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Properties of Copper Chromite Catalysts in Hydrogenation Reactions

R. Rao, A. Dandekar, R. T. K. Baker,[1] and M. A. Vannice[2]

Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802-4400

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A pretreatment involving a 4-h reduction under H_2 at 573 K, compared to either 473 or 673 K, gave the highest specific activity for furfural and crotonaldehyde hydrogenation over an unpromoted copper chromite catalyst. Both H_2 and CO chemisorption declined monotonically with increasing reduction temperature, but turnover frequencies also showed a maximum after a pretreatment at 573 K. DRIFTS identified a band, associated with CO adsorbed on Cu^{+1} sites, which reached a maximum intensity after a 573 K pretreatment, while XRD patterns also provided evidence for a $CuCrO_2$ phase and showed a continuous increase in Cu^0 as temperature increased. Selectivity to furfuryl alcohol ranged from 35–80% and reaction orders on furfural and H_2 were near unity. In contrast, crotonaldehyde hydrogenation gave primarily butyraldehyde with only around 3% crotyl alcohol and a near zero-order dependence on crotonaldehyde, although the H_2 dependence was still near first order. IR spectra under reaction conditions revealed adsorbed crotonaldehyde, provided evidence for an unsaturated alkoxide intermediate and detected no butyraldehyde on the surface. A simple Langmuir–Hinshelwood sequence nicely explained both reactions, it was consistent with the DRIFTS results obtained during crotonaldehyde hydrogenation, and the resultant rate expression gave meaningful entropies and enthalpies of adsorption for H_2 and crotonaldehyde.

INTRODUCTION

Copper chromite catalysts have been used extensively for years in various industrial processes such as the partial hydrogenation of vegetable oils and fatty acids as well as the decomposition or dehydration of alcohols (1). The utilization of these catalysts in hydrogenation reactions stems from their capability to selectively hydrogenate carbonyl bonds while leaving unsaturated C=C bonds virtually untouched. New restrictions now prevent used copper chromite catalysts from being deposited in landfill sites, thus providing an incentive for new replacement Cu catalysts containing no chromium. Consequently, we are currently studying Cu dispersed on different types of carbon and have chosen furfural and crotonaldehyde hydrogenation as two test reactions to probe catalytic behavior and to allow comparisons among these Cu-containing systems. Furfural, C_4H_3OCHO, is an important compound in the fragrance industry and the vapor-phase hydrogenation of furfural is perhaps the best method of producing furfuryl alcohol. Furthermore, because of the presence of both C=O and unsaturated C=C bonds, furfural is a suitable compound to test the ability of a catalyst to selectively hydrogenate a carbonyl bond. Crotonaldehyde also contains a carbonyl group as well as a conjugated C=C bond, which makes selective hydrogenation of the former more difficult. Despite decades of use, however, the number of fundamental kinetic studies of hydrogenation reactions over copper chromite catalysts reported in the open literature has been limited, with only three pertaining to furfural (2–4) and one referring to crotonaldehyde (5).

In addition, there have not been many studies characterizing these copper chromite systems, especially the state of the surface, and, although Cu^{+1} species have most frequently been associated with activity in various hydrogenation reactions, the participation of Cu^0, and even Cu^{+2}, has been proposed (5–15). Chudinov *et al.* investigated changes in the oxidation state of a copper-chromium-zinc-alumina catalyst during reduction in H_2 between 323 and 673 K and reported that significant amounts of Cu^0 began to form only above 573 K (6). Pillai examined the influence of a variety of pretreatments on copper chromite used for the reductive alkylation of aniline with acetone and concluded that Cu^{+1} species were the active sites in the reaction (7). Herman and co-workers also suggested that Cu^{+1} was the active species in copper chromite used for methanol synthesis (8), and similar conclusions were reached by Monnier *et al.*, who proposed that the Cu^{+1} species existed in a crystalline $CuCrO_2$ phase (9). Hubaut and co-workers studied the hydrogenation of dienes on copper chromite and again proposed that Cu^{+1} species constituted the active sites (5). Makarova and co-workers suggested that, after pretreatment in hydrogen between 453 and 643 K, two phases coexisted in the catalyst, i.e., metallic Cu and a cation-deficient, controlled-disordered spinel (10). In contrast, Imura *et al.* have stated that the active form of copper for methanol decomposition can vary, and they proposed that Cu^{+2}, Cu^{+1}, and Cu^0 species are present

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[1] Current address: Chemistry Department, Northeastern University, Boston, MA 02115.

[2] To whom inquiries should be sent.

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in different catalysts (11). Capece and co-workers determined the oxidation states and surface composition of copper chromite at various stages of catalytic use and after reductive pretreatments, and they concluded that Cu^{+1} is the active species for double-bond isomerization while Cu^0 is required for hydrogenation of conjugated dienes (12). Nishimura *et al.* have reported that olefin hydrogenation proceeds on metallic copper (13), and Stroupe reported that copper chromite catalysts used in low temperature hydrogenations showed partial or complete reduction to Cu^0 (14). Finally, Yurchenko *et al.* used XPS and XRD to observe Cu^0 formation during reduction under H_2 (15). Thus, despite these characterization studies of copper chromite catalysts, uncertainty still remains about the relationships between pretreatment procedures, composition, and active sites.

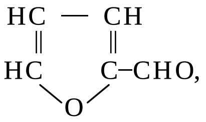
This paper describes the characterization of a commercial, unpromoted copper chromite catalyst after a series of different pretreatments. In particular, the effect of reduction temperature was examined by physical adsorption, H_2, CO, and N_2O chemisorption, X-ray diffraction, and IR spectroscopy of adsorbed CO, while the hydrogenation of furfural and crotonaldehyde was used as a catalytic probe of the reduced surface. A high resolution TEM examination of this catalyst after different reduction temperatures is reported elsewhere (16). These investigations not only provide a basis for comparison with Cu/carbon catalysts, but also contribute additional insights into the surface sites associated with their catalytic behavior.

EXPERIMENTAL

The catalyst used was a commercial, unpromoted copper chromite sample (Cu-1800P, Engelhard Corp.). One of three pretreatments was utilized—reduction in 40 cm^3 H_2 (STP)/min ($WHSV = 5 \times 10^4$ $cm^3/h \cdot g$) at 1 atm at either 473, 573, or 673 K for 4 h, because a 4-h reduction period was reported to be optimum by Pillai (7). The state of the surface was probed by H_2 and CO chemisorption at 300 K using a stainless steel adsorption system giving a vacuum below 10^{-7} Torr at the sample (17). After the initial isotherm, the sample was evacuated at 300 K for 30 min and a second isotherm was measured to determine reversible adsorption. The H_2 (MG Ind., 99.999%) and CO (Matheson, 99.99%) were flowed through molecular sieve traps (Supelco) and Oxytraps (Alltech Asso.) for additional purification. BET surface areas were measured using Ar at 77 K.

XRD spectra were obtained *ex situ* using a Rigaku Geigerflex diffractometer equipped with a CuKα radiation source and a graphite monochromator. Each sample was given one of the pretreatments described above, and afterwards it was passivated by exposure to a flowing mixture of 1% O_2 in He for 1 h prior to handling in air during XRD measurements.

Vapor-phase rate measurements were performed at atmospheric pressure in a pyrex reactor which was placed inside a heating mantle equipped with a temperature controller (Omega, Model CN2011). The catalyst was reduced *in situ* for 4 h at either 473, 573, or 673 K under flowing H_2 and the reactor was then cooled to the reaction temperature. A constant flow of vapor-phase furfural,



or crotonaldehyde, $CH_3CH{=}CHCHO$, was established by bubbling the H_2 carrier gas through a saturator containing pure liquid furfural (Alfa, 99.99%) or crotonaldehyde (Aldrich, 99.5+%) which was kept in a constant-temperature liquid bath (Fisher Scientific, Model 90). This eliminated the problem of line blockage, presumably due to polymerization, that was experienced with furfural when it was introduced via a syringe pump. The partial pressure of the organic reactant in the feed was controlled by changing the temperature of the bath. All stainless steel lines after the bath, as well as the sampling valve of the gas chromatograph, were heated to ensure that no condensation of either the reactant or the products occurred. Mass flow rates of hydrogen and helium (used as a diluent) were regulated by mass flow controllers (Tylan, Model FC-260). Furfural (FURFAL) hydrogenation was studied between 423 and 473 K, standard reaction conditions were 730 Torr H_2 and 10 Torr furfural unless otherwise noted, and at 413 K the H_2 partial pressure dependency was determined at a furfural partial pressure of 10 Torr and the furfural pressure dependence was determined at a hydrogen partial pressure of 730 Torr. For the companion reaction, standard conditions were 35 Torr crotonaldehyde (CROALD) and 720 Torr H_2, with Arrhenius plots obtained over a temperature range of 333 to 453 K. A more detailed study of this reaction was conducted, and partial pressure dependencies on crotonaldehyde were obtained between 110 to 240 Torr at a H_2 pressure of 400 Torr while dependencies on H_2 were measured over a range of 200 to 600 Torr at a crotonaldehyde pressure of 160 Torr, and these reaction orders were acquired at 353, 373, and 393 K. Products from both reactions were analyzed by a gas chromatograph (Hewlett–Packard, Model 5730A) equipped with a 10-ft column packed with Carbowax 20M on 80/100 Supelcoport. All kinetic measurements were made at atmospheric pressure and under differential conditions as conversions were routinely below 15%, except for one run to determine selectivity to furfural alcohol at higher conversions.

