Hydrogenation of Furfural over Copper-Containing Catalysts

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Furfuryl alcohol is the main product of the vapor-phase hydrogenation of furfural over copper-containing catalysts such as copper–chromium oxide and palladium-loaded CuY. The amount of furan adsorbed on CuY increases with increasing degree of Cu(II) ion exchange. The evidence of interaction between Cu(II) ion and the furan ring is demonstrated in the ir and EPR spectra. High selectivity to furfuryl alcohol and the absence of tetrahydrofurfuryl alcohol formation over copper-containing catalysts is interpreted in terms of the interaction between Cu(II) ion and the furan ring of furfural preventing the furan ring from being hydrogenated. This interaction also explains the enhancement of conversion to furfuryl alcohol on Pd–CuY. Here the active site for the selective formation of furfuryl alcohol is the Cu(II) ion interacting with the furan ring while Pd activating the hydrogen.

INTRODUCTION

In the gas-phase hydrogenation of furfural the products that can be produced are furfuryl alcohol, 2-methylfuran, and tetrahydrofurfuryl alcohol. Resinous material and ring-decomposed products are also found in the liquid-phase hydrogenation reaction (*1*). For a copper–chromium oxide catalyst, furfuryl alcohol is obtained, while a Raney nickel catalyst produces tetrahydrofurfuryl alcohol (*2*). Although copper–chromium oxide is widely used as a hydrogenation catalyst, little is known about its selective hydrogenation ability for the aldehyde group.

Zeolites are often used as a matrix for the study of active sites in catalytic reactions. Catalytically active metal ions can be introduced into the zeolite, with the number of ions introduced controlled by ion-exchange techniques. It is possible to prepare zeolite catalysts containing both metal and metal ions.

Our studies with Pd–CuY and Ni–CuY zeolite catalysts, containing both Cu(II) ion and palladium or nickel metal, have indicated that they have high selectivity for furfuryl alcohol. The main purpose of the present investigation is to study the role of copper in these catalysts for the selective formation of furfuryl alcohol in the furfural hydrogenation reaction.

METHODS

Copper–chromium oxide catalysts were prepared by coprecipitating solutions of CrO_3 and $Cu(NO_3)_2$ in appropriate ratios in aqueous NH_3 at pH 6.5. The samples were carefully calcined in air at 280°C. Copper–barium–chromium oxide was precipitated from a solution of CrO_3, $Cu(NO_3)_2$, and $Ba(NO_3)_2$.

Silica-supported metal oxide catalysts were prepared by impregnation of cylindrical silica from Davison (surface area, 300 m^2g^{-1}). The amount impregnated as cupric oxide was 10%.

The Linde synthetic zeolite NaY (Lot No. 968050009) was used as the starting material for zeolite catalysts. Sodium ions in the zeolite were exchanged for nickel, copper, chromium, and cobalt ions in their respective nitrate solutions; for palladium ion in tetraammine palladium ion solution; and for ammonium ion in ammonium chloride solution. The degree of exchange was expressed as the percentage of original Na^+

ions replaced by exchanged ions and designated by n as in $Cu(n)Y$. Palladium and nickel ion-exchanged samples were reduced with hydrogen for 2 hr at 300°C and designated as Pd–Y and Ni–Y. The reagents used in preparation of catalyst and in ion exchange of the zeolite were Mallinckrodt analytical grade; cupric nitrate was Fisher Certified Reagent and nickel nitrate was E. Merck GR. Furfural was distilled in a nitrogen atmosphere and kept in ampules and stored in the dark. The gases used in the experiments, hydrogen, helium, and nitrogen were Matheson ultrahigh pure grade.

The catalytic activity for furfural hydrogenation of various catalysts was measured in a fixed-bed stainless-steel tubular integral reactor. The hydrogenation reaction was studied between 160 and 350°C with the hydrogen flow rate of 30–850 ml min^{-1} and the furfural feed rate of 2.0–8.5 ml hr^{-1}. The reaction products were collected at 10-min intervals and were analyzed by a gas chromatograph using a 10-ft column packed with 15% Carbowax 20 M on Chromosorb w(60/80) previously impregnated with 2% KOH.

