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Gel Entrapped Catalysts

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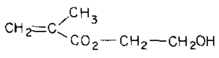
A new type of catalyst has been prepared consisting of small particles of transition type metals uniformly dispersed in a swollen, nonporous, polymer gel. The activity and selectivity of such catalysts has been investigated in several hydrogenation reactions. The influence of the solvent on hydrogen solubility and extent of swelling of the gel has been noted with regard to the rate and selectivity of the reaction.

INTRODUCTION

A number of recent reports have been concerned with the use of insoluble polymers as supports for metal catalysts. In all of the previous reports the metal has been deposited either on the surface of a polymer or in the pores of a macroreticular resin (*1–3*). In this paper we report on the preparation and use of metals deposited *within* a homogenous gel. The gel used in this work was prepared by crosslinking polymerization of 2-hydroxyethyl methacrylate (HEMA), I, in such a way that it contained no pores. For the purpose of this work a "pore" is considered to be a void in the gel which is continuous in space and permanent in time. Diffusion in nonporous gels has been well described (*4*) and increases exponentially with increasing swelling of the gel by a solvent.



$CH_2{=}C(CH_3){-}CO_2{-}CH_2{-}CH_2OH$

I

Crosslinked poly(HEMA) is a well studied member of a class of acrylic polymers commonly described as hydrogels (*5*), in reference to their facility for swelling to varying degrees in water and polar organic solvents such as alcohols. Poly(HEMA) itself has found considerable use in biomedical applications (*6*). Previous work by one of us has been concerned with the entrapment of enzymes within the matrices of homogenous hydrogels such as poly (HEMA) (*7*).

METHODS

The gel catalysts were prepared by immersing 7.2 g of small pieces (ca. 1 × 2 mm) of poly(HEMA) (with 0.3 to 1.0 mole% ethylene dimethacrylate (EDMA) crosslinking agent) in 40 ml of a 0.1 *M* aqueous or alcoholic solution of a metal complex such as $Li_2PdCl_4 \cdot 3H_2O$. After the gel particles had reached osmotic equilibrium with the external solution they were removed and washed free of surface solvent. The imbibed solvent was then removed under diminished pressure. Visual examination of sections of a number of larger gel pieces, which were treated as described above, indicated a uniform distribution of metal complex throughout the gel. The metal complex thus entrapped was subsequently reduced by allowing the polymer particles to imbibe a 1 *M* ethanolic $NaBH_4$ solution. Reaction byproducts were removed by immersing the metal containing gel in a large volume of water or an alcohol. The wash solvent was then removed under diminished pressure and the gel pieces were ground to the desired particle size (ca. 600 μm for this

TABLE 1
Hydrogenation of Cinnamaldehyde in Various Solvents[a]

Solvent	Vol% swelling[b]	H_2 Solubility (ml H_2/ml solvent)[c]	Initial rate ($\times 10^6$, M sec^{-1})	%III[d]	Relative rates with Pd/C[e]	% III with Pd/C[e]
Methanol	65	0.068	56.0	74	6	55
Ethanol	55	0.065	17.6	81	7	50
n-Propanol	50	—	5.4	89	2.7	57
i-Propanol	15	0.042	3.2	91	2.7	59
n-Butanol	15	—	0.7	—	3	54
Acetic acid	70	0.053	45.0	70	9.7	73
Dimethylformamide	85	0.037	16.2	80	2.7	59
Water	40	0.015	5.2	80	1	88

[a] 55 mg 0.3 wt% Pd in poly(HEMA) gel, 0.1 ml (0.80 mmole) cinnamaldehyde, 4.9 ml solvent, 30°C, 70 cm Hg total pressure.

[b] Ref. (*5*).

[c] Estimated for conditions of this work from data given in Ref. (*9*).

[d] % III = % hydrocinnamaldehyde.

[e] Rates relative to rate reported for hydrogenation in water at room temperature; Ref. (*9*).

study). The technique has also been used to prepare gel entrapped Pt, Rh, Ru, Co and Ni. Convenient starting complexes in these cases are H_2PtCl_6, $RhCl_3 \cdot 3H_2O$, $RuCl_3 \cdot XH_2O$, $CoCl_2 \cdot 6H_2O$, and $Ni_2(OOCCH_3)_2 \cdot 4H_2O$, respectively. In all cases the colloidal size metal particles exhibited no shock sensitivity or pyrophoric character. Line broadening of X-ray diffraction and scanning electron microscopy studies on a sample of gel entrapped Pt indicate the trapped metal particles are about 15 nm in size.

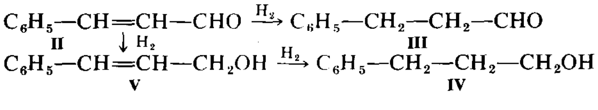
Hydrogenation rate measurements were made by following the consumption of hydrogen at constant pressure using the apparatus and procedure described earlier (*8*). The use of a small volume of solution (5 ml) in a 25 ml creased reaction flask, together with a high speed of shaking, resulted in vigorous agitation of the reaction solution. The reproducibility of the rate measurements of the hydrogenation systems investigated in the present study was to within 10%.

