Catalysis Letters 60 (1999) 51–57

Furfural hydrogenation over carbon-supported copper

Rajeev S. Rao [a], R. Terry K. Baker [b] and M. Albert Vannice [c,*]

[a] Akzo-Nobel Chemicals, 1 Livingstone Avenue, Dobbs Ferry, NY 10522, USA
[b] Department of Chemistry, Northeastern University, Boston, MA 02115, USA
[c] Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802-4400, USA

Received 24 February 1999; accepted 20 April 1999

Furfural hydrogenation over copper dispersed on three forms of carbon – activated carbon, diamond and graphitized fibers – were studied. Only hydrogenation of the C=O bond to form either furfuryl alcohol or 2-methyl furan occurred at temperatures from 473 to 573 K. Reduction at 573 K gave the most active catalysts, all three catalysts had activation energies of 16 kcal/mol, and turnover frequencies were 0.018–0.032 s^{-1} based on the number of $Cu^0 + Cu^+$ sites, which were counted by N_2O adsorption at 363 K and CO adsorption at 300 K, respectively. The Cu/activated carbon catalyst showed no deactivation during 10 h on stream, in contrast to the other two catalysts. A simple Langmuir–Hinshelwood model invoking two types of sites was able to fit all kinetic data quite satisfactorily, thus it was consistent with the presence of both Cu^0 and Cu^+ sites.

Keywords: furfural hydrogenation, Cu/carbon catalysts, kinetics

1. Introduction

Furfural, C_4H_3OCHO, is an important compound in the fragrance industry, and the vapor-phase hydrogenation of furfural is commonly used to produce furfuryl alcohol. Depending on the catalyst employed, the vapor-phase hydrogenation of furfural can yield a variety of products, such as furfuryl alcohol, 2-methylfuran, furan, tetrahydrofuran, tetahydrofurfuryl alcohol and even ring-decomposition products, such as pentanols and pentanediols. For over five decades copper chromite has been utilized successfully as a catalyst for the selective hydrogenation of furfural to furfuryl alcohol. However, new environmental restrictions now prevent deactivated copper chromite catalysts from being used in landfill sites, and this has provided an incentive to develop new replacement Cu catalysts which contain no chromium. Consequently, copper has been dispersed on three different forms of carbon, namely activated carbon, synthetic diamond powder and graphitic fibers, and investigated as a catalyst in furfural hydrogenation. Surprisingly, despite decades of use, the number of fundamental kinetic studies of furfural hydrogenation over copper catalysts is very limited and, in addition, there is still considerable controversy over the type of copper active sites involved in this reaction. Therefore, these two issues were examined in some detail.

Recently, the hydrogenation of furfural was studied over a commercial, unpromoted copper chromite catalyst which was characterized by physical and chemical adsorption, X-ray diffraction, and IR spectra of adsorbed CO [1]. This investigation indicated that both Cu^+ and Cu^0 are integral for optimum catalytic performance. In this paper, furfural hydrogenation over these three types of Cu/C catalysts is examined and compared to the previous results. The effect of pretreatment temperature as well as the type of carbon support on the kinetic behavior was examined. Characterization of the pure supports as well as the Cu/C catalysts has been described elsewhere [2,3]. By associating specific activity, i.e., turnover frequencies, with the IR spectra of adsorbed CO, which can identify the surface oxidation states of Cu, additional information can be obtained about the nature of the surface sites involved in this reaction.

2. Experimental

The activated carbon used in this study (Norit Corp., A8933) had a BET surface area of 800 m^2/g. One portion, designated AC-HNO_3, was pretreated by boiling in 12 N nitric acid for 48 h to increase the concentration of oxygen-containing functional groups on the surface and its acidity. Subsequent to the boiling procedure, the sample was repeatedly washed in distilled water until a pH close to 7 was attained, dried in air in an oven at 393 K, and stored in a desiccator. The graphitic fibers (GF) were Thornel P25 pitch-based commercial fibers (Amoco Performance Products) with a BET surface area of 6 m^2/g, and they were manually cut and ground to a fine powder with a mortar and pestle prior to the impregnation step. The synthetic diamond powder (DM) (Alfa Aesar, designated “99.9%” metals basis) was used as received and had a BET surface area of 25 m^2/g. Elemental analyses for all the carbon samples are listed in table 1. Our analytical results indicate a somewhat higher metal content than specified. The 5% Cu/C catalysts were prepared by a wet impregnation (WI) technique involving copper nitrate (Aldrich, 99.999%) dissolved in distilled, deionized water in the following amounts for the three supports: AC-HNO_3:

---

[*] To whom correspondence should be addressed.

Table 1
Elementary analysis of carbons.