Surface area was obtained by conventional BET techniques at liquid-nitrogen temperature. Measurements of furan and tetrahydrofuran adsorption were made at 25°C in a flowing nitrogen atmosphere using a Perkin–Elmer TGS-2 system. The zeolite catalysts were pretreated at 200°C for 1 hr prior to the adsorption measurements. X-Ray diffraction patterns of copper oxide (10 wt%) on silica catalysts were recorded by a Norelco spectrometer ($CuK\alpha$, 30 kV, 20 mA). The EPR spectra were recorded at X-band frequencies on a Varian E-4 spectrometer at room temperature and occasionally at liquid nitrogen temperature. The DPPH standard was used for the determination of g factor. The EPR sample tube was directly connected to a portable vacuum and gas-handling system. The electronic reflectance spectra were obtained using a Shimadzu MPS-5000 spectrometer

and the infrared spectra with a Perkin–Elmer IR-267 spectrometer using Nujol mulling techniques.

RESULTS

The major hydrogenation products obtained with the various catalysts investigated are shown in Table 1. Table 2 shows examples of product distributions of the furfuryl hydrogenation reaction over various catalysts. Furfuryl alcohol was mainly produced on copper oxide group catalysts. On these catalysts, especially on copper–chromium oxide, small amounts (<2%) of methylfuran and water were formed together with furfuryl alcohol. Pd- or Ni-loaded CuY catalysts (Pd–CuY and Ni–CuY) were also highly selective toward furfuryl alcohol formation. With a nickel oxide catalyst, the product was tetrahydrofurfuryl alcohol. Upon increasing the reaction temperature beyond 250°C, gaseous products such as methane were mainly produced. Pd–HY and Pd–LaY catalysts were very selective toward formation of furan. No significant amount of hydrogenation

TABLE 1

Major Products of Furfural Hydrogenation for Various Catalysts[a]

Catalysts	Products
Copper–chromium oxide Copper–barium–chromium oxide Copper oxide/silica or alumina Copper–chromium oxide/silica Copper–cobalt oxide/silica Pd–CuY	Furfuryl alcohol
NiO/silica or alumina	Tetrahydrofurfuryl alcohol (above 250°C decomposed products were produced)
Pd–HY Pd–LaY	Furan
Pd–Y Pd/silica	Methylfuran, H_2O Furfuryl alcohol
Chromium oxide/silica Cobalt oxide/silica HY, CrY, NiY, CuY	No significant amount of product formation

[a] Reaction conditions: Temperature, 160–350°C; feed rate of furfural, 2.0–8.5 ml hr^{-1}; H_2 flow rate, 30–850 ml min^{-1}; catalyst weight, 0.30 g.

TABLE 2

Some Typical Examples of Product Selectivity of Furfural Hydrogenation Reaction

Catalyst	Reaction temperature (°C)	Percentage conversion	Product selectivity (vol. %)					
			Furfuryl alcohol	Methyl furan	Water	Penta-diol	Tetrahydro-furfuryl alcohol	Furan
Copper–chromium oxide	260	53	98	1	1			
CuO(10%)/silica	200	17	>99					
Pd–CuY	300	58	>99					
Ni–CuY	300	10	>99					
NiO(10%)/silica	200	15					>99	
Pd–Y	300	17	40	12	12	36		
Pd–LaY	350	38						>99
Pd–HY	350	50						>99

product of furfural was observed over silica-supported cobalt or chromium oxide and cation-exchanged zeolite catalysts.

In most cases the catalysts were observed to deactivate over the course of a run. At temperatures below 200°C and above 350°C, the activity decreased to 50% of the initial rates in about 2 hr. Minimum deactivation was observed between 260 and 300°C. Copper oxide catalysts prepared by coimpregnating cobalt oxide or chromium oxide showed much smaller deactivation rates. The used, deactivated copper oxide group catalysts could be regenerated to 95% of their initial activity by heating in an air stream at 260°C for 3 hr.

Figure 1 shows X-ray diffraction patterns of fresh and used catalysts of copper oxide supported on silica. Copper oxide which was present as cupric oxide on a fresh catalyst (A) was reduced to metallic copper (B) after using the catalyst at 350°C. Thus the deactivation of copper oxide catalysts above 350°C is due primarily to the reduction of copper oxide to metallic copper. The deactivation of the catalyst observed below 200°C is not due to this reduction of copper oxide since no difference was observed in the X-ray diffraction patterns of fresh and used copper oxide/silica catalysts. The formation of coke on the surface can be sug-

gested as a possible cause of the deactivation of the catalyst below 200°C.

