methane did not adsorb at all under these conditions. When the propylene or hexane were transformed to the carbonate at about 130°C, only one unidentate carbonate group was initially observed. On raising the temperature, the second unidentate carbonate band appeared also. After these unidentate carbonates have formed on the surface, they behave essentially the same as the carbonates formed from CO adsorption given above, i.e., they decompose near 200°C to give CO_2.







The source of the oxygen required to form the unidendate carbonates is the catalyst and not gaseous oxygen, implying substantial lability of surface oxygen. It is interesting that in the absence of gaseous oxygen above about 200°C, there is a sufficient affinity for oxygen by the catalyst surface for the unidentate carbonate to partially transform to a bidentate carbonate.

For kinetic evaluation, it will be necessary to know if any of the reactions so far discussed are reversible. Spectra showed that once the carbonates form they desorb as CO_2 only, not as CO. With propylene, the only desorption products are H_2O when the adsorbed propylene is transformed to the carbonate at 130°C, and CO_2 at temperatures above 200°C.

Before proceeding to the second oxidation mechanism, one can summarize the reactions so far discussed as follows. Carbon monoxide reacts with the CuO + copper chromite mixture to form carbonyl groups and unidentate carbonate groups. Hydrocarbons adsorb on the surface and at about 130°C are cracked, liberating H_2O and transforming to unidentate carbonates. From this point the reactions of CO and of hydrocarbons are similar. At 200°C in air the unidentate carbonates decompose to CO_2. In the absence of air at a temperature above 200°C the unidentate carbonates transform to a bidentate carbonate and a carbonate ion. At higher temperatures these carbonates decompose to give CO_2.

Another mechanism for carbon monoxide oxidation, via the carbonyl group M—C≡O, occurs at temperatures above 80°C. This terminal carbonyl group is weakly bound to the metal atom, since it can be largely removed reversibly by evacuation. At temperatures above 80°C this terminal carbonyl group is oxidized to CO_2 by either reacting with gaseous oxygen or in its absence, with oxygen associated with the catalyst. One can detect the absorption band due to adsorbed CO_2, as well as gaseous CO_2, the product of the reaction. On evacuation the adsorbed CO_2 also desorbs rapidly, indicating that it is weakly bound to the surface.

The reaction between the CO and the oxygen of the catalyst continuously generates CO_2 at temperatures in excess of 80°C, and can be easily observed in the spectrometer cell. The amount of CO_2 produced is greatly in excess of the amount of oxygen which could possibly be on the catalyst surface, and thus must come from the bulk of the material. With air as well as CO in the system, the rate of CO_2 production is much faster. This reaction between CO and copper chromite was followed in a vacuum balance using various pressures of CO in a range of temperatures between 134 and 180°C. This temperature range was chosen to obtain a convenient reaction rate for measurement. A maximum temperature of 180°C was used, since the surface carbonate groups start to decompose at higher temperatures.

When propylene was added to the copper chromite, only an initial weight gain was observed at low temperatures. Above 200°C the copper chromite continuously loses weight. This, of course, is the temperature at which the surface carbonates start to decompose and produce CO_2.

Some typical results are shown in Fig. 2, presented as $-(\Delta X)^2$ against the time, where (ΔX) is the weight change of the catalyst. This "parabolic plot" is typical of certain diffusional processes in solids. The plots are satisfactorily linear, indicating that the rate-determining step of this reduction reaction is diffusion in the catalyst. Since the times of the experiments were only of the order of tens of minutes, the diffusing species must have a large degree of mobility at this relatively low temperature. The intercepts of these plots give a positive value of (ΔX), due to the initial weight gain when the carbonate and carbonyl groups form. In Fig. 3 is given a plot of the reaction rates, taken from the slopes of the parabolic plots, against the ambient CO pressures. This plot is linear. In the absence of gaseous diffusion this indicates that the surface of the catalyst is sparsely covered with carbonyl groups, which is to be expected in this temperature range.