Element	Wt%		
	Activated carbon	Graphitized fibers	Diamond powder
Al	0.07	0.02	0.22
Ca	0.06	0.04	0.03
Fe	0.08	0.26	0.14
Mg	0.07	0.01	0.01
Na	0.11	0.26	0.15
Si	1.69	0.19	0.09
Ti	0.02	<0.01	0.03
C	83.52	95.01	97.68
H	1.28	0.05	0.08
N	0.71	0.05	0.18
O[a]	14.49	4.89	2.06

[a] Oxygen plus inorganic impurities.

1 cm^3/g; DM: 0.5 cm^3/g; GF-WI: 0.5 cm^3/g. This solution was added to the support, stirred and the catalysts were then dried in an oven for 24 h at 423 K and stored in a desiccator.

XRD spectra were obtained *ex situ* using a Rigaku Geigerflex diffractometer equipped with a Cu $K\alpha$ radiation source and a graphic monochromator. Each sample was reduced at either 573 or 673 K for 4 h in flowing H_2 and then passivated by exposure to a flowing mixture of 1% O_2 in He for 1 h prior to handling in air. Crystallite sizes were then determined using the Scherrer equation with Warren's correction for instrumental line broadening (0.12° at $2\theta = 38°$). These passivated samples were also examined in a Philips 420T transmission electron microscope which was operated at a voltage of 120 kV. The sample was directly dispersed on a 400 mesh carbon-coated copper grid.

The number of metallic Cu surface atoms (Cu_s^0) was determined by dissociative N_2O adsorption at 363 K according to the stoichiometry $N_2O_{(g)} + 2Cu_s^0 \rightarrow Cu_2O + N_{2(g)}$ [4,5]. The oxygen uptake was measured gravimetrically in a Perkin–Elmer TGS2 TGA apparatus after 10–20 mg catalyst was reduced *in situ* in accordance with one of the pretreatments described below. After reduction under flowing H_2 for 4 h at either 573 or 673 K, the sample was cooled to 363 K and purged for 30 min in pure He. The inlet gas was switched to a 50% N_2O/50% He mixture and the increase in weight was monitored. Once the weight reached a steady value, the N_2O was shut off and the sample was purged in pure He to remove any weakly adsorbed species. After the weight stabilized again, the difference in weight before and after N_2O exposure was calculated to determine the oxygen uptake.

Vapor-phase kinetic studies were performed at atmospheric pressure using a standard reactor system described elsewhere [1]. The number of surface Cu^+ sites was determined by CO chemisorption at 300 K [3]. Prior to each kinetic study, the catalyst was pretreated *in situ* at either 573 or 673 K for 4 h under 1 atm of hydrogen flowing at 40 sccm. A constant partial pressure of furfural was established in the feed by bubbling the H_2 carrier gas through a saturator containing pure furfural (Alfa, 99.99%), which was held in a constant temperature bath. It was verified that in the absence of the catalyst there was no reaction between the hydrogen and the furfural (F) over the temperature range used in this study. A gas chromatograph utilizing a column packed with Carbowax 20M on 80/100 Supelcoport was used for product analysis. The activity of each catalyst was measured at a furfural partial pressure of 5 Torr and a hydrogen partial pressure near 730 Torr between temperatures of 370 to 470 K. During the hydrogen partial pressure runs, the partial pressure of furfural was maintained at 5 Torr with He being used as the makeup gas, whereas during the furfural partial pressure studies, the partial pressure of hydrogen was maintained at 730 Torr. The H_2 (MG Ind., 99.999%) and He (MG Ind., 99.999%) were flowed through molecular sieve traps (Supelco) and Oxytraps (Alltech Associates) for additional purification. After a change in the reaction conditions such as temperature or the partial pressure of a reactant, 30 min were allowed to reach steady state before the product stream was sampled.

3. Results

XRD patterns are shown in figure 1 for the three catalysts after reduction at 573 K and passivation. In the case of the activated carbon sample, the distinct peak at 26.5° in figure 1(a) indicates that the support contains a significant fraction of graphitic crystallites. The peak at 43.5° for the Cu/DM sample in figure 1(b) is characteristic of diamond. In all three cases, the copper is present as a mixture of copper metal and cuprous oxide and no evidence