The amounts of furan and tetrahydrofuran adsorbed on various zeolites are shown in Table 3. The amount of furan adsorbed on CuY increased with increasing degree of copper ion exchange ranging from 0.19 g furan/g zeolite on Cu(15)Y to 0.23 g furan/g zeolite on Cu(42)Y. There was no change, however, in the amount of tetrahy-
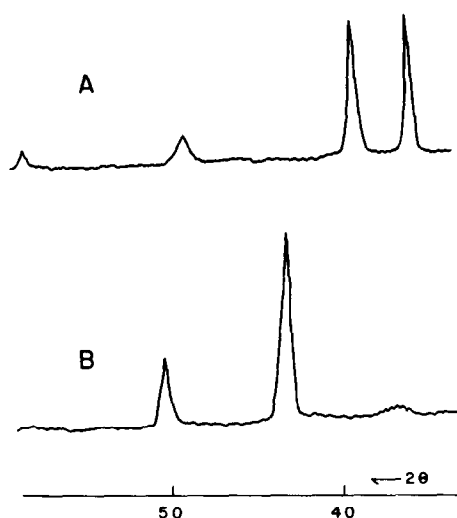

FIG. 1. X-Ray diffraction patterns of CuO/silica. (A) Activated in air at 300°C for 2 hr; (B) after furfural hydrogenation reaction at 350°C for 4 hr.

TABLE 3

The Amount of Furan and Tetrahydrofuran
Adsorbed on Various Zeolite Catalysts at 25°C

Zeolite	Amount adsorbed[a] (g adsorbent/g zeolite[b])	
	Furan	Tetrahydrofuran
NaY	0.18	—
H(25)Y	0.17	—
Cu(15)Y	0.19	0.170
Cu(29)Y	0.22	0.165
Cu(42)Y	0.23	0.165

[a] Precision ±0.003 g adsorbent/g zeolite.

[b] Dehydrated base.

drofuran adsorbed on CuY with increasing degree of Cu(II) ion exchange. The significance of this will be discussed later.

Figure 2B shows the infrared spectrum of adsorbed furfural on Cu(15)Y at room temperature. The absorption bands, at 3140, 1570, 1390, and 880 cm^{-1} are identified as those of liquid furfural. The absorption band of furfural at 2840, 2800, and 1460 cm^{-1} were not observable because of the use of Nujol mulling technique.

The absorption band at 1570 cm^{-1}, representing conjugated double-bond stretching, was relatively strong. When furfural was adsorbed at 150°C, the 1570-cm^{-1} band was shifted to lower frequency by 15 cm^{-1} and

weakened. This shift was also observed when furfural was adsorbed at 150°C on Pd–CuY and Ni–CuY, but not on HY, CrY, NiY, and NaY. The shift was also observed when furan was adsorbed at room temperature on CuY. No shift was observed when CuY was reduced with hydrogen at 300°C.

Also with the adsorption of furan the electronic spectra of CuY showed the absorption bands at 480 and 580 nm.

When CuY was evacuated at 200°C for 3 hr, the EPR spectrum shown in Fig. 3A was obtained. Spectra B and C were obtained when furan was adsorbed on CuY. With the adsorption of furan on CuY, a new high-field band appeared and increased with increasing amount of furan adsorbed, while the original signal of Cu(II) decreased. This narrow band had a width of 8 G and a g factor of 2.002. No hyperfine structure was observed at liguid-nitrogen temperature. The intensity of the signal of Cu(II) did not regain its original value with the evacuation of the sample at room temperature. Heating to 300°C changed the color of the catalysts from purple-blue to black. Among zeolite catalysts only CuY types showed the appearance of the new band with the adsorption of furan at room temperature. The new band, however, was not observed for CuY treated with hydrogen at 350°C. A new band in the EPR spectrum was also ob-

FIG. 2. Infrared spectra of CuY. (A) Evacuated at 200°C for 4 hr; (B) furfural adsorbed at room temperature.
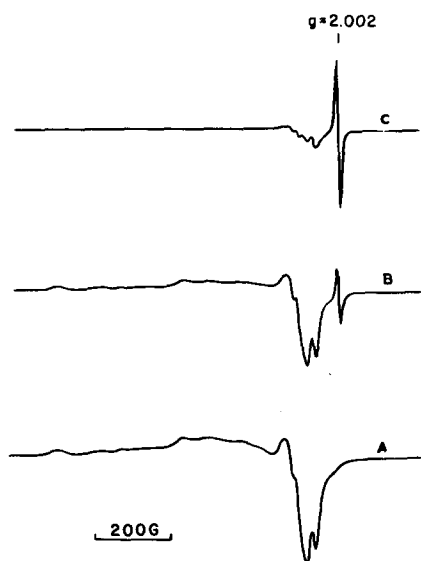
g = 2.002

