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Time Dependence for the Selective Hydrogenation of Crotonaldehyde

Recently Noller and Lin reported that they were able to selectively reduce the carbonyl bond of crotonaldehyde, an α,β-unsaturated aldehyde (*1*). The authors reported a maximum yield of 54 mol% of crotyl alcohol, the β-unsaturated alcohol, which is not the normal hydrogenation product. This alcohol has been observed for platinum (*2, 3*), nylon-supported platinum–tin (*4*), and copper (*5*) mixed-metal systems but had not been reported for the nickel–copper system prior to the Noller and Lin paper.

This result seemed very interesting and we thought we might try to extend this work to other nickel mixed-metal systems. Prior to starting experiments with the other systems we made numerous attempts to reproduce their result but were only able to obtain much smaller amounts than their reported values. We were concerned that there may have been some ill-defined experimental condition that allowed them to produce the less-favored product. In the process of trying to reproduce their results and possibly find the cause of this discrepancy, we found experimental conditions that allowed us to obtain only crotyl alcohol and to thus confirm their result, while showing that this selectivity was only temporary. After enough time elapsed, butyraldehyde became the only product.

Three supported catalysts containing at least one metal and one sample of only support were prepared according to a coprecipitation method whereby the metal(s), if any, and support are coprecipitated from an aqueous solution by addition of a base. This was the same technique that was used by Noller and Lin (*1*) and was further elucidated by Lin (*6*). The starting materials for the catalysts were the Fisher reagent-grade nitrates of each of the components (Al, Cu, and Ni) which were weighed out in the correct molar ratios to give the desired weight percent for the oxide of each component after calcination. These were dissolved into the same beaker using a minimum amount of water (about 150 ml per 15 g of finished catalyst) and were precipitated from solution by slowly (dropwise) introducing 300 ml of 2.5 *M* aqueous ammonia into this solution. After removing most of the water, catalyst pellets were formed by extruding the gel-like precipitate through an 8-mm hole in stainless-steel using a hand-powered press. The pellets were then dried overnight in an oven at 100–110°C. Finally, all of the catalysts and the support were calcined at 300°C in air at a flow rate of 15 ± 1 ml/min for 12 h.

The mixed-metal catalyst contained 30% NiO, 14% CuO, while the nickel catalyst contained 30% NiO and the copper catalyst 14% CuO. The only other component of each catalyst was Al_2O_3. The surface areas of each of these were 239, 244, and 251 m^2/g, respectively, and the surface area of the pure alumina support was 255 m^2/g. These were measured by the low-temperature multi-point adsorption of N_2, had a reproducibility of about ± 11 m^2/g, and were in good agreement with those reported in the Noller and Lin paper.

The typical weight of catalyst pellets for a hydrogenation was 0.74 ± 0.01 g which occupied a space of 3–4 mm in diameter and 4–8 mm in length between two glass wool plugs in the center of the reactor. Immediately prior to performing a catalysis run, the catalysts were preconditioned with nitrogen (Airco 99.8%) for 2 h at a flow rate

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of 15 ± 1 ml/min and a temperature of 300°C, and then reduced with hydrogen (Airco 99.9%) which had been further purified by allowing the gas to pass through an Engelhard Deoxo catalytic purifier. Both gases had to flow through a trap which contained Davison molecular sieve (5 Å) and were cooled with liquid nitrogen before coming in contact with either the crotonaldehyde or the catalysts. Catalysts were reduced for 12 h at 430°C with a hydrogen flow rate of 26 ± 1 ml/min and hydrogenations were carried out by bubbling the purified hydrogen at a flow rate of 25 ml/min through crotonaldehyde and then directing it through the catalytic reactor.

Since 80°C was the temperature at which the catalyst in the Noller and Lin paper was most selective, this temperature was chosen as the first attempt at producing the alcohol with the nickel/copper catalyst. After hydrogen flow had been established through the reactor system, no sampling of the effluent was performed for 75 min so that the result would be a steady-state value. After this waiting period, gas chromatographic analysis revealed that butyraldehyde was the predominant component in the gas effluent. Although the unsaturated alcohol was usually present (the amount of which varied from one experiment to the next), the relative amount of it was always less than about 15%. At hydrogenation temperatures of 150 and 200°C, the catalyst was more active but produced very little or no crotyl alcohol with butyraldehyde and butanol being the predominant products at the two respective temperatures.

At each of these three temperatures there was another peak in the gas chromatographic (GC) analysis which was later to be identified as a mixture of C_1–C_4 alkanes and small amounts of CO and CO_2. The total area of this peak under these experimental conditions was about 5% of the total area of all peaks in a particular analysis.

It was thought that the concentrations of the various products might be varying with time and that the waiting period prior to sampling of the effluent was either too long or too short and caused the discrepancy in results.