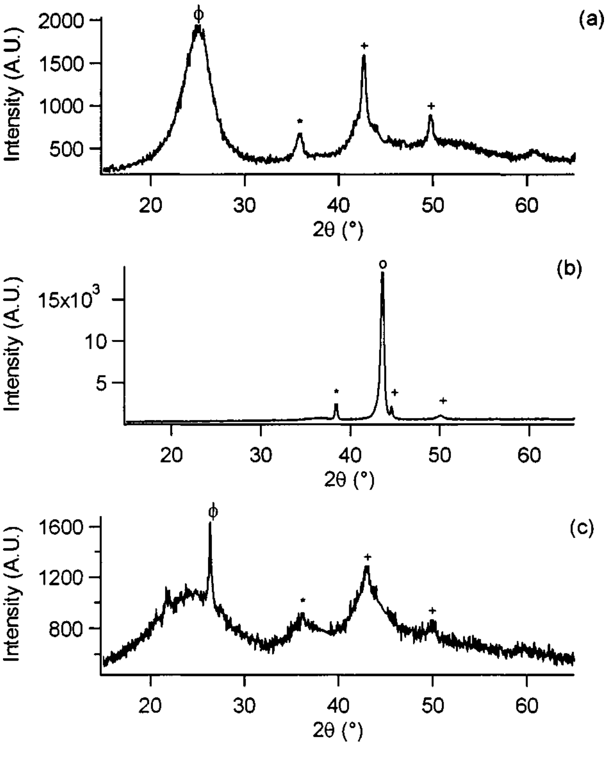

Figure 1. XRD patterns for (a) Cu/GF-WI, (b) Cu/DM and (c) Cu/AC-HNO_3 following reduction in H_2 at 573 K for 4 h. The following phases are denoted: Cu^0 (+), Cu_2O (∗), diamond (O), graphite (ϕ).

Table 2
Comparison of copper crystallite sizes calculated from various methods following reduction at 573 K.

	CO uptake[a] (μmol/g)	"O" uptake (μmol/g)	d_{ad}[b] (nm)	d_{XRD} (nm)	TEM	
					d_{sur} (nm)	d_{vol} (nm)
5.1% Cu/DM	35	25	9	13	20	23
4.8% Cu/AC-HNO$_3$	10	56	7	5	13	13
5.1% Cu/GF-WI	6	5[a]	120	20	78	88

[a] From [8].

[b] Based on combined "O" and CO adsorption (i.e., $Cu^0 + Cu^+$).

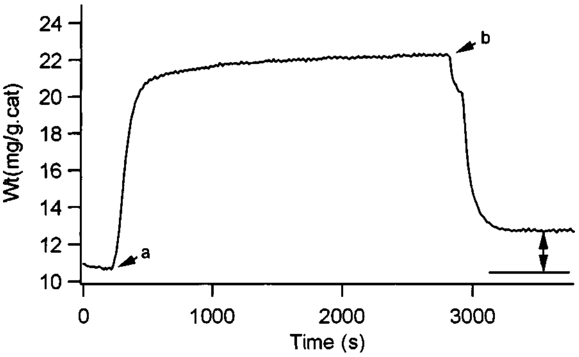

Figure 2. Typical N_2O adsorption experiment for Cu/AC-HNO$_3$ reduced at 573 K for 4 h: (a) 50% N_2O/50% He started and (b) He purge started.

Table 3
Dependence of activity of Cu/C catalysts on the reduction temperature. $T_{rxn} = 498$ K, $P_{H_2} = 730$ Torr, $P_F = 5$ Torr.

	Activity (μmol/(s g))		TOF (s^{-1}), $T_{red} = 573$ K	
	$T_{red} = 673$ K	$T_{red} = 573$ K	a	b
5.1% Cu/DM	0.9	1.6	0.018	0.030
4.8% Cu/AC-HNO$_3$	0.6	1.6	0.013	0.022
5.1% Cu/GF-WI	0	0.23	0.032	0.023

[a] Based on surface $Cu^0 + Cu^+$ sites.

[b] Based on spherical particles with d_{sur} from TEM.

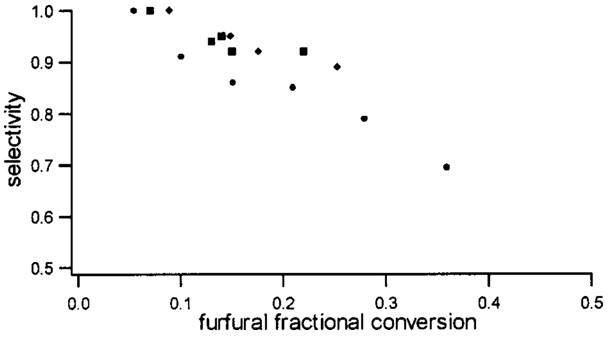

Figure 3. Selectivity to furfurol as a function of conversion during furfural hydrogenation over Cu/C catalysts: 4.8% Cu/AC-HNO$_3$ (●), 5.1% Cu/DM (◆) and 5.1% Cu/GF-WI (■); $P_{FRFAL} = 5$ Torr, $P_{H_2} = 730$ Torr, $T = 370$–470 K.