FIG. 3. EPR spectra of Cu(15)Y and effect on furan adsorption at 25°C. (A) Evacuation at 200°C for 4 hr; (B) furan on Cu(15)Y; (C) additional furan added to B.

served when 2-methylfuran was adsorbed on CuY. The *g* factor of the signal was the same as that observed for furan adsorption. However, there were hyperfine structures that changed with the degree of Cu(II) ion exchange as shown in Fig. 4. When furfural was adsorbed on CuY at room temperature, there was no change in the EPR spectrum from that of CuY. When furfural was adsorbed at 150°C, however, the appearance of the new band was observed.
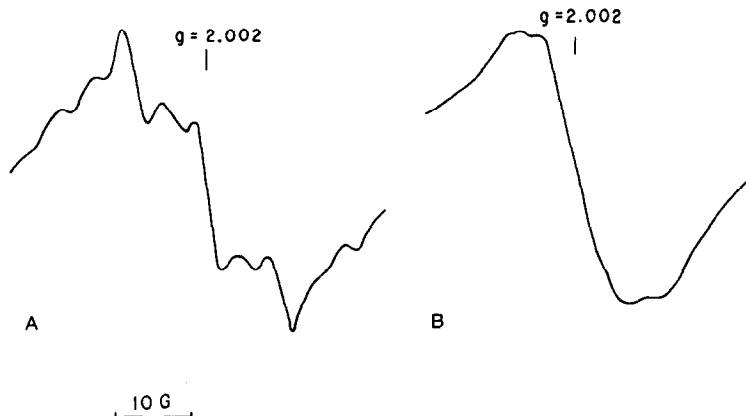
DISCUSSION

Furfuryl alcohol is essentially the only product produced in the hydrogenation of furfural over a wide variety of copper-containing catalysts. These include copper oxide, copper–chromium oxide, copper–cobalt oxide, Pd–CuY, and Ni–CuY. This observation suggests that copper, in particular Cu(II), is the active component of the catalyst for this selective formation.

Furan is essentially the only product made with Pd–HY and Pd–LaY catalysts. Since HY and LaY are typical acid catalysts having strong acid sites (*3, 4*), this product results from the interaction of the polar carbonyl group of furfural with these Brönsted acid sites. The role of Pd probably was to activate the hydrogen.

The amounts of furan adsorbed on NaY and HY are almost the same. On CuY, however, the amount of furan adsorbed increased with increasing degree of Cu(II) ion exchange. The amount of tetrahydrofuran, which has no conjugated double bond, did not increase with increasing degree of Cu(II) ion exchange. This suggests that Cu(II) ion serves as the adsorption site for the furan ring.

Infrared studies of furan and furfural adsorbed on CuY showed that the absorption peak of 1570 cm^{-1}, representing the conjugated double bond of furan and furfural, was shifted to lower frequency by 15

FIG. 4. EPR spectrum of methylfuran adsorbed on Cu(*n*)Y. (A) Cu(15)Y; (B) Cu(30)Y.

cm^{-1}. It may be that the electron density of the conjugated double bond in the furan ring was transferred to Cu(II) ion in zeolite and this interaction prevented the furan ring from being hydrogenated.

The evidence of interaction between Cu(II) ion and the furan ring is also demonstrated in the EPR spectra. Rupert has shown that radical cations are formed from a series of polynuclear aromatic compounds adsorbed on Cu(II)-exchanged montmorillonite, and electron exchange between radical cations or between radical and neutral diamagnetic species results in the single, exchange-narrowed EPR band (5). The appearance of the single narrow band, with g factor close to a free electron, when furan was adsorbed on CuY may be attributed to the Cu–furan complex similar to the Cu–arene complex observed on Cu(II)-exchanged montmorillonite.

High selectivity to furfuryl alcohol and the absence of tetrahydrofurfuryl alcohol formation on copper-containing catalysts is interpreted in terms of the interaction between Cu(II) ion and the furan ring of furfural preventing the furan ring from being hydrogenated. This interaction also explains the enhancement of conversion to furfuryl alcohol on Pd–CuY. Here the active site for the selective formation of furfuryl alcohol is the Cu(II) ion interacting with the furan ring while Pd activating the hydrogen.

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