By adsorbing CO below 80°C where little reaction occurs, the weight increase corresponds to the summation of the number of adsorbed carbonate and terminal carbonyl groups. Then, by evacuating, the amount remaining corresponds to the number of carbonate groups only. The number of

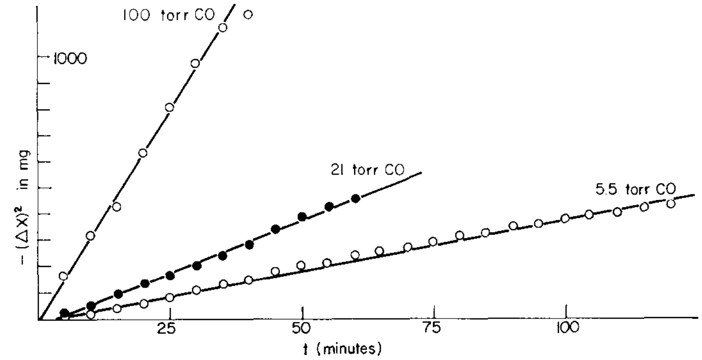


FIG. 2. Plots of the square of weight change against time, for the reactions between various pressures of CO, and 1.166 g Harshaw copper chromite 1800P, at 173°C.

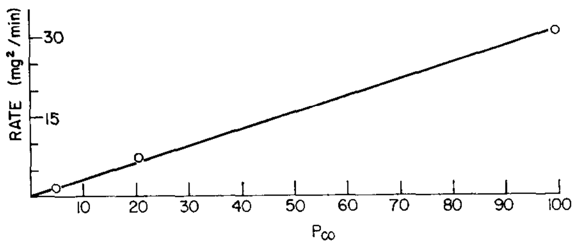
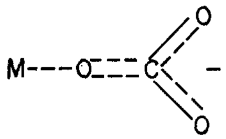


FIG. 3. Plot of the reaction rate between CO and copper chromite against the ambient CO pressure. The rates were taken from the slopes of the plots given in Fig. 2.

terminal carbonyl groups will depend on the temperature and the ambient gas pressure, since these groups are only weakly bound. Similarly, by adding propylene or hexane and then evacuating, one obtains the number of hydrocarbon molecules strongly bound to the surface. The results of these experiments indicate sparse coverage for all surface species.



$\simeq$ 1 group/100 Å²,
Cu—C≡O $\simeq$ 0.5 group/100 Å²,
Propylene$_{ADS}$ $\simeq$ 0.2 molecules/100 Å²,
Hexane$_{ADS}$ $\simeq$ 0.1 molecules/100 Å².

With the identification of the surface intermediates which exist for both reaction mechanisms, we can now consider the surface sites on which these species are adsorbed.

When CO adsorbs to form the terminal carbonyl group (i.e., M—C≡O), it has an absorption frequency of 2110 cm^{-1}. This is very close to that observed in copper carbonyl complexes (2120 cm^{-1}) (*12*). The chromium carbonyl complex (*13*) $Cr(CO)_6$ has an infrared absorption band at 2000 cm^{-1}. These data indicate that the metal on which the carbonyl forms is the copper.

When any adsorption takes place on the copper chromite, the small band which appears as a shoulder at 990 cm^{-1} is perturbed. With added CO or H_2 it is completely removed; with added propylene below 80°C, or SO_2 at any temperature, it is only reduced in intensity; with added methane the band remains unchanged (cf. Fig. 1). With exposures to CO the large broad band near 850 cm^{-1} (±50) also decreases in intensity.

Cupric oxide has no absorption bands in this vicinity (*14*), but α-chromia does have bands at 990 and 890 cm^{-1} (*15*). Since these bands must clearly be associated with Cr–O stretching frequencies, the bands near these frequencies in the copper chromite must be more closely associated with the chromium atoms than with the copper atoms. One of the carbonates which forms from the CO or hydrocarbon must be adsorbed on one of these surface chromium oxygens. Since at least two discrete unidentate carbonate species are observed, it is probable that this other carbonate species is formed on an oxygen associated with copper.