exists for the presence of cupric oxide in the XRD patterns after reduction at 573 K. Crystallite sizes for all three catalysts were calculated from these XRD spectra, as well as from the TEM data. Weight changes associated with a typical N_2O adsorption run are shown in figure 2 for a Cu/AC-HNO$_3$ sample reduced at 573 K, and other similar uptake isotherms are shown elsewhere [6]. Uptakes of O atoms and chemisorbed CO are provided in table 2 along with crystallite sizes calculated from the sum of the "O" uptake and the irreversible CO adsorption uptakes according to the equation $d_{ad} = 1.15/D$ [4,5,7,8]. Crystallite sizes determined from XRD as well as TEM particle size distributions are also listed in table 2. Particle sizes are smallest in the Cu/AC-HNO$_3$ system, thus indicating the highest copper dispersion (Cu_{surf}/Cu_{total}) for this catalyst.

Table 3 shows the effect of reduction temperature on the activity of these Cu/C catalysts. A combination of "O" adsorption via N_2O decomposition and CO chemisorption was used to calculate the total number of exposed surface copper atoms assuming a stoichiometry of $O : Cu^0 = 1 : 2$ and $CO : Cu^+ = 1 : 1$ [8], hence the turnover frequency (TOF) can be based on this value. The CO uptakes used here from table 2 have been reported previously [8]. It is evident that in the case of all three catalysts, a pretreatment at 573 K in hydrogen yielded the catalyst with the higher activity; therefore, unless mentioned otherwise, all reported kinetic data were obtained after this pretreatment. In accordance with reports for other copper-containing catalysts [1,9–11], no products corresponding to the hydrogenation of the C=C bond were detected in this study and the only products were furfuryl alcohol and 2-methylfuran. Figure 3 represents the selectivity to furfural alcohol (defined here as (mole furfurol)/(mole furfurol + mole 2-methylfuran)) as a function of the furfural conversion using data obtained during the Arrhenius runs, i.e., temperature also varied. Selectivity to furfurol at conversions below 0.1 was close to unity for all three catalysts; however, selectivity decreased with increasing conversion and temperature, although at different rates. With Cu/AC-HNO$_3$, the selectivity fell to 70% at a conversion of 36%. Arrhenius plots for furfural hydrogenation on each catalyst after reduction at 573 K, shown in figure 4, give nearly identical apparent activation energies of 15.9 ± 2.0, 15.9 ± 2.0 and 15.6 ± 2.0 kcal/mol for the Cu/GF-IW, Cu/DM and the Cu/AC-HNO$_3$ catalysts, respectively, where the uncertainty is represented by 95% confidence limits.

Catalyst deactivation has been observed in all previous investigations of furfural hydrogenation [1,9–11], and various causes have been suggested, such as formation of coke on the catalyst surface, poisoning of the catalyst by either a reaction intermediate or a by-product, sintering of the

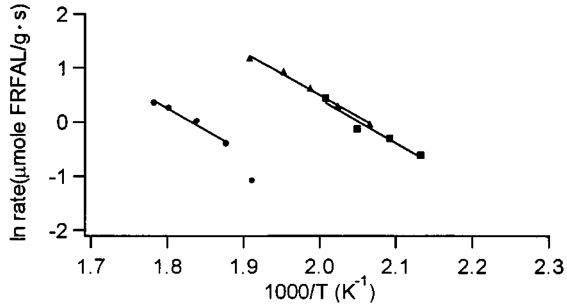

Figure 4. Arrhenius plots for furfural hydrogenation over Cu/C catalysts: $T_{red} = 573$ K, $P_F = 5$ Torr, $P_{H_2} = 730$ Torr; 5.1% Cu/GF-WI (●), 5.1% Cu/DM (■) and 4.8% Cu/AC-HNO$_3$ (▲).

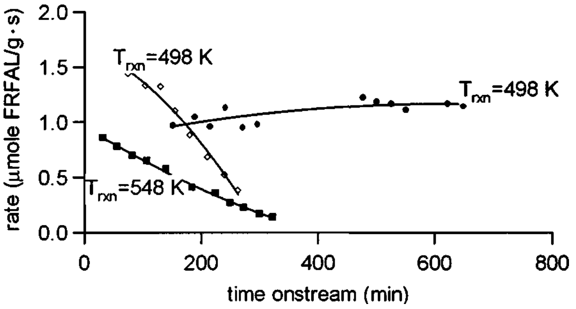

Figure 5. Activity maintenance of Cu/C catalysts reduced at 573 K, $P_F =$ 5 Torr, balance H$_2$: 4.8% Cu/AC-HNO$_3$ (●), 5.1% Cu/DM (◊) and 5.1% Cu/GF-WI (■).

