

A KINETIC AND DRIFTS STUDY OF CROTONALDEHYDE HYDROGENATION OVER CARBON-SUPPORTED COPPER

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Introduction

For consideration as a replacement for copper chromite catalyst, novel copper catalysts utilizing high surface area activated amorphous carbon (AC), graphitized carbon fibers (GF) and diamond powder (DM) as supports were prepared. The catalysts were characterized using CO adsorption, N₂O adsorption and decomposition, XRD, temperature-programmed desorption (TPD) and diffuse reflectance FTIR spectroscopy (DRIFTS). The vapor-phase hydrogenation of crotonaldehyde (CROALD) to butyraldehyde (BUTALD) or crotyl alcohol (CROALC) was studied at low conversions over these catalysts after reduction at different temperatures between 423 to 773 K. The oxidation state of the surface Cu atoms was probed by DRIFTS spectra of CO adsorbed on these Cu/AC, Cu/GF and Cu/DM samples after pretreatment at different temperatures. In addition, DRIFTS spectra were obtained *in situ* under reaction conditions in order to gain additional insights into the surface sites and adsorption configurations associated with the catalytic behavior of these systems.

Results and Discussion

DRIFTS spectra of the pure carbon supports, together with their TPD spectra, indicated the presence of strongly as well as weakly acidic functional groups on their surfaces. These groups were partially removed after a high temperature treatment at 773 K in H₂. Bands for surface nitrate, nitrite and nitrito groups were observed after impregnation of these carbons with an aqueous copper nitrate solution. After reduction at 423 K, these groups decomposed to form unidentate and bidentate copper carboxylate complexes presumably

via the participation of the carboxylic acid functional groups present initially.

The dispersion as well as reducibility of Cu were found to be strongly dependent on the nature of the carbon used as support. The crystallite sizes varied from 4 nm on the nitric acid treated AC and 17 nm on DM to about 193 nm on GF. This is similar to the observations by Ryndin et al. (1) who attributed the differences in the dispersion and sintering characteristics of Pd on graphite and diamond to the peculiarities in the interaction of Pd particles with these surfaces in a hydrogen atmosphere. DRIFTS spectra of CO adsorbed on these Cu/AC, Cu/GF and Cu/DM samples after reduction at different temperatures indicated that the relative amounts of Cu⁺¹ ions and metallic Cu atoms varied as function of reduction temperature. The IR band wavenumbers at 2115 cm⁻¹ for CO adsorbed on the pretreated Cu/AC and Cu/GF samples and 2130 cm⁻¹ for CO adsorbed on the Cu/DM sample were close to those reported for CO adsorbed on Cu⁺¹ species. Similarly, bands at 2060 cm⁻¹ for CO adsorbed on pretreated Cu/GF and 2090 cm⁻¹ for CO adsorbed on pretreated Cu/DM were close to those reported for CO adsorbed on Cu⁰ species (2).

The activities of these catalysts for crotonaldehyde hydrogenation also varied with the nature of the support and the reduction temperature employed. Whereas the 5% Cu/AC catalyst exhibited the highest overall activity per gram catalyst, maximum enhancement in selectivity for crotyl alcohol was obtained over the 5% Cu/GF catalyst prepared using ion-exchange technique. Similar enhancement in the selectivity to the unsaturated alcohol has been reported by Giroir-Fendler et al. during the hydrogenation of cinnamaldehyde over group VIII metals dispersed on graphite (3). The effect was interpreted to be due to an electron

transfer from graphite to the metal particles decorating the edges of the basal planes. The selectivity of 15% over this catalyst compares to a value of 3% over Cu chromite. A mixture of Cu^0 and Cu^{+1} species was observed on the surface of each catalyst after pretreatment at the temperature which gave that particular catalyst the highest activity. This is consistent with the hypothesis that the presence of both Cu^0 and Cu^{+1} species is required for optimum performance of these copper catalysts, which has been proposed earlier to explain the maximum in activity that occurs as a function of reduction temperature for copper chromite (4). Activation energies for the hydrogenation of crotonaldehyde varied from 3 kcal/mole over Cu/AC to 24 kcal/mole over Cu/GF, with near zero-order dependence on crotonaldehyde and first-order dependence on H_2 over all the catalysts. Turnover frequencies, based on total Cu surface area, were an order of magnitude higher over Cu/GF as compared to those over Cu/AC.

The low selectivities obtained over copper in this study are in general agreement with a previously noted analysis that the carbonyl group selectivity in a conjugated system is lower than that expected from the relative reactivities of isolated double bonds (5). It has been suggested that this low selectivity could be due to strong adsorption of the allylic alcohol on copper and its subsequent high reactivity (6). DRIFTS spectra of the catalysts exposed to crotonaldehyde, crotyl alcohol and butyraldehyde provided strong evidence for the preferential adsorption of these molecules through the C=C double bond. To verify the relative rates of isomerization and hydrogenation of these monohydrogenation products, hydrogenation of crotyl alcohol and butyraldehyde were examined. Whereas crotyl alcohol rapidly isomerized to butyraldehyde at low temperatures, with selectivity shifting more towards butanol at higher temperatures, butyraldehyde showed negligible activity at reaction temperatures in the range of interest. This is consistent with the proposal that strong adsorption of CROALC and its preferential isomerization to BUTALD under mild conditions limits the final selectivity achievable for CROALC during the hydrogenation of CROALD (6).

In situ FTIR spectra, obtained during crotonaldehyde hydrogenation, revealed the

formation of a possible phenolate-type intermediate on the catalyst surface and clearly verified the presence of crotonaldehyde adsorbed strongly through the C=C double bond and weakly through the C=O bond. It has been proposed before that both butyraldehyde and crotyl alcohol can originate from a common adsorbed intermediate (7). Evidence was found for a surface phenolate-type species, possibly formed through the interaction of the terminal carbonyl bond in adsorbed CROALD with surface cuprous ions. Whereas the adsorption of H_2 was found to be the slow step during the hydrogenation over Cu/GF, a Langmuir-Hinshelwood sequence with the hydrogenation of such an intermediate species as the rate-determining step (rds) nicely explained the kinetics of the reaction over Cu/AC.

References

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