The infrared studies were conducted with a Sirius 100 FTIR system (Mattson Instr.) using a DRIFTS cell (HVC-DPR, Harrick Sci. Corp.) that was extensively modified to allow *in situ* treatments up to 800 K under flowing gases

(18, 19). Ultrahigh purity H_2 and Ar (99.999%, MG Ind.) were further purified by passing them through indicating Oxytraps (Alltech Assoc.) and molecular sieve traps, and precise gas flow rates were maintained using mass flow controllers (Tylan Corp., Model FC-260). The recorded interferograms typically consisted of 10,000 signal-averaged scans obtained using a postamplifier gain of 8, an iris setting of 50, and a resolution of 4 cm^{-1}. Each sample and corresponding background interferogram was then Fourier-transformed to its equivalent frequency component spectrum and the ratio of these two spectra gave the transmittance spectrum from which either the absorbance or the Kubelka–Munk spectrum was obtained. Further details of the data handling procedure have been described elsewhere (20). After loading the copper chromite into the DRIFTS reactor cell, a standard procedure was used to collect the interferograms, all of which were obtained at 300 K. The first interferogram was that of the initial "as-is" sample at 300 K under flowing Ar (20 cm^3 (STP)/min). The catalyst was then subjected to one of the three *in situ* pretreatments previously discussed then cooled to 300 K for the second interferogram. Following this, the catalyst was exposed to a mixture of 10% CO and 90% Ar at 300 K for 30 min and then purged with pure Ar for 1 h. Interferograms were collected before and after the purging step. Spectra were also obtained during crotonaldehyde hydrogenation after one of the three pretreatments under reaction conditions of 720 Torr H_2, 30 Torr crotonaldehyde, and 333 K. In each case the reference spectrum was that obtained just prior to the introduction of crotonaldehyde. Additional spectra were taken after a 30-min purge with Ar at each temperature.

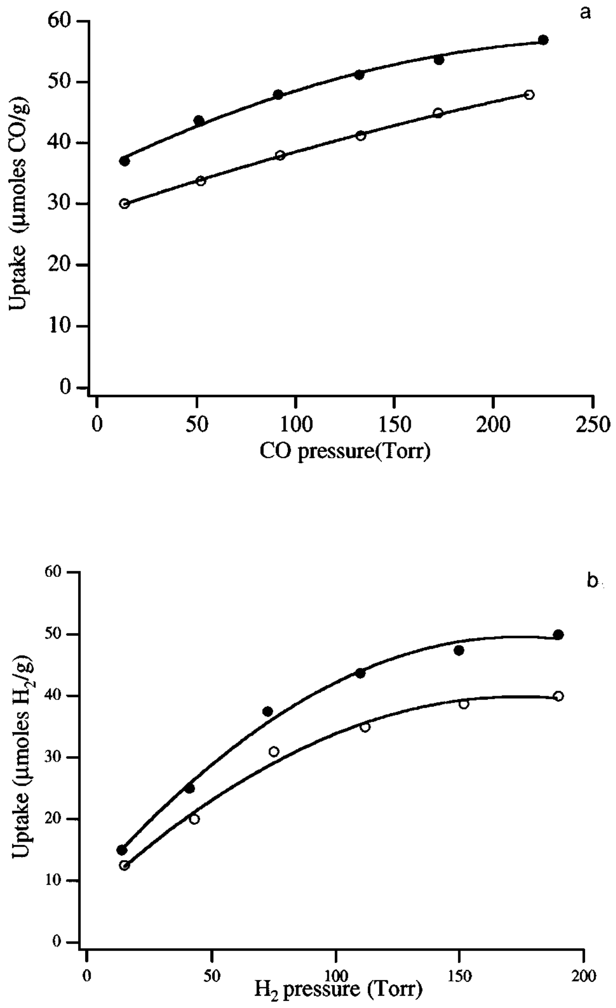


FIG. 1. Adsorption isotherms at 300 K for copper chromite after reduction in hydrogen at 573 K: (a) CO, (b) H_2; (●)—total adsorption, (○)—reversible adsorption.

RESULTS

A typical set of chemisorption isotherms is shown in Fig. 1, and Table 1 lists the BET surface areas as well as both the total and irreversible hydrogen and CO uptakes after each pretreatment temperature. The irreversible adsorption is defined as the difference between the total (initial) and reversible uptakes. The BET measurements indicate that after reduction in hydrogen, the available catalyst surface area more than doubles from the initial value of 28 m^2/g, and the surface area increased with higher pretreatment temperatures. The H_2 and CO uptakes were utilized to count adsorption sites and provide turnover frequencies on these catalysts.

The XRD patterns are given in Fig. 2. That of the unreduced catalyst was in general agreement with the pattern

TABLE 1

BET Surface Areas and CO and H_2 Uptakes for Copper Chromite as a Function of the Pretreatment Temperature

Reduction temperature (K)	Surface area (m^2/gm)	Wt. loss (mg/g)	H_2 uptake (μmol H_2/g)[a]		CO uptake (μmol/g)[a]		O uptake (μmol O/g)
			Total	Irreversible	Total	Irreversible	
Untreated	28	—	—	—	—	—	—
473	58	16.1	94	25	95	20	1046
573	66	20.7	50	8	57	6	1408
673	72	31.3	26	5	32	4	1240

[a] At 100 Torr.

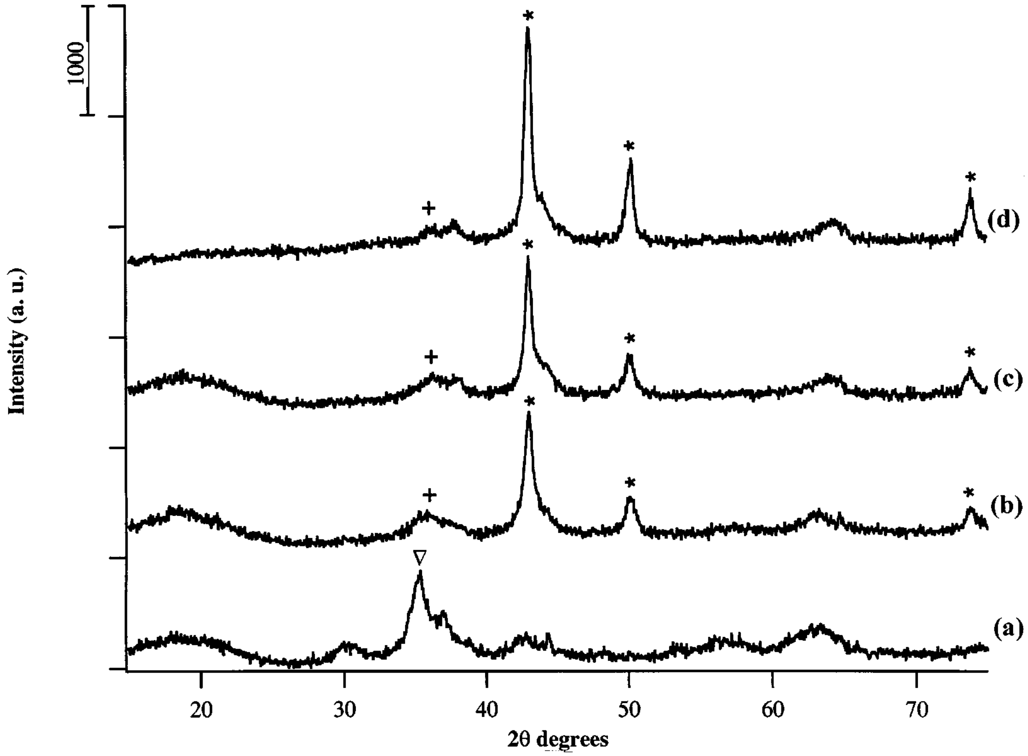


FIG. 2. XRD patterns for Cu chromite catalysts after: (a) He treatment at 473 K; (b) reduction at 473 K; (c) reduction at 573 K; and (d) reduction at 673 K. The following phases are denoted: Cu^0 (∗), $CuCr_2O_4$ (▽), $CuCrO_2$ (+).

previously reported for copper chromite, with the dominant peak at a 2 θ value of 35.4° corresponding to cupric chromite (2). After pretreatment in hydrogen, narrow, well-defined peaks appeared at 43.0, 51.0, and 75.0° which correspond to metallic Cu. A broad, weaker peak can be seen at 36.5°, which is assigned to $CuCrO_2$ based on Pillai's work (7). As the pretreatment temperature was increased from 473 to 673 K, the intensity of the peak at 36.5° slowly decreased while the peaks for Cu^0 intensified.