As mentioned above, 80°C was chosen as the best match of the previously reported condition for the most selective catalyst. After reducing a fresh portion of the bimetallic catalyst, a sample of the effluent gas was taken as soon as hydrogen flow had been established through the bubbler containing crotonaldehyde and then every 15 min thereafter. The results are presented in Fig. 1 and show how the concentration of crotyl alcohol varied with time for this freshly prepared catalyst (open circles). The first two samples from the sampling port on the outlet of the reactor contained no observable peaks from any of the possible organic components. At this point 15 min had elapsed since the start of the experiment, which was clearly longer than it took for the organic material to pass through the reactor system and could be accounted for by retention of reactants and products on the catalyst. When the next sample was analyzed, 93% of the total amount of organic compounds observed was crotyl alcohol. After this, its relative amount decreased with time, reaching a steady-state level of about 6% when 160 min had elapsed. The closed circles in Fig. 1 show how butyraldehyde varied with time. After the first two samples, butyraldehyde was present at about a 7% level and increased with time until a steady-state concentration of about 94% was reached after 160 min.

Since the product distribution was clearly a very large function of the recent history of the catalyst, it seemed that the catalyst might exhibit marked variations in selectivity or activity if the catalyst had been used, regenerated, and then reused. The open squares in Fig. 1 show the time-dependent yield of crotyl alcohol for the catalyst used to produce the results described above after it had been regenerated in flowing hydrogen for 12 h. As was observed above there was an induction period before anything other than hydrogen ap-

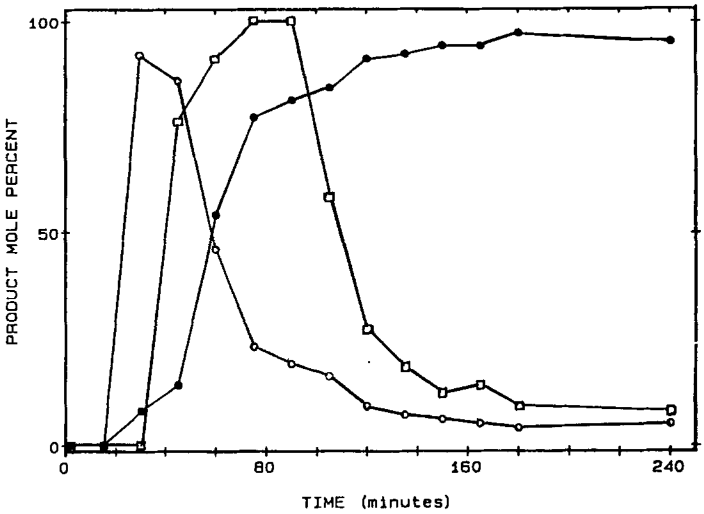

FIG. 1. Product mole percent for the Ni/Cu catalyst as a function of time during the hydrogenation of crotonaldehyde at 80°C and an H_2 flow rate of 25 ml/min. Open circles represent the yield of crotyl alcohol while filled circles represent the yield of butyraldehyde. The squares show the time dependent yield of crotyl alcohol for this catalyst which after 240 min of catalytic hydrogenation had been regenerated (rereduced) for 12 h under standard reduction conditions.

peared at the sampling port. After this, crotyl alcohol was again the predominant product until the end of the first 100 min and then began to decrease until a steady-state level of 10% was attained after 160 min. While this was occurring, butyraldehyde grew in relative concentration to its steady-state value. To the best of our knowledge this short-term selectivity has not been observed before for crotonaldehyde.

Since there was such a strong time dependence on the amount of crotyl alcohol produced, it seemed important to reconfirm that both metals must be present to produce crotyl alcohol from crotonaldehyde. The single component catalysts were run under identical experimental conditions to see if the alcohol was produced by either or both metals.

When the copper catalyst was reduced and used, very little reaction occurred, with at least 95% of the organic effluent being unreacted crotonaldehyde and the rest butyraldehyde. Pure alumina support showed a similar result.

The supported nickel catalyst had a much higher activity producing butyraldehyde and butanol. As in the mixed-metal experiment there was an induction time of about 30 min before product was observed. After this, butyraldehyde became the major component with small amounts of butanol and crotyl alcohol also being produced. Steady-state levels of each were attained after only 80 min.

A turnover number based on the total number of metal atoms and the total yield of crotyl alcohol in the first experiment (6×10^{-6} moles) was calculated for the duration of the experiment. This provided a calculated turnover number of 0.02. Thus, there is only one crotyl alcohol molecule produced for every 50 metal atoms. This makes it appear possible that the formation of crotyl alcohol may not even be a catalytic process at all, but instead may be the result of a stoichiometric reaction with a small number of nickel sites that have the correct electronic environment and/or ensemble size to allow this reaction to take place. Our results do not allow us to comment on this with any degree of certainty since the unsaturated alcohol was only produced during the initial stages of the catalyst's lifetime when, as mentioned above, there were also large amounts of reactant and products that were retained on the catalyst. These could be poisoning or blocking active sites, or changing the ensemble size of these sites. No matter which of these is the cause for this short-term selectivity, the regeneration experiment clearly causes the sites to be available again for reaction. If the reaction is catalytic, there must be a very small percentage of the sites that are selective for reduction of the aldehyde since only a small amount of crotyl alcohol was detected.

Our results also confirm that both metals are absolutely necessary since the selectivity was only observed when both were present. Thus, regardless of whether or not it is a catalytically activated reaction, copper plays an important role in the selectivity of the catalyst. This role was explained by Noller and Lin (*1*) as being the result of an interaction between the metals in which copper tended to donate electron density to the nickel to make it more electron-rich. This interpretation is consistent with our results.

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