2. Cornaz, P. F., Van Hooff, J. H. C., Pluijm, F. J., and Schuit, C. G. A., *Discussions Faraday Soc.* **41**, 290 (1966).
3. Iyengar, R. D., Codell, M., Karra, J. S., and Turkevich, J., *Discussions Faraday Soc.* **41**, 323 (1966).
4. Mastikhim, V. M., Kefeli, L. M., and Keier, N. P., *Kinetics Catalysis* (*USSR*) (*Engl. Transl.*) **6**, 157–158 (1965).
5. Iyengar, R. D., Codell, M., Karra, J. S., and Turkevich, J., *J. Am. Chem. Soc.* **88**, 5055 (1966).
6. Reyerson, L. H., and Honig, J. M., *J. Phys. Chem.* **56**, 140 (1952).
7. Reyerson, L. H., and Honig, J. M., *J. Am. Chem. Soc.* **75**, 3917 (1954).
8. Dzenentski, Z., *Zh. Fiz. Khim* **40**, 2309–2312 (1966).
9. Iyengar, R. D., and Zettlemoyer, A. C., unpublished results.

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A Method for Studying Catalytic Hydrogenation of Aqueous Cinnamaldehyde over Platinum and Nickel Wire

Prevention of catalyst poisoning is a general problem in the hydrogenation of aldehydes in aqueous solution over nickel and platinum catalysts, apparently, because of the accompanying formation of polymeric products that are strongly adsorbed on the catalyst surface. To measure this type of catalyst poisoning and to learn how to regenerate used nickel and platinum catalysts in aqueous medium, the hydrogenation of cinnamaldehyde (β-phenylacrolein) was employed as a convenient test reaction. This aldehyde has an intense absorption band at 2900 Å that enables measurement of the concentration changes that occur during the catalytic hydrogenation of dilute aqueous solutions (10^{-4} to 10^{-5} M) at 25°C. Extremely low rates of hydrogenation can, therefore, be determined—even as low as those occurring over massive platinum or nickel wire. Use of a catalytic metal in the form of wire rather than in the form of a dispersion on a porous support enables rapid changes in catalyst treatment, and precludes diffusion limitations.

The high intensity of the 2900-Å band in cinnamaldehyde arises because of conjugation of the phenyl, vinyl, and carbonyl groups in this molecule. Hydrogenation of the carbonyl group to form cinnamyl alcohol would shift the above band to 2500 Å but this did not occur. The other probable hydrogenation products, 3-phenyl-1-propanol and 3-phenyl-1-propanol, have maximum absorptivities one-hundredth of that for cinnamaldehyde, so these products are not detected. However, since former studies of the catalytic hydrogenation of a conjugated aldehyde (acrolein) have shown that initial attack occurs at the carbon–carbon double bond during hydrogenation over nickel (*1*) and platinum (*2*), it is likely that cinnamaldehyde is hydrogenated to 3-phenyl-1-propanal in all the following experiments.

An all-glass flow apparatus was devised that would enable measurement of the extent of conversion of cinnamaldehyde (10^{-4} M) as the aqueous solution was passed over platinum wire at a constant rate (0.2 ml/sec) at 25°C. The solution was saturated with hydrogen at atmospheric pressure (the solubility of hydrogen is sufficient to give 10 moles of hydrogen per mole of cinnamaldehyde), then passed through the catalyst bed into a quartz absorption cell in a Cary spectrophotometer. When it was so desired, the flow of cinnamaldehyde solution could be stopped, and another solution (poison or regenerant) passed over the catalyst. A satisfactory level of conversion, in the range 60% to 90%, could be attained by means of disks of platinum gauze (45 mesh) having a total surface area of 140 cm².

The effects of successive pretreatments on platinum catalyst are shown in Table 1.

TABLE 1

POISONING AND REGENERATION OF PLATINUM CATALYST[a] FOR CINNAMALDEHYDE HYDROGENATION AT 25°C

Pretreatment[b]	Decay time (min)[c]
4.5% H_2O_2	62
Water	48
30% Aqueous α-hydroxyadipaldehyde	25
4.5% H_2O_2	73
4.5% H_2O_2, then conc. HNO_3	75

[a] 71 circles of 45-mesh platinum gauze, 1 cm in diameter, surface area 140 cm².

[b] 15-Minute duration at room temperature.

[c] Time for conversion to decrease to 50% of its initial value.

After each pretreatment, a cinnamaldehyde hydrogenation test was made. Even with clean catalyst, the conversion gradually decreased due to poisoning during the cinnamaldehyde hydrogenation. However, with previously poisoned catalyst, the conversion decreased faster. The table lists times required for the conversion to fall to 50% of its initial value. We conclude that (1) water washing does not restore activity after cinnamaldehyde hydrogenation; (2) α-hydroxyadipaldehyde poisons platinum; (3) 4.5% hydrogen peroxide restores the catalyst activity after poisoning with α-hydroxyadipaldehyde; and (4) concentrated nitric acid is no more effective as a regenerant than 4.5% hydrogen peroxide.

From experiments of this kind, the effect of pretreating platinum with a number of substances was determined. It was found, for example, that aqueous solutions of sodium sulfide and α-hydroxyadipaldehyde were strong poisons. Ethanol or 10% aqueous 1,2,6-hexanetriol did not act as poisons. Platinum partially deactivated by hydrogenation of hydroxyadipaldehyde could be regenerated with 4.5% hydrogen peroxide, concentrated nitric acid, 0.1 M potassium persulfate, 0.01 M oxalic acid, or 0.1 M maleic acid. The latter two reagents restored the catalyst to better than the original condition.

Experiments with nickel catalysts were made in a static system, consisting of a magnetically stirred solution through which hydrogen was bubbled at atmospheric pressure. The catalyst was 50-mesh nickel gauze having a geometric surface area of 12.4 cm². Hydrogenation of 10^{-4} M cinnamaldehyde was again monitored spectrophotometrically as a function of time.

Initial tests showed that the nickel catalyst was inactive immediately after treatment with 4.5% hydrogen peroxide. However, hydrogenation slowly set in over a 1-hr period. It thus appeared that hydrogen in solution at room temperature was able to remove an inhibiting oxygen film formed on the nickel surface by exposure to hydrogen peroxide. Next, it was found that treatment of the catalyst with concentrated ammonium hydroxide after the hydrogen peroxide treatment greatly shortened the induction period in the hydrogenation. Finally, it was found that if the hydrogen peroxide and ammonium hydroxide treatments were followed by exposure to hydrogen for 1.5 hr, the induction period in the subsequent hydrogenation test was completely eliminated.

REFERENCES

1. BRENDLEIN, H., German Patent 755,524 (to Deutsche Gold und Silber Scheideanstalt) (1952).
2. HERNANDEZ, L., AND NORD, F. F., *Experientia* 3, 489 (1947).

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