IR spectra of $CuCr_2O_4$, referenced to the untreated sample, were obtained in Ar after reduction at different temperatures. They showed intensity losses in the regions of OH stretching and bending, but no loss of bands which could be associated with any structural or functional change occurring during the pretreatments. All the spectra discussed henceforth are referenced to the spectrum of the corresponding pretreated catalyst prior to CO admission, unless stated otherwise. Upon exposure of the pretreated catalyst surfaces to a 10% CO/90% Ar mixture, a distinct absorption band developed around 2115 cm^{-1} in all the three cases (Fig. 3). The gas-phase CO spectrum, which has a characteristic doublet at 2170 and 2121 cm^{-1}, has been subtracted from these spectra. The absorption band at 2115 cm^{-1} corresponds to CO adsorbed linearly on Cu^{+1} sites (21, 22). Absorption bands at 2140–2160 cm^{-1} and 2080–2105 cm^{-1} can be associated with CO on Cu^{+2} and Cu^0 sites, respectively (22); however, no such bands were detected in these spectra.

Calculation of the Weisz–Prater number gave values of 0.05 and 0.012 for the most active catalysts during hydrogenation of furfural and crotonaldehyde, respectively, thus indicating the absence of diffusional limitations. Table 2A lists the specific activities for furfural hydrogenation at 413 K per square meter as well as on a turnover frequency basis (based on chemisorbed H atoms) after each of the three different pretreatments. Initial runs indicated that the catalyst pretreated at 573 K gave the highest rate, specific activity, and turnover frequency; therefore, unless mentioned otherwise, the reported kinetic data were obtained after this pretreatment. A thorough kinetic study of furfural hydrogenation was very difficult to conduct because in all experiments significant catalyst deactivation was observed, in agreement with previous reports (2, 4), and the extent of this process was more severe at higher furfural partial pressures. The deactivation profile of the catalyst used in the present study at 413 K is displayed in Fig. 4a and, as indicated, the reciprocal of the rate was linearly dependent on time on-stream. Two possible reasons have been suggested for the deactivation: the formation of coke and/or poisoning of the catalyst by either adsorbed furfural or some product that is formed, or a change in the oxidation state of the copper during the course of the reaction. The

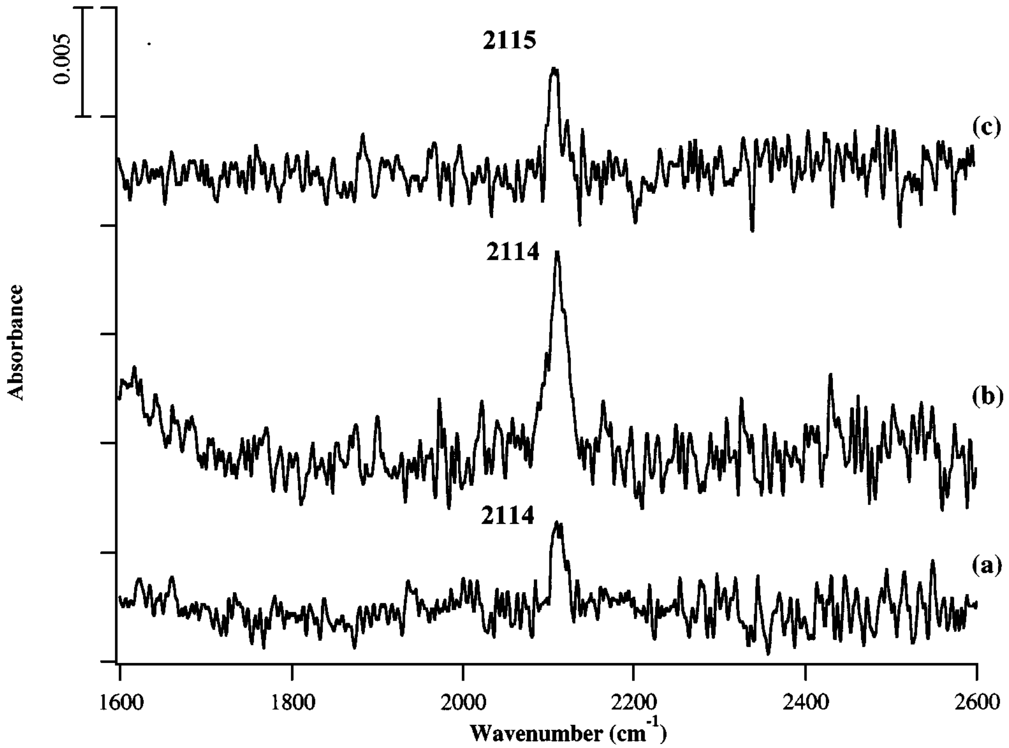


FIG. 3. IR spectra of CO adsorbed at 300 K on copper chromite after different reduction temperatures: total pressure = 750 Torr, $P_{CO} = 75$ Torr, balance Ar: (a) $T_{red} = 473$ K; (b) $T_{red} = 573$ K; (c) $T_{red} = 673$ K.

Arrhenius plot for the most active copper chromite catalyst for furfural hydrogenation is shown in Fig. 4b, and it gives an apparent activation energy of 11 ± 2 kcal/mol, where the uncertainty is represented by 95% probability limits. For this reaction, Borts and co-workers (4) report an activation energy of about 21 kcal/mol; however, the marked deactivation they observed could easily affect this value and, in addition, it is possible that their catalyst composition was different from that used here. In accordance with other reports (2, 4), the only two products observed were furfural alcohol and 2-methylfuran, and Fig. 5 represents selectivity, defined as mole furfural/(mole furfurol + mole 2-methylfuran), at higher furfural conversions. Partial pressure dependencies on hydrogen and furfural for furfural hydrogenation were determined at 413 K, using the most active catalyst, i.e., that after reduction at 573 K. In order to correct for the deactivation occurring during these experiments, after the activity was measured at each chosen set of conditions, the reaction conditions were returned to a predefined set of standard conditions and the activity was remeasured. The activities at the different reaction conditions were then normalized to those collected at these standard conditions to correct for deactivation, and the results are shown in Fig. 6. Dependencies from a power rate law fit gave a value of 0.9 for either hydrogen or furfural. These results compare to the study of Borts *et al.* (4) which reported a first-order dependence on furfural but a second-order dependence on H_2.

TABLE 2

A. Furfural Hydrogenation over Copper Chromite at 413 K, 720 Torr H_2, 10 Torr FURFAL

Pretreatment temperature (K)	Rate[a] (μmol/g · s)	Specific activity[a] (μmol/m^2 · s)	TOF[b] (s^{-1})	TOF[c] (s^{-1})	E_a (kcal/mol)	S[d] (%)
473	12.4	0.21	0.25	0.13	—	80
573	16.8	0.26	1.05	0.34	11 ± 2	70
673	6.4	0.09	0.64	0.24	—	80

B. Crotonaldehyde Hydrogenation at 333 K, 725 Torr H_2, 35 Torr CROALD

Pretreatment temperature (K)	Rate[e] (μmol/g · s)	Specific activity[e] (μmol/m^2 · s)	TOF[b] (s^{-1})	TOF[c] (s^{-1})	E_a (kcal/mol)	S[f] (%)
473	9.9	0.17	0.20	0.053	4.6 ± 0.4	2.1
573	15.0	0.23	0.94	0.150	3.4 ± 0.3	3.1
673	8.2	0.11	0.82	0.158	4.4 ± 0.3	2.8

[a] Based on furfural disappearance.
[b] Based on irreversible hydrogen adsorption.
[c] Based on total hydrogen adsorption.
[d] Selectivity for furfuryl alcohol.
[e] Crotonaldehyde disappearance.
[f] Selectivity for crotyl alcohol.