With this information about the course of the surface reactions, one is now in a position to make meaningful kinetic studies. In order to avoid the complicating factor on the kinetics of using a copper chromite which contains cupric oxide, the leached copper chromite was used.

By measuring the rate of the reaction at various partial pressures, one can determine the pressure dependencies of the reactants and products.

For the general reaction,

$$a\,(CO) + b\,(O_2) \rightarrow c\,(CO)_2.$$

The empirical rate equation of this reaction is

$$R = k\frac{(CO)^a(O_2)^b}{(CO_2)^c},$$

where the exponent c may be equal to zero if the CO_2 has no inhibiting effect on the reaction. On thermodynamic grounds the reverse reaction may be considered negligible in the temperature range studied here.

With a large excess of oxygen, varying the CO partial pressure established the CO rate dependence close to first order. Curve A in Fig. 4 shows CO conversion at various temperatures up to 160°C.

Using a constant partial pressure of CO, no influence on rate was observed by varying the oxygen-to-CO mole ratios from 2.5 to 1.22 (stoichiometric being a ratio of 0.5). This gives a pseudo-zero-order oxygen dependence.

For low conversions the amount of CO_2 produced had no influence on the overall reaction. Large amounts do inhibit the CO oxidation reaction as shown in curve B of Fig. 4, where the partial pressure of CO_2 was initially 32.4 Torr. Retardation is most significant at the lower temperatures and is gradually removed at temperatures in excess of 150°C, where the concentration of adsorbed CO_2 approaches zero. The extent of inhibition by $CO_{2(g)}$ was determined at 144°C by maintaining the initial partial pressures of CO and O_2 constant and varying the CO_2 partial pressure between 32.4 and 4.6 Torr, and monitoring the changes in percentage conversion of CO. The exponent for CO_2 in our empirical equation is approximately $\frac{1}{3}$ for CO_2 levels greater than 4.6 Torr in the low temperature region studied.

The overall rate expression at 144°C for the catalytic oxidation of CO via the carbonyl species in the presence of added CO_2 is

$$R = k\,(CO)^1(O_2)^0(CO_2)^{-1/3},$$

where

$$R = \frac{\%\ \text{CO conversion}}{\text{catalyst vol}}.$$

From the empirical rate equation, it is seen that in the absence of added CO_2 and using a constant flow of O_2 and CO, the value of k is proportional to the amount of CO converted. In Fig. 5 is given a plot of log (% CO converted) against $1000/T$ for three different samples, viz, Harshaw copper chromite, leached copper chromite, and SO_2 poisoned copper chromite. On the two unpoisoned samples, it is seen that the behavior is essentially the same, indicating that the presence of CuO in the $CuCr_2O_4$ does not alter the mechanism. One can observe both the low-temperature oxidation path via the carbonyl group and the high-temperature oxidation path via the carbonate species. This appears as a sharp break on the Arrhenius plot and occurs at about 180°C, in agreement with the spectroscopic studies.

The "activation energies" given in Fig. 5

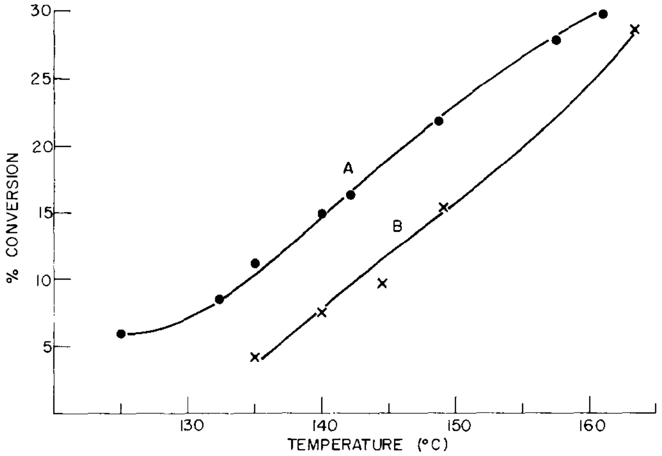


FIG. 4. Comparison of percentage CO converted at various temperatures without added CO_2 (A) and with 4% added CO_2 (B). The data were taken using the supported leached copper chromite. CO = 35.1 cm³/min, air = 84 cm³/min, N_2 = 475 cm³/min.