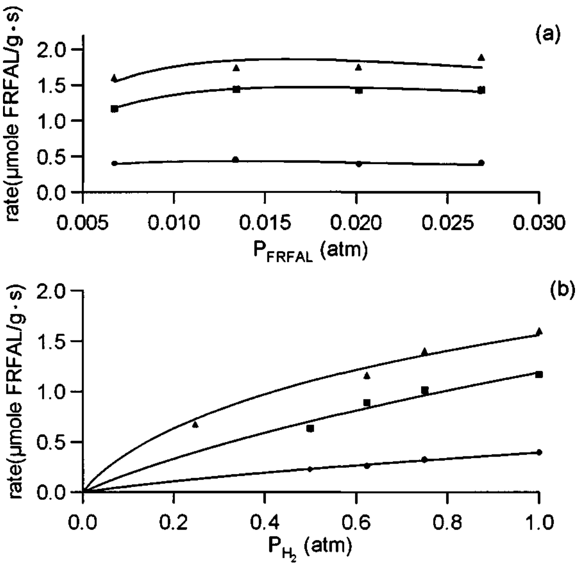

Figure 6. Rate vs. partial pressure of (a) furfural and (b) hydrogen for furfural hydrogenation over 5.1% Cu/DM at 498 K (▲), 4.8% Cu/AC-HNO$_3$ at 498 K (■) and 5.1% Cu/GF-WI at 513 K (●). Solid lines represent fit by equation (6).

catalyst under reaction conditions, or a change in the oxidation state of the copper during the reaction. Activity maintenance profiles for all the three catalysts are shown in figure 5. Because of its lower activity, this run with Cu/GF-IW was conducted at a higher temperature of 548 K rather than 498 K. Although both Cu/DM and Cu/GF-WI catalysts exhibit significant deactivation, the Cu/AC-HNO$_3$ catalyst with the highest dispersion did not exhibit any activity loss during a 10 h period on stream.

The partial pressure dependence of the rate of furfural (FRFAL) disappearance on both P_{FRFAL} and P_{H_2} was investigated. Due to the problems associated with catalyst deactivation, the partial pressure data were more limited than those obtained in a parallel study of crotonaldehyde hydrogenation [8]. The procedure for correcting the measured rates for deactivation has been described previously [1]. The rate dependences on P_{H_2} and P_{FRFAL} are shown in figure 6 for Cu/GF-WI at 513 K, Cu/AC-HNO$_3$ at 498 K, and Cu/DM at 498 K. The reaction order in H$_2$ was close to 0.8 for Cu/GF-WI and Cu/AC-HNO$_3$ and around 0.6 for Cu/GF, while the reaction order in furfural was about 0.1 for Cu/DM and Cu/AC-HNO$_3$ and zero for Cu/GF-WI.

4. Discussion

Furfural can be quantitatively reduced to furfuryl alcohol over Pt oxide by the addition of one molecular equivalent of hydrogen [12], and upon further hydrogenation, the ring becomes saturated to yield tetrahydrofurfuryl alcohol together with ring-opening products. Ni-based catalysts lead to hydrogenation of the furan ring and the accompanying products [11]. In the present study, the only products detected were furfuryl alcohol and 2-methylfuran, which is consistent with previous results with copper-based catalysts [1,9–11], which have been the most widely used to achieve selective hydrogenation of the C=O bond while leaving the C=C bonds in the furan nucleus intact. Bremner and Keeys made an exhaustive investigation of furfural hydrogenation 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 at higher temperatures around 523 K [9]. Seo and Chon reported that furfuryl alcohol was the primary product obtained over a variety of copper-based catalysts between 473 and 573 K [11], but they did not mention any significant change in the selectivity with temperature. Borts and co-workers investigated the kinetics of furfural hydrogenation over a commercial copper–chromium oxide catalyst around 400 K and reported that furfuryl alcohol was the main product, with up to 3 wt% 2-methylfuran being formed [10].

In the present investigation, Cu/C catalysts reduced at 573 K displayed a higher furfural hydrogenation activity than those reduced at 673 K. In previous studies, copper chromite catalysts reduced at 573 K had also displayed the highest specific activity for furfural and crotonaldehyde hydrogenation [1], acetone hydrogenation to isopropanol [13], and reductive alkylation of aniline with acetone [14]. Therefore, it is likely that not only the same states of copper represent the active phase in all these reactions, but they also reach optimal concentrations after this particular pretreatment. A comparison of the XRD patterns in figure 1 indicates that after reduction at 573 K, the copper exists in a mixture of Cu^0 and Cu^+ oxidation states. The broad peak at 36.5° is assigned to cuprous oxide, whereas the peaks around 43.5 and 50.5° are associated with metallic copper. Calculation of crystallite size from the principal Cu^0 peak indicates that the copper crystallite size (and hence the dispersions) are dependent on the type of support used. The smallest crystallites are formed in the Cu/AC-HNO_3 catalyst and are on the order of 5 nm in diameter. Consistent trends are exhibited in the N_2O adsorption and the TEM data, as shown in table 2. The presence of a maximum in the Cu^+ concentration after reduction at 573 K, as shown by both the XRD data as well as the FTIR spectra for adsorbed CO on these Cu/C catalysts [3,8], indicates that Cu^+ is involved in the catalytic cycle, in agreement with previous proposals [1,15–18]. However, activation of molecular H_2 is more likely to occur on a metallic Cu surface; therefore, the presence of both Cu^+ and Cu^0 sites is required for optimal performance, although a surface consisting of only Cu^0 can display some activity because the aldehyde can also be adsorbed and activated on a Cu^0 surface [1,8]. This statement is supported by the fact that a sample of Cu/GF-WI which was used in a reaction without first being reduced in H_2 displayed no activity initially. In this regard, the commonly held belief that Cu^0 is the active site for such reactions is perhaps not without some merit, although a surface consisting of only Cu^0 is not optimal.