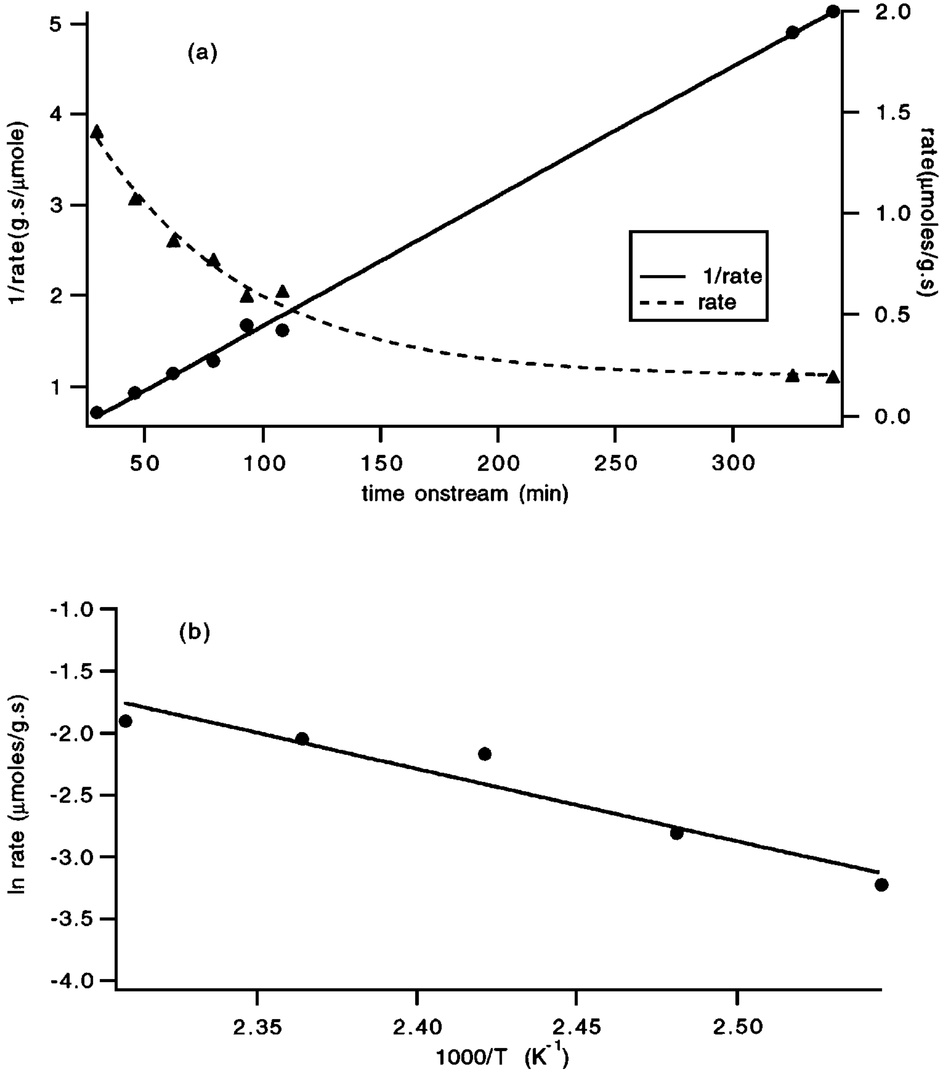


FIG. 4. Furfural hydrogenation over copper chromite after reduction at 573 K, $P_{\mathrm{FURFAL}} = 10$ Torr, $P_{\mathrm{H_2}} = 730$ Torr. (a) Deactivation during reaction at 413 K and (b) Arrhenius plot.

Activities and turnover frequencies (TOFs) at 333 K for crotonaldehyde hydrogenation are listed in Table 2B. Again, the $CuCr_2O_4$ sample reduced at 573 K gave the highest rate and specific activity. Based on irreversible hydrogen adsorption, the TOF was also maximized after a reduction at 573 K, whereas the TOF values were similar after reduction at either 573 or 673 K if total H_2 adsorption is used to count sites. An Arrhenius plot for the sample reduced at 573 K is shown in Fig. 7; others are provided elsewhere (23). All plots gave activation energies close to 4 kcal/mol, which are slightly lower than those reported over Pt catalysts (24). In contrast to furfural, no significant deactivation was observed in any of these activity runs. Partial pressure dependencies for crotonaldehyde hydrogenation were obtained using $CuCr_2O_4$ reduced at 573 K, and data, shown in Fig. 8, were obtained at three temperatures to facilitate kinetic modeling. At all temperatures, the reaction order of H_2 was near unity and that of crotonaldehyde was near zero.

Vapor-phase crotonaldehyde gave peaks at 2940, 2830, 2730, 1724, 1646, 1455, 1145, 1078, and 970 cm^{-1}, as shown in Fig. 9, and these peaks have been subtracted from the other spectra in Fig. 9. The IR spectra of copper chromite under reaction conditions with H_2 and crotonaldehyde are shown in Fig. 9. Three strong absorption bands developed at 1428, 1529, and 1704 cm^{-1} along with weak bands near 968, 1130, 1636, 2740, and 2960 cm^{-1}. The band at 1704 cm^{-1}, red-shifted by 20 cm^{-1} from the vapor-phase species, can be assigned to the carbonyl stretch frequency of unreacted crotonaldehyde adsorbed on the copper chromite surface. Similarly, the bands at 968, 1130, 1636, 2740, and 2960 can also be assigned to weakly adsorbed crotonaldehyde (21, 25). Purging with Ar after reaction leaves two strong bands at 1428 and 1529 cm^{-1} and a weak band at 1660 cm^{-1},

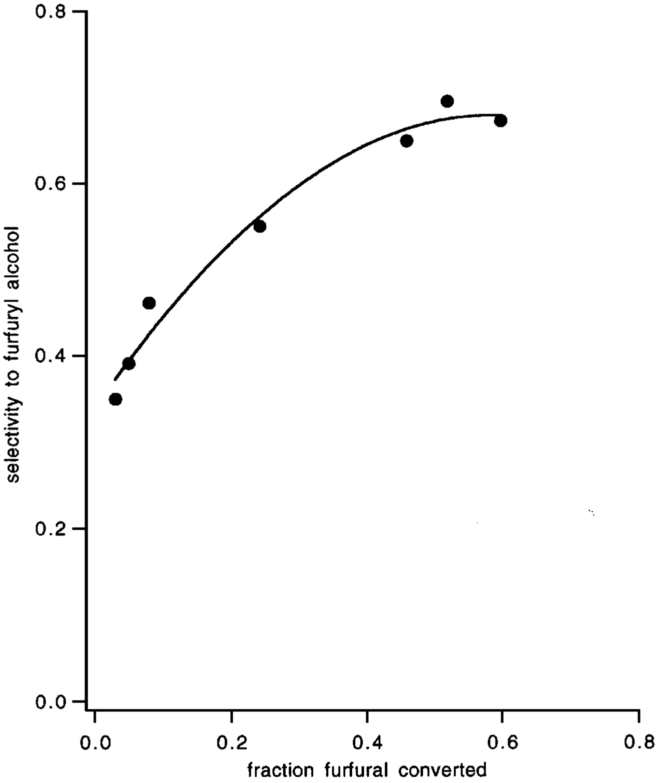


FIG. 5. Selectivity to furfuryl alcohol in furfural hydrogenation over copper chromite pretreated at 573 K.

as shown in Fig. 10. No IR investigation of this reaction over any catalyst has been previously reported to provide an assignment for a species with only these bands; however, bands at 1475 cm^{-1} have been associated with ethylene π-complexes with Cu metal and bands around 1530 cm^{-1} have been assigned to C=C π bonds interacting with Cu^{+1} cations (21, 26). However, bands around 1430 cm^{-1} can also be associated with CH_3 asymmetrical deformation modes (25), and the weak bands at 2740 and 2960 cm^{-1} are representative of C–H stretches, with the former indicative of that between H and a carbon atom attached to a carbonyl group (25). If the oxygen atom interacts with Cu^{+1} or Cu^0 to form an alcoholate (an alkoxide), the 1704 cm^{-1} band would not be present and a weaker band in the 1000–1100 cm^{-1} region might be expected to occur (21). The spectra in Fig. 10 do not disallow this possibility; thus both the 1529 and 1428 bands can be assigned to an intermediate consisting of crotonaldehyde with one H atom added to the carbonyl bond and the O atom interacting with Cu^{+1} while the C=C bond forms a π-complex with another Cu^{+1} cation, although the possibility of the 1428 band representing a π-complex with Cu^0 cannot be discounted. The absence of the C–H 2830 cm^{-1} band in these adsorbed species probably reflects this interaction between the C=C π bond and the Cu species. Table 3 lists the assignments of the IR bands associated with the species observed on a copper chromite surface. It is important to note that no band at 1751 cm^{-1}, indicative of butyraldehyde, was detected. Exposure of this sample to 30 Torr of butyraldehyde in Ar at 333 K produced no detectable bands, indicating very weak adsorption of butyraldehyde on this surface.