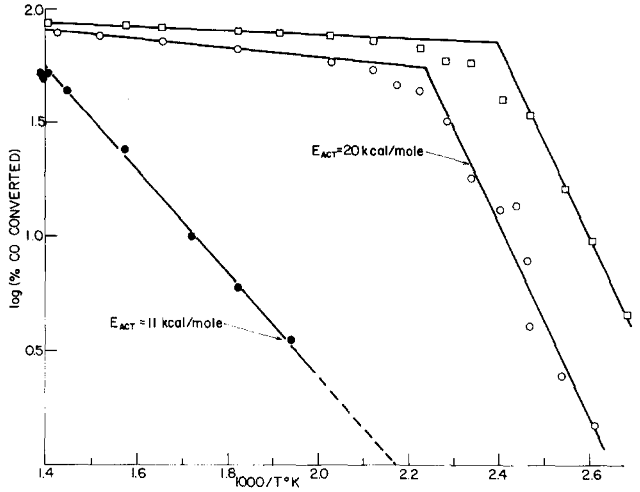


FIG. 5. Arrhenius plot of percentage CO conversion over unsupported catalyst powders. (□) Harshaw copper chromite 1800P; (○) Leached copper chromite; (●) SO_2-poisoned leached copper chromite. The gas flows used were: air = 200 cm^3/min, CO = 4 cm^3/min.

are merely a convenient way of expressing the temperature dependence of the reaction rate. Since the CO can be reversibly adsorbed on the copper, the amount adsorbed will decrease with increasing temperature. Thus, although the reaction between the carbonyl group and oxygen undoubtedly goes faster with increasing temperature, the surface concentration of $Cu—C\equiv O$ groups decreases with increasing temperature. The true activation energy will thus be higher than the experimental value.

The slope of the plot above 200°C has no fundamental significance, since the rates in this region represent the summation of oxidation reactions via two different mechanisms.

Sulfur dioxide is a well-known poison for oxidation catalysts. Spectroscopically one can observe bonded SO_2 and/or SO_3 on the copper chromite. This bonded SO_2 and/or SO_3 is stable in vacuum or air and does not desorb or transform in the temperature range used here (to 400°C).

In the vacuum balance, the reaction between CO or propylene and cupric oxide, chromia, or copper chromite was carried out both before and after the addition of SO_2. The cupric oxide and copper chromite are reduced by CO at 135°C. After the addition of SO_2, no weight losses indicative of catalyst reduction were observed until one exceeded 250°C with CO and 300°C with propylene. With chromia in the presence of CO or propylene, no weight losses were observed up to 320°C (the highest temperature used). This resistance to reduction by CO is consistent with thermodynamic data. An initial weight gain of several tenths of a milligram was observed when the CO was admitted to the system.

The catalytic activities of the copper chromite and chromia were also measured at various temperatures in the flow reactor, both before and after SO_2 poisoning. With unpoisoned chromia, both CO and propylene are oxidized to CO_2 at temperatures above 270°C. After treating with SO_2, the activity of the chromia for CO and propylene oxidation was reduced, but not badly. After adding SO_2 to copper chromite, no CO conversion to CO_2 was observed until one exceeded 200°C. The data for this poisoned copper chromite are also given on the Arrhenius plot in Fig. 5. It is seen that the extrapolated value to 1% conversion is at approximately the same temperature at which the break occurs in the plots for the unpoisoned catalysts. One can conclude that the low-temperature mechanism for CO oxidation via the terminal carbonyl groups is blocked, due to the adsorption of SO_2 on the copper atoms. The higher temperature mechanism via carbonate group decomposition (for CO and hydrocarbons) is affected to a lesser extent.

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