After reduction at 573 K, TOFs for furfural hydrogenation on all three Cu/C catalysts are comparable, with an average value and standard deviation of $0.021 \pm 0.006\ s^{-1}$ based on the total number of surface Cu atoms (Cu^0+Cu^+). This is strong evidence that these carbon supports do not play a significant role in the reaction, which is confined to the copper surface and appears to be structure insensitive. Values of the Weisz parameter [19] ranged from 1.8×10^{-3} for Cu/GF-WI to 3.3×10^{-6} for Cu/DM, verifying the absence of any significant mass transfer effects. Under similar reaction conditions, a TOF of $0.03\ s^{-1}$ can be calculated for copper chromite [1], which is quite similar to the values obtained here. This again supports both the conclusion that copper is the principal catalytically active component in all these catalysts and the accepted belief that chromium acts primarily as a stabilizing agent rather than as a participant in copper chromite catalysts. In an effort to determine the relative importance of the Cu^0 and the Cu^+ sites, TOFs are plotted in figure 7 as a function of the fraction of the surface copper atoms present as Cu^0 for these three Cu/C catalysts as well as copper chromite (described in [1]). A trend common to all catalysts is that the TOF decreases as the Cu^0 surface fraction approaches unity, which is similar to that observed in a parallel study of crotonaldehyde hydrogenation in which TOFs on surfaces comprised only of Cu^0 were also much smaller than TOFs on a surface with a Cu^0 fraction close to 0.5 [8]. However, in the latter investigation when the fraction of Cu^0 sites fell below 0.5, the TOF decreased dramatically and fell to zero with catalysts containing no Cu^0 [8]. The observation of a TOF maximum for crotonaldehyde on a surface comprised of roughly equal amounts of Cu^0 and Cu^+ is very strong evidence that the optimal catalyst for these types of reactions requires both types of sites.

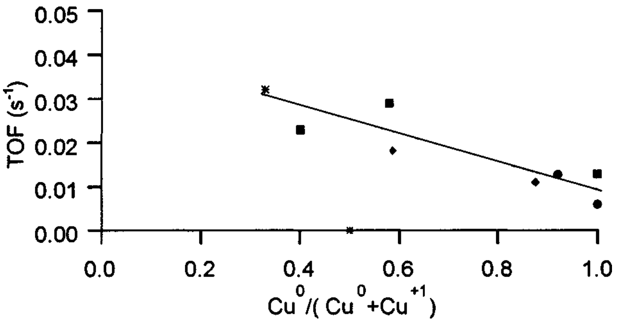

Figure 7. Dependence of the TOF on the fraction of Cu^0 surface sites: $T_{rxn} = 498$ K, 5 Torr furfural, balance H_2: 4.8% Cu/AC-HNO_3 (●), 5.1% Cu/DM (♦) and 5.1% Cu/GF-WI (∗), and Cu chromite (■) (from [1]).

Selectivity to furfuryl alcohol was very high at low conversions but decreased as conversion (and temperature) increased. Different selectivities have been reported by different authors under different reaction conditions, and this is likely a consequence of catalyst composition as well as the reaction conditions. Borts and coworkers reported a maximum selectivity to 2-methylfuran of 3% at 400 K [10], and Seo and Chon also reported a selectivity to furfuryl alcohol greater than 98% with copper–chromium oxide, CuO/silica, Pd–CuY and Ni–CuY between 573 and 673 K at respective fractional conversions of 0.53, 0.17, 0.58 and 0.10 [11]. Bremner and Keeys found that the yield of 2-methylfuran was greatest between 473 and 573 K on copper/alumina and copper chromite, and a maximum yield of 66% furfuryl alcohol was obtained around 470 K [9].