TABLE 3

Wavenumber (cm^{-1}) and Assignment of Bands Observed during Crotonaldehyde (CROALD) Hydrogenation on Copper Chromite

Observed Wavenumber (cm^{-1})	Assignment	Reference
1704	C=O stretch in adsorbed CROALD	21
1636	Olefinic C=C stretch in adsorbed CROALD	21–25
1529	C=C π interaction between alcoholate and Cu^{+1}	25
1428	CH_3 deformation modes, or possible C=C π complex with Cu^0	25
1130	C–C stretch in adsorbed CROALD	26
968	CH wagging vibrations in adsorbed CROALD	25
2740, 2960	CH_x stretches in adsorbed CROALD	21, 25

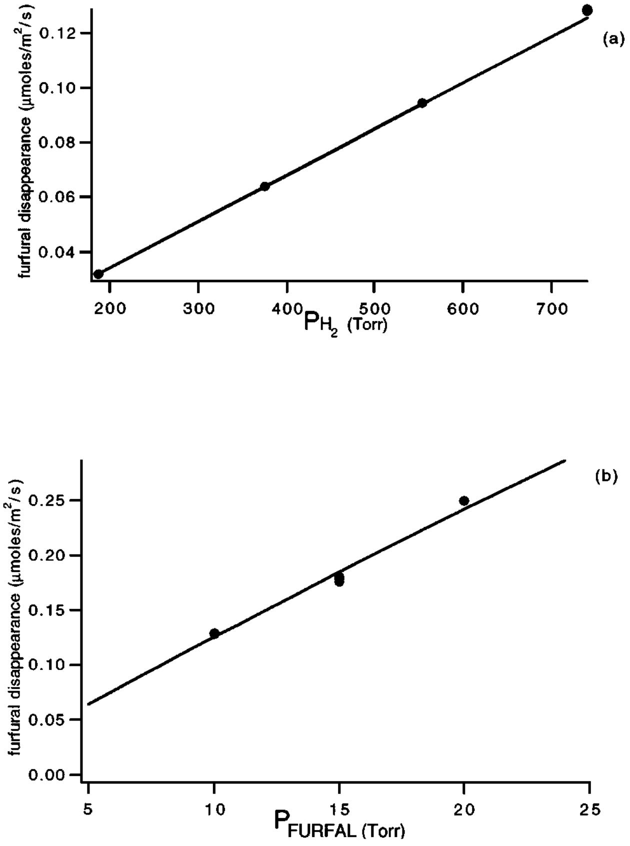


FIG. 6. Pressure dependencies for furfural hydrogenation on copper chromite: (a) H_2; (b) furfural. The fit is that obtained with Eq. [2].

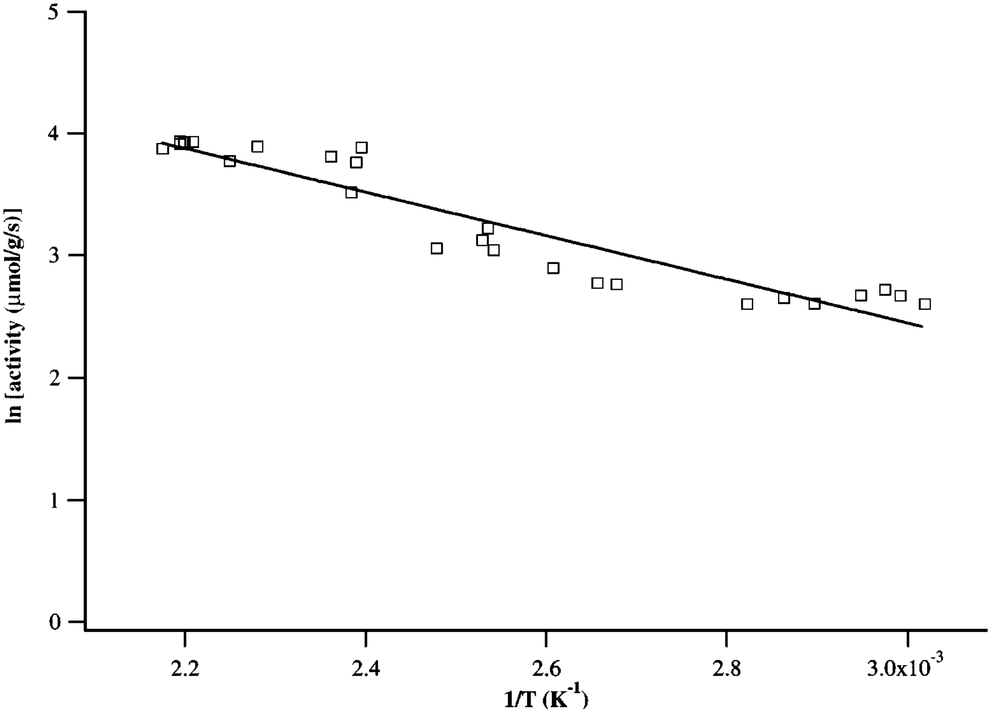


FIG. 7. Arrhenius plot of crotonaldehyde hydrogenation over copper chromite after reduction at 573 K: $P_{\mathrm{CROALD}} = 35$ Torr; $P_{\mathrm{H_2}} = 710$ Torr.

DISCUSSION

Previous studies of copper chromite catalysts have shown that catalytic activity is dependent upon the reduction temperature. In their study of acetone hydrogenation to isopropanol over copper chromite, Makarova and co-workers reported that the maximum activity was obtained after reduction at 573–593 K (10), and Pillai also found that copper chromite reduced at 573 K showed the highest activity for the reductive alkylation of aniline with acetone (7). As shown in Table 2, the catalyst pretreated in H_2 at 573 K showed the highest activity; therefore, our results agree with these previous studies and indicate that the same active form(s) of Cu may be involved in all these reactions. This would imply that the copper sites involved in the reaction reach a maximum concentration after this particular pretreatment. Comparison of the XRD patterns obtained for the catalyst after the three different pretreatment temperatures shows that the only identifiable peak that may be maximized after reduction at 573 K is that at 36.5°, which has been associated with $CuCrO_2$ and implies that the cuprous ion plays some role in the catalytic cycle. The broad peak at 36.5° in the XRD pattern is assigned to a Cu^{+1} species, designated as $CuCrO_2$, based on previous studies (7, 9). Its presence along with metallic copper is evident in each reduced sample, and the relative amount of Cu^0 clearly increases as reduction temperature increases, although the fraction at the surface cannot be ascertained. Peak widths of the principal Cu^0 peak indicate Cu crystallites on the order of 12–15 nm. The DRIFTS results provide evidence only for Cu^{+1} species at the surface, which reach a maximum concentration after the 573 K pretreatment. The absence of Cu^{+2} is not surprising, but the inability to detect CO adsorbed on Cu^0 is certainly somewhat unexpected. The broad 36.5° peak implies a low level of crystallinity, whereas the linewidth of the Cu^0 peaks indicates larger metallic copper crystallites; thus one possible interpretation is the formation of Cu^0 particles that are almost completely covered by an oxide phase, such as $CuCrO_2$. The verification of Cu^{+1} sites and the coincidence of maximum specific activity with maximum Cu^{+1} concentration is strong evidence that these sites are involved in the catalytic cycle, in agreement with previous conclusions (7–10). However, H_2 activation should be more likely to occur on Cu^0 surfaces, thus the presence of both Cu^{+1} and Cu^0 species is probably required for optimum performance.

The effect of pretreatment temperature under flowing H_2 was monitored by a variety of adsorption techniques. The BET surface area, as determined by Ar physisorption, doubled after pretreatment at 473 K, and continued to increase with increasing reduction of temperature to reach a value of 72 m^2/g after pretreatment at 673 K, as shown in Table 1. This is presumably a consequence of the opening of small pores due to the removal of strongly adsorbed water plus dehydroxylation. The IR spectra and the increasing weight loss with higher pretreatment temperature are

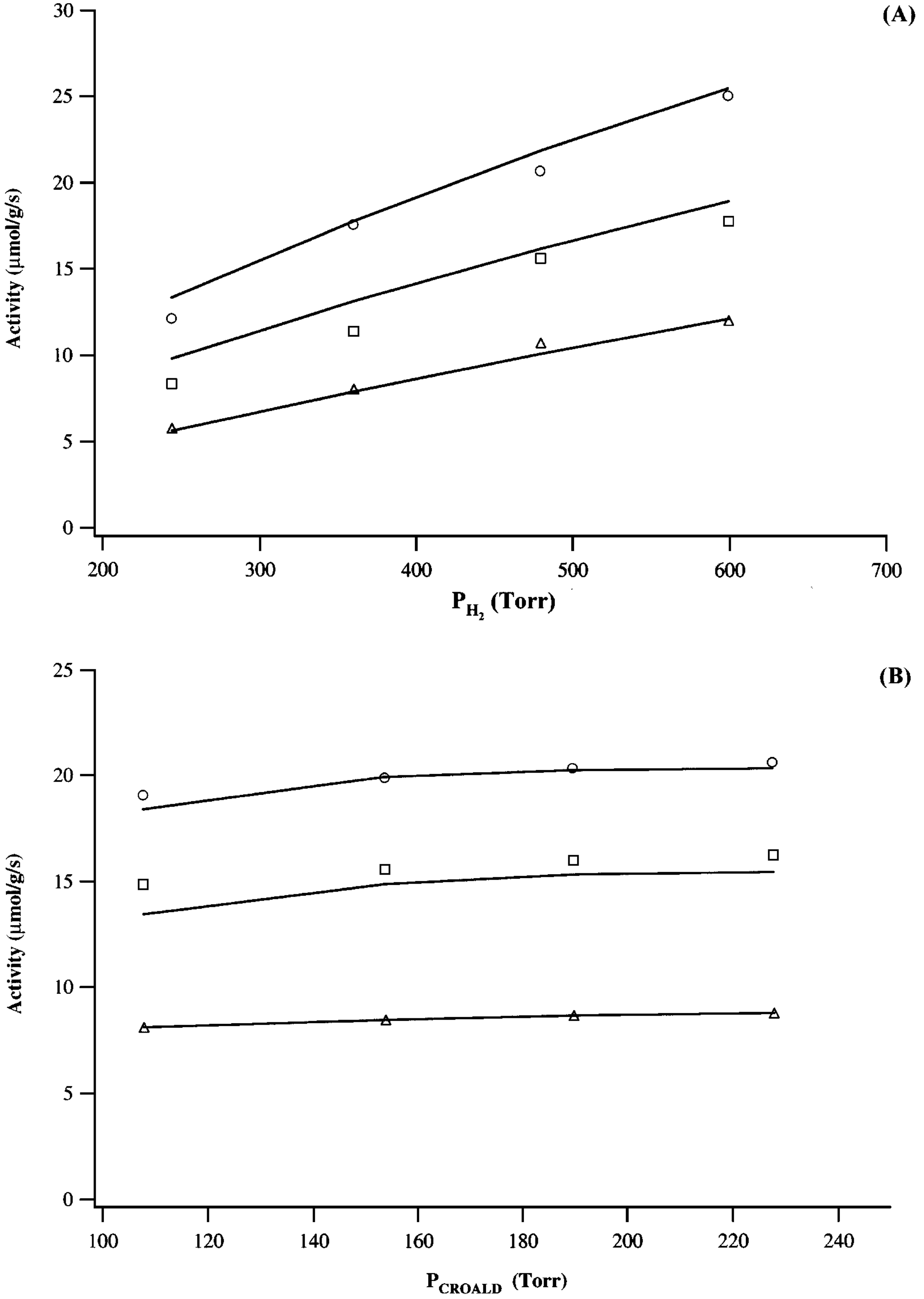


FIG. 8. Pressure dependencies at different reaction temperatures for crotonaldehyde hydrogenation over copper chromite after reduction at 573 K: (△), 353 K; (□), 373 K; (○), 393 K. (A) Dependence on H_2, $P_{CROALD} = 160$ Torr; (B) dependence on CROALD, $P_{H_2} = 400$ Torr.

consistent with this proposal. The total uptake of either H_2 or CO at 100 Torr is very similar for each sample and both values decline as pretreatment temperature increases. The irreversible adsorption follows the same pattern and the number of sites capable of strongly adsorbing hydrogen, presumably in the form of H atoms, is about double that which strongly adsorb CO. Since H_2 must be activated in the reactions examined, hydrogen chemisorption, especially the irreversibly adsorbed form, is probably the best choice to calculate turnover frequencies, i.e., molecule

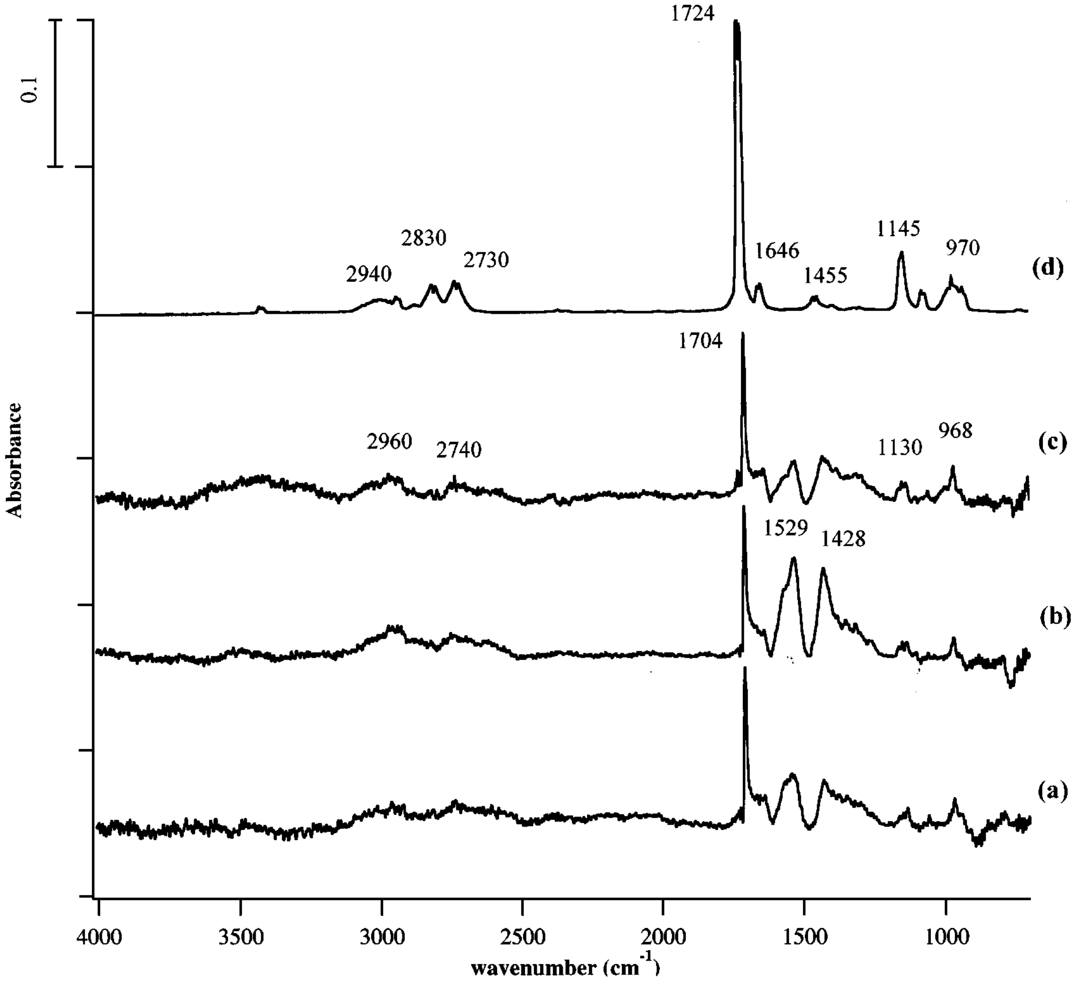


FIG. 9. DRIFT spectra of copper chromite under reaction conditions at $T = 333$ K, $P_{\mathrm{CROALD}} = 30$ Torr, $P_{\mathrm{H_2}} = 720$ Torr. Reduction temperature: (a) 473 K; (b) 573 K; (c) 673 K; and (d) DRIFT spectrum of vapor-phase crotonaldehyde at 333 K. The reference spectrum in each case is that of the sample in H_2 prior to introduction of CROALD. Gas-phase CROALD bands have been removed.

reacted/s/site, where a H atom counts an adsorption site. Irreversible hydrogen (and to a lesser extent CO) adsorption does occur on Cu^0 surfaces at 300 K, but at less than monolayer coverages (27). Dissociative N_2O adsorption at 363 K has been used to measure metallic Cu surface area based on the stoichiometry; $N_2O_{(g)} + 2\,Cu_s^0 \rightarrow Cu_2O + N_{2(g)}$ (28), where Cu_s is a surface atom. The results in Table 1 show that very large amounts of oxygen are adsorbed during this reaction, regardless of the pretreatment temperature, if all the weight gain is attributed to O atoms. No correlation with the amount of Cu^0 detected by XRD is observed. The oxygen coverages of $1.0\text{–}1.3 \times 10^{19}$ O atoms/m^2 represent very high fractional coverages and were not especially sensitive to the pretreatment. The catalytic decomposition of N_2O over CuO and Cr_2O_3 at higher temperature has been associated with coordinatively unsaturated cations at the surface (29, 30); thus N_2O adsorption on these sites, either with or without dissociation, is likely and appears to obviate this technique for determining metallic surface Cu atoms in this system.