The apparent activation energy of 16 kcal/mol for these three carbon-supported Cu catalysts is higher than the value of 12 kcal/mol obtained for copper chromite [1], and is somewhat lower than the value of 21 kcal/mol reported by Borts and coworkers for their copper chromite catalyst [10]. The essentially identical activation energies among these three Cu/C catalysts implies that the mechanism of furfural hydrogenation may be similar on all these catalysts.

A sample of deactivated Cu/DM exhibited an XRD pattern consisting of only Cu^0, as compared to a freshly reduced catalyst which contained both Cu_2O and Cu metal. This indicates that a gradual transformation of cuprous oxide to metallic copper during the course of the reaction may be at least a partial cause for the observed deactivation. The question then arises as to why no deactivation was observed with the Cu/AC-HNO_3 catalyst. One possible explanation could be related to the higher concentration of oxygen-containing surface groups on the AC-HNO_3 support compared to the DM and GF supports. The presence of these oxygen-containing groups on the surface may stabilize the Cu nitrate precursor and make it kinetically and thermodynamically less favorable to reduce to metallic copper, and the smaller Cu particles in the Cu/AC catalyst should favor this interaction. Alternatively, if catalyst poisoning

Table 4

Parameters from rate expression for furfural hydrogenation on Cu/C catalysts (see figure 6). Model 1 is a Langmuir–Hinshelwood (L-H) expression assuming 1 type of site (equation (1)), and model 2 is a L-H expression assuming 2 types of sites (equation (6)).

Catalyst	T_{rxn} (K)	k' (μmol/(s g))		K_{H_2} (atm^{-1})		K_F (atm^{-1})	
		Model 1	Model 2	Model 1	Model 2	Model 1	Model 2
5.1% Cu/GF-WI	513	362	6000	0.18	0.078	130	9300
4.8% Cu/AC-HNO$_3$	498	941	1400	0.16	0.063	93	540
5.1% Cu/DM	498	5081	4400	120	0.67	270	690

occurred due to adsorption of either a particular intermediate or a by-product, it may be either that the different adsorption properties of the activated carbon may make the Cu/AC-HNO$_3$ catalyst less susceptible to deactivation by poisoning or that the small Cu particles have different adsorption behavior compared to large crystallites. None of the other possible causes for deactivation discussed in the previous section can be ruled out at this time and, in fact, Bremner and Keeys found that the catalytic activity could be regenerated by removal of poisons or other carbonaceous residue (coke) blocking the active sites [9].

A simple Langmuir–Hinshelwood (L-H) model was proposed previously for furfural hydrogenation over copper chromite which assumed one type of adsorption site and a surface reaction between an adsorbed H atom and a partially hydrogened furfural species as the rate-determining step [1]. The derived rate equation

$$r = k'P_{H_2}P_F/\left(1 + K_{H_2}^{1/2}P_{H_2}^{1/2} + K_FP_F\right)^2 \qquad (1)$$

is able to fit the results in figure 6 and provides the parameters listed in table 4 [6]. Alternatively, a similar L-H model invoking two types of sites, i.e., primarily one for dissociative adsorption of H_2 (Cu^0) and the other primarily for furfural adsorption (Cu$^+$, for example), can be proposed as shown below:

$$H_2 + 2S_1 \overset{K_{H_2}}{\rightleftharpoons} 2H\text{–}S_1 \qquad (2)$$

$$F + S_2 \overset{K_F}{\rightleftharpoons} F\text{–}S_2 \qquad (3)$$

$$F\text{–}S_2 + H\text{–}S_1 \overset{K}{\rightleftharpoons} S_2\text{–}F{\cdot}H\text{–}S_1 \qquad (4)$$

$$S_2\text{–}F{\cdot}H\text{–}S_1 + H\text{–}S_1 \xrightarrow{k} \text{furfurol} + S_2 + 2S_1 \qquad (5)$$

Assuming H atoms are the principal species on S_1 sites and furfural is the predominant species on S_2 sites, the following rate expression can be readily derived:

$$r = k'P_FP_{H_2}/\left(1 + K_{H_2}^{1/2}P_{H_2}^{1/2}\right)^2(1 + K_FP_F), \qquad (6)$$

where $k' = kKK_FK_{H_2}$.

This equation also fits the kinetic data very well, as shown in figure 6, and the corresponding parameters are also listed in table 4. Although one cannot choose between the two models based on the limited data here, the two-site model is certainly consistent and perhaps more descriptive of the roles proposed for Cu^0 and Cu$^+$ sites. With the latter model, two of the K_{H_2} values are very similar and two of the K_F values are quite similar, and in each case an order of magnitude variation exists in each set of values. The noticeably higher K_F and K_{H_2} values could reflect significant differences in Cu^0 crystallite size or the Cu^0/Cu$^+$ ratios, but these variations may well be due to the presence of deactivation with two of these catalysts even though rates were continually normalized in an effort to correct for deactivation effects. Further studies will be required to clarify this.