The kinetic behavior of Cu chromite can now be examined. Depending on the catalyst, vapor-phase hydrogenation of furfural can give rise to a variety of products such as furfuryl alcohol, 2-methylfuran, furan, tetrahydrofuran, tetrahydrofurfuryl alcohol, and even ring-decomposition products such as pentanols and pentanediols. Furfural has been reduced quantitatively to furfuryl alcohol with Pt oxide, provided that the reduction was stopped after the addition of one molecular equivalent of hydrogen (31). On further hydrogenation, the ring is first saturated to yield tetrahydrofurfuryl alcohol, together with smaller amounts of ring-opening products, i.e., pentanediols and pentanols.; Ni-based catalysts lead to hydrogenation of the furan ring and the accompanying products (3, 32). Cu-based catalysts have been most widely used for the selective hydrogenation of the C=O bond in the side group while leaving

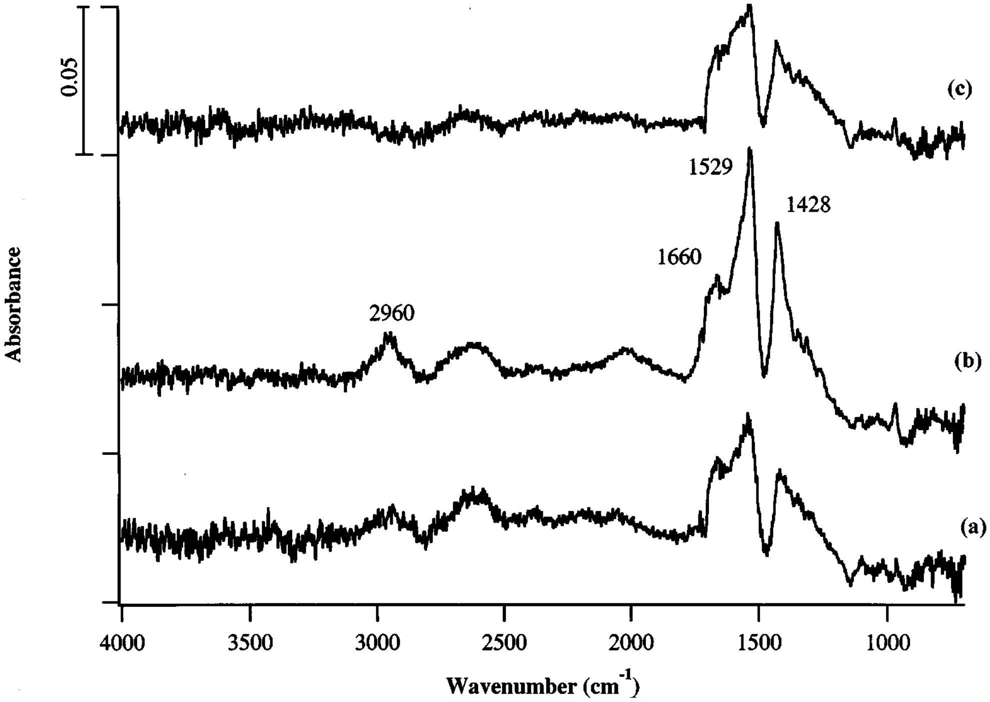


FIG. 10. DRIFT spectra of copper chromite after crotonaldehyde hydrogenation and purging in Ar at 333 K; (a) $T_{\text{RED}} = 473$ K, (b) $T_{\text{RED}} = 573$ K, and (c) $T_{\text{RED}} = 673$ K.

the C=C bonds in the furan nucleus intact. Bremner and Keeys made an exhaustive investigation of furfural hydrogenation to furfuryl alcohol and 2-methylfuran over several copper catalysts, including copper-alumina and copper chromite, and they found that furfuryl alcohol was the primary product below 473 K while 2-methylfuran was the primary product around 523 K (2). Seo and Chon also reported that furfuryl alcohol was the primary product formed in furfural hydrogenation over a variety of copper-based catalysts, but they did not mention any significant change in selectivity with temperature (3). Borts and co-workers investigated the kinetics of furfural hydrogenation over a copper chromium catalyst and reported that furfuryl alcohol was the main product with less than 3 wt% 2-methylfuran being formed (4).

Despite the preference of copper chromite for hydrogenation of furfural to furfuryl alcohol and 2-methylfuran, there is surprisingly little fundamental information on the kinetics and mechanism of this reaction over this catalyst, and a definitive understanding of the active state of copper involved in furfural hydrogenation does not exist. In this study, an unpromoted copper chromite catalyst was reduced at either 473, 573, or 673 K and then examined for furfural hydrogenation. As indicated in Fig. 5, at conversions up to 60%, only furfural and 2-methylfuran are produced, and the selectivity to furfural alcohol ranges from 35 to 70%, consistent with the earlier studies discussed above. The reaction orders near unity (i.e., 0.9) for both furfural and H_2 are consistent with the first-order dependence on furfural reported by Borts *et al.*, but clearly differ from the second-order H_2 dependence reported by this group (4). Very severe deactivation was also observed by Borts *et al.* and, if not correctly accounted for, this could explain the difference in H_2 dependency, especially if nondifferential conversions were achieved.

The partial pressure data suggest that a simple bimolecular surface reaction as a rate determining step (rds) is capable of explaining the hydrogenation of furfural over this copper chromite catalyst, and a Langmuir–Hinshelwood model invoking either one type of site with competitive adsorption between furfural and hydrogen or two types of sites, i.e., one for each reactant, fits the data well. For example, with the former sequence, assuming that H_2 activation requires dissociation, the steps are

$$H_{2(g)} + 2\,S \xrightleftharpoons{K_{H_2}} 2\,H{-}S \qquad [1a]$$

$$C_4H_3OCHO_{(g)} + S \xrightleftharpoons{K_F} C_4H_3OCHO{-}S \qquad [1b]$$

$$C_4H_3OCHO{-}S + H{-}S \xrightleftharpoons{K} C_4H_3OCH_2O{-}S \qquad [1c]$$

$$C_4H_3OCH_2O{-}S + H{-}S \xrightarrow{k} C_4H_3OCH_2OH{-}S \quad \text{(rds)} \qquad [1d]$$

$$C_4H_3OCH_2OH{-}S \xrightleftharpoons{I/K_A} C_4H_3OCH_2OH_{(g)} + S, \qquad [1e]$$

where S designates an active site.

Step (4) is the rate determining step (rds) and the other four are in quasi-equilibrium. Should the adsorbed furfuryl alcohol in step (5) react further with hydrogen rather than desorb, 2-methylfuran is formed. If only adsorbed furfural and hydrogen are considered to be significant surface species, the site balance is then $L = [S] + [C_4H_3OCHO{-}S] + [H{-}S]$ and the derived rate expression is

$$r = kKK_{H_2}K_F P_{H_2} P_F / \left(1 + K_{H_2}^{1/2} P_{H_2}^{1/2} + K_F P_F\right)^2, \qquad [2]$$

which fits the data well, as shown in Fig. 6. The value of the apparent rate constant ($kKK_{H_2}K_F$) is 1.8×10^{-5} μmole/($s \cdot m^2 \cdot atm^2$), and the values of the equilibrium adsorption constants are $K_{H_2} = 1.1 \times 10^{-4}$ atm^{-1} and $K_F = 1.4$ atm^{-1} which provide near first-order behavior for each reactant. An equally good fit of the data is obtained with the 2-site model because of the near first-order dependence on each reactant (33); thus a choice between the two models cannot be made.

In regard to crotonaldehyde hydrogenation, only the paper by Hubaut *et al.* has addressed this reaction over copper chromite catalysts (5), although Jenck and Germain did examine competitive hydrogenation of aldehydes and olefins over copper chromite (34). Noller and Lin studied crotonaldehyde hydrogenation over Cu–Ni catalysts (35), and this reaction over various Pt catalysts has been investigated recently (36–38). Hubaut *et al.* reported that at 313 K and atmospheric pressure, selectivity to crotyl alcohol decreased from 15 to 6% as the overall conversion of crotonaldehyde increased from 0.1 to 49%, and butanol was obtained at conversion levels above 10%. Apparent reaction orders of 0.75 for hydrogen and 0.17 for crotonaldehyde were reported at 313 K, but no activation energies, rates, or specific activities were reported and the effect of pretreatment temperature was not investigated.

In the present study, the partial pressure dependencies of 0.88 for hydrogen and 0.08 for crotonaldehyde are in good agreement with the values of Hubaut *et al.* The sample reduced at 573 K exhibited the highest rate and specific activity, and it yielded an activation energy of 3.4 ± 0.3 kcal/mol between 333 and 453 K. Selectivities to crotyl alcohol at 333 K and a 10% conversion level were near 3%, which is about half that reported by Hubaut *et al.* (5). This low selectivity towards the allyl alcohol during hydrogenation of an α,β-unsaturated aldehyde is somewhat surprising, given the high selectivity of $CuCr_2O_4$ for diene hydrogenation (5). However, it is consistent with the conclusion of Jenck and Germain that the functional group selectivity in a conjugated system is lower than that expected from the relative reactivities of isolated double bonds and carbonyl groups (34). The results obtained in this study are in general agreement with previous studies in that the highest selectivity of 3% for crotyl alcohol is much lower than that achieved with some other catalysts such as Pt/TiO_2 (24).