5. Summary

Furfural hydrogenation was studied over three carbon-supported Cu catalysts, namely Cu/activated carbon, Cu/diamond and Cu/graphitic fibers, which represent possible replacements for current commercial copper chromite catalysts. Two different reduction temperatures of 573 and 673 K were used to pretreat the catalysts. Similar to other copper-containing catalysts, only products corresponding to hydrogenation of the C=O bond were detected, and the selectivity to furfuryl alcohol was comparable to that obtained with commercial copper chromite catalysts. All three catalysts displayed a higher activity after reduction in hydrogen at 573 K rather than 673 K. After pretreatment at the former temperature for 4 h, the copper existed as a mixture of Cu^0 and Cu$^+$ oxidation states, indicating that both types of sites may be involved in the catalytic cycle. Arrhenius runs yielded apparent activation energies close to 16 kcal/mol for all the three catalysts, suggesting a similar reaction mechanism may exist on all of them. Orders in furfural were close to zero on these catalysts while those in hydrogen fell between 0.6 and 0.8. A comparison of TOFs based on total Cu surface sites (Cu$^0+$Cu$^+$) indicated that the catalytic activity was independent of the support and the TOFs on all three catalysts were very similar. For all catalysts, including copper chromite, the TOF decreased steadily as the fraction of surface Cu$^+$ sites decreased from 0.3 to zero (i.e., 100% Cu^0). Simple Langmuir–Hinshelwood models involving a bimolecular surface reaction as the rate-determining step described these data well and a two-site model, which could represent Cu^0 and Cu$^+$ sites, is shown here to provide very satisfactory fits of the data for all three catalysts. Similar to copper-based catalysts in previous reports, the Cu/DM and the Cu/GF-WI catalysts exhibited deactivation during the course of the reaction but, in contrast, the Cu/AC-HNO$_3$ catalyst displayed no deactivation whatsoever. The superior activity maintenance displayed by the Cu/AC-HNO$_3$

catalyst coupled with its high selectivity to furfural alcohol indicates that it is a viable candidate to replace copper chromite.

Acknowledgement

Support for this study was provided by the National Science Foundation under Grant CTS-9415335.

References

[1] R. Rao, A. Dandekar, R.T.K. Baker and M.A. Vannice, J. Catal. 171 (1997) 406.

[2] A.B. Dandekar, R.T.K. Baker and M.A. Vannice, Carbon 36 (1998) 1821.

[3] A.B. Dandekar and M.A. Vannice, J. Catal. 178 (1998) 621.

[4] R.M. Dell, F.S. Stone and P.F. Tiley, Trans. Faraday Soc. 49 (1953) 195.

[5] J.J.F. Scholten and J.A. Konvalinka, Trans. Faraday Soc. 65 (1969) 2465.

[6] R. Rao, Ph.D. thesis, The Pennsylvania State University (1998).

[7] W.E. Garner, F.S. Stone and P.F. Tiley, Proc. Roy. Soc. London 211 (1952) 472.

[8] A. Dandekar, R.T.K. Baker and M.A. Vannice, J. Catal., in press.

[9] J.G.M. Bremner and R.K.F. Keeys, J. Chem. Soc. (1947) 1068.

[10] M.S. Borts, N.D. Gil'chenok, V.M. Ignate'ev and G.S. Gurevich, Zh. Prikl. Khim. 59 (1986) 126.

[11] G. Seo and H. Chon, J. Catal. 67 (1981) 424.

[12] A. Kaufman and J.C. Adams, J. Am. Chem. Soc. 45 (1923) 3029.

[13] O.V. Makarova, T.M. Yu'reva, G.N. Kustova, A.V. Ziborov, L.M. Plyasova, T.P. Miyukova, L.P. Davydova and V.I. Zaikovskii, Kinet. Catal. 34 (1993) 683.

[14] R.B.C. Pillai, Catal. Lett. 26 (1994) 365.

[15] S. Mehta, G.W. Simmons, K. Klier and R.G. Herman, J. Catal. 57 (1979) 339.

[16] J.R. Monnier, M.J. Hanrahan and G. Apai, J. Catal. 92 (1985) 119.

[17] R. Hubaut, M. Daage and J.P. Bonnelle, Appl. Catal. 22 (1986) 231.

[18] O.V. Makarova, T.M. Yur'eva, G.N. Kustova, A.V. Ziborov, L.M. Plyasova, T.P. Minyukova, L.P. Davydova and V.I. Zaikovskii, Kinet. Katal. 34 (1993) 683.

[19] P.B. Weisz, Z. Phys. Chem. 11 (1957) 1.