It has been suggested that this low selectivity could be due to the strong adsorption of the allylic alcohol on copper chromite and its subsequent high reactivity (39). Other than desorb, the allylic alcohol can either isomerize to form the saturated aldehyde or further hydrogenate to form the saturated alcohol. In the present study, the *in situ* FTIR spectra suggested the formation of a possible unsaturated alkoxide-type intermediate on the catalyst surface, clearly verified the presence of adsorbed crotonaldehyde via the frequency of the C=O and C=C stretches, and indicated the absence of butyraldehyde on the surface. It has been previously proposed that both butyraldehyde and crotyl alcohol can originate from this type of common intermediate (24, 40). This adsorbed complex can react with adsorbed H to give either butyraldehyde or crotyl alcohol. Since no butanol was detected in the product analysis, secondary hydrogenation activity can be assumed to be negligible at these reaction temperatures giving low conversions. However, a very low fraction of the final product corresponds to crotyl alcohol, thus rapid isomerization of crotyl alcohol must occur in the adsorbed state to yield butyraldehyde. This is consistent with the results of Hubaut *et al.* which demonstrated a low hydrogenation activity of crotyl alcohol relative to its isomerization over copper chromite (39).

The *in situ* FTIR studies of crotonaldehyde hydrogenation suggest that an unsaturated alkoxide-type species is a detectable organic intermediate whose hydrogenation rate could control the overall rate of reaction. Therefore, a Langmuir–Hinshelwood model with the hydrogenation of such an intermediate species as the rate determining step (rds) was utilized to describe crotonaldehyde hydrogenation over copper chromite. This approach, which assumes all steps other than the rds to be quasi-equilibrated, generates the same general sequence of elementary steps as shown previously, i.e.,

$$H_{2(g)} + 2\,S \overset{K_{H_2}}{\rightleftharpoons} 2\,H{-}S \qquad [3a]$$

$$C_3H_6CO_{(g)} + S \overset{K_{CROALD}}{\rightleftharpoons} C_3H_6CO{-}S \qquad [3b]$$

$$C_3H_6CO{-}S + H{-}S \overset{K^*}{\rightleftharpoons} C_3H_6CHO{-}S + S \qquad [3c]$$

$$C_3H_6CHO{-}S + H{-}S \xrightarrow{k} C_3H_6CHOH{-}S + S \quad \text{(rds)} \qquad [3d]$$

$$C_3H_6CHOH{-}S \overset{K_{ISO}}{\rightleftharpoons} C_3H_8CO_{(g)} + S, \qquad [3e]$$

where S again represents an active site, k is a rate constant, K_{H_2} and K_{CROALD} are adsorption equilibrium constants while K^* is the equilibrium constant for reaction [3c]. The assumptions that an alkoxide-like species is an adsorbed reactive intermediate, whose formation is given by step [3c], and that adsorbed butyraldehyde concentrations are very low, both of which are supported by our DRIFTS data, give

TABLE 4

Parameters Obtained from Rate Expression for Crotonaldehyde Hydrogenation

Reaction temp. (K)	k (μmol/s/m^2)	$K_{\mathrm{H_2}}$ (atm^{-1})	K_{CROALD} (atm^{-1})	K^*
353	2.0	0.46	5.4	0.29
373	3.9	0.36	3.6	0.45
393	5.7	0.21	3.3	0.78

TABLE 5

Thermodynamic and Kinetic Parameters for Crotonaldehyde Hydrogenation

$-\Delta H^\circ_{ad}$ (kcal/mol)		ΔS°_{ad} (cal/mol/K)		E_{rds} (kcal/mol)
H_2	CROALD	H_2	CROALD	
5.6	3.6	−17.2	−6.7	8.5

a site balance of

$$L = [S] + [H\text{–}S] + [C_3H_6CO\text{–}S] + [C_3H_6CHO\text{–}S] \quad [4]$$

and result in the rate expression:

$$r = \frac{kK_{\mathrm{H_2}}K_{\mathrm{CROALD}}K^*P_{\mathrm{H_2}}P_{\mathrm{CROALD}}}{\left(1+K_{\mathrm{H_2}}^{1/2}P_{\mathrm{H_2}}^{1/2}+K_{\mathrm{CROALD}}P_{\mathrm{CROALD}}+K_{\mathrm{H_2}}^{1/2}K_{\mathrm{CROALD}}K^*P_{\mathrm{H_2}}^{1/2}P_{\mathrm{CROALD}}\right)^2}. \quad [5]$$

The capability of this equation to fit all the experimental results is excellent, as shown in Fig. 8, and the correlation constants obtained for the four fitting parameters were near unity. The parameters obtained from these linear regressions are listed in Table 4, and their physical consistency was checked by obtaining enthalpies and entropies of adsorption for H_2 and crotonaldehyde from the plots of these adsorption constants versus reciprocal temperature (Fig. 11), and these values are listed in Table 5. The values of $K_{\mathrm{H_2}}$, K_{CROALD}, and K^* are such that a near first-order dependency on H_2 and a near zero-order dependency on CROALD are obtained over the pressure range studied. The enthalpies of −5.6 and −3.6 kcal/mol indicate weak chemisorption on the copper chromite surface, and the entropy losses of −17.2 and −6.7 e.u. correspond to values close to that expected for the loss of one degree of translational freedom (41).

SUMMARY

Both the specific activity and the TOF for furfural and crotonaldehyde hydrogenation reached their highest values over unpromoted copper chromite after reduction under H_2 at 573 K, compared to 473 and 673 K, whereas both H_2 and CO chemisorption declined monotonically with increasing temperature. *In situ* DRIFTS spectra showed that

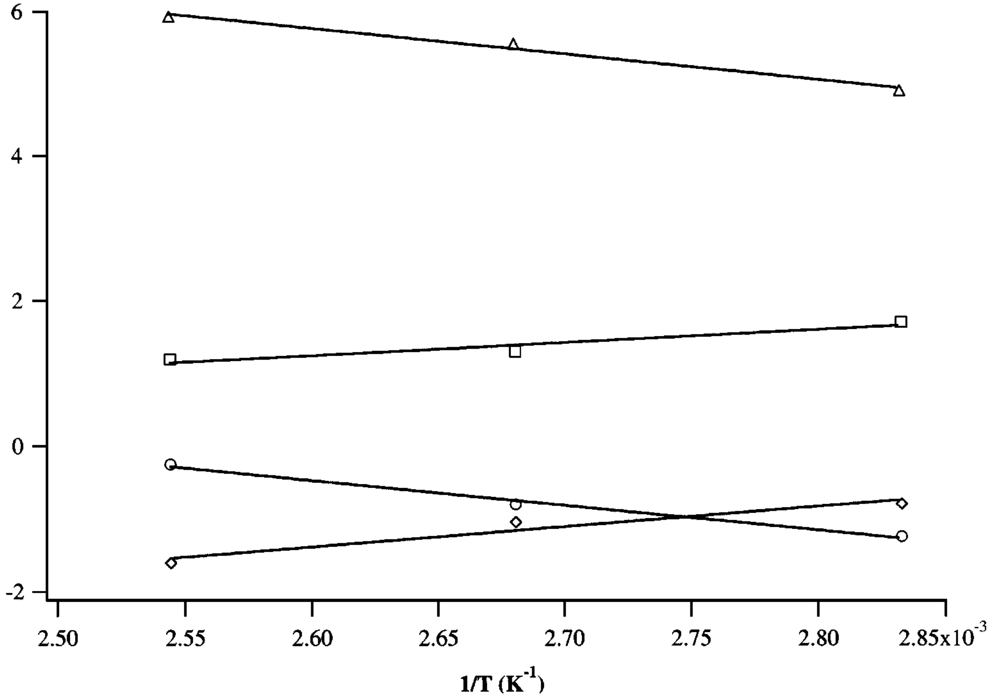


FIG. 11. Kinetic parameters from rate expression (Eq. [5]) for crotonaldehyde hydrogenation versus inverse temperature: ln $K_{\mathrm{H_2}}$ (◇), ln K_{CROALD} (□), ln k (△), and ln K^* (○). Units of k are μmole/s/g cat.

a peak associated with CO adsorption on Cu^{+1} sites reached a maximum after the 573 K pretreatment, and XRD patterns also provided evidence for a Cu^{+1} phase ($CuCrO_2$), although they also showed a continuous increase in the Cu^0 phase as reduction temperature increased. Consequently, Cu^{+1} sites correlate with activity and appear to be involved in the catalytic process, as proposed by previous workers, but the presence of Cu^0 sites is probably also required, thus providing one explanation for the maximum in activity that occurs as a function of reduction temperature. Selectivity to furfural alcohol ranged from 35–70%, significant deactivation occurred, and reaction orders on furfural and H_2 were near unity after correction for deactivation. A straightforward Langmuir–Hinshelwood model described these data well. In contrast to furfural, little deactivation was observed during crotonaldehyde hydrogenation, a lower apparent activation energy was observed, and the dependency on the organic reactant was near zero order, although that on H_2 was still near first order. IR spectra taken under reaction conditions indicated the presence of adsorbed crotonaldehyde, provided evidence for an unsaturate alkoxide intermediate, and detected no butyraldehyde. A simple Langmuir–Hinshelwood reaction sequence incorporating this intermediate gave an excellent fit of the data, along with physically meaningful values for enthalpies and entropies of adsorption that imply weak adsorption for both crotonaldehyde and hydrogen.

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