The hydrogenation products were identified by glc using a Hewlett Packard Model 5780 unit fitted with a flame ionization detector. Product separation was achieved on a 6 ft column of 10% squalane on Chromosorb W, 80/100 mesh.

RESULTS AND DISCUSSION

To investigate the hydrogenation properties of the gel catalysts we chose substrates whose reductions had been extensively studied over conventional supported catalysts.

Table 1 summarizes the results obtained in the reduction of cinnamaldehyde, II, using a Pd/poly(HEMA) gel catalyst together with data reported for reduction over Pd/C (*9*). With this substrate, hydrogen absorption ceases after an uptake of slightly more than 1 equiv of gas/mole of II. Analyses of the reaction mixtures revealed the presence of the saturated aldehyde III and saturated alcohol **IV**. The absorption in excess of 1 equiv represents the extent of initial carbonyl reduction leading to the formation of the unsaturated alcohol, V, which is readily reduced to **IV**. No other reaction products were observed by glc.



$$\begin{array}{ccc} C_6H_5{-}CH{=}CH{-}CHO & \xrightarrow{H_2} & C_6H_5{-}CH_2{-}CH_2{-}CHO \\ \text{II} \quad \downarrow H_2 & & \text{III} \\ C_6H_5{-}CH{=}CH{-}CH_2OH & \xrightarrow{H_2} & C_6H_5{-}CH_2{-}CH_2{-}CH_2OH \\ \text{V} & & \text{IV} \end{array}$$

In most solvents the Pd/poly(HEMA) catalyst is noticeably more selective towards the formation of **III** than the conventional catalyst. The relative rates of reduction with the gel catalyst in the various solvents reveal the intervention of internal diffusional effects on both hydrogen and substrate transport. These effects are illustrated graphically in Fig. 1 which is a plot of the rate (normalized by hydrogen solubility) vs percentage swelling of the gel by the solvent.[1] Thus, methanol is an efficient solvent due to a combination of its relatively high solubility towards hydrogen and its propensity for swelling the polymer matrix (thus increasing substrate diffusion), while a low rate is observed in isopropanol due to low hydrogen solubility and poor swelling ability. Acetic acid is an efficient solvent since it is able to swell the gel catalyst to a considerable extent. Reduction in DMF proceeded with gradual slowing of the reaction rate as the reaction progressed. Inspection of the reaction mixture indicated that the extremely high swelling capacity of this solvent permitted the loss of catalyst from the gel.

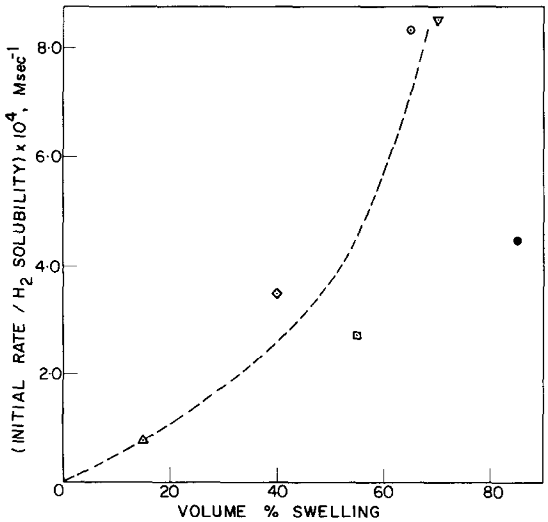
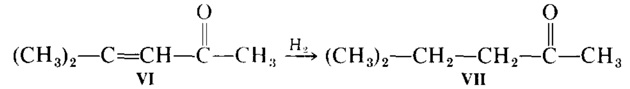


FIG. 1. Effect of swelling of gel on the rate of cinnamaldehyde hydrogenation in various solvents: (○) methanol; (□) ethanol; (△) *i*-propanol; (▽) acetic acid; (●) dimethylformamide; (◇) water.

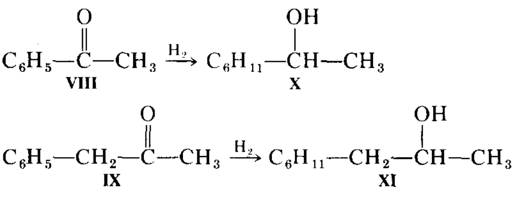
A Pd/poly(HEMA) catalyst exhibited selectivity analogous to Pd/C for the reduction of mesityl oxide **VI**, absorbing 1 mole of hydrogen/mole of **VI** to provide the saturated ketone, **VII** (Table 2).



$$\underset{\text{VI}}{(CH_3)_2\text{—}C\text{=}CH\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3} \xrightarrow{H_2} \underset{\text{VII}}{(CH_3)_2\text{—}CH_2\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3}$$

Methanol and acetic acid are efficient solvents for this reduction with both the Pd/poly(HEMA) and Pd/C catalysts. Ethyl acetate, a good solvent for the reduction over Pd/C, permits only a very low rate with the gel catalyst, consistent with its poor swelling properties towards the polymer matrix.

We found that a Rh/poly(HEMA) catalyst was efficient for the conversions of acetophenone **VIII** and phenylacetone **IX** to the saturated alcohols **X** and **XI** (Tables 3 and 4).



$$\underset{\text{VIII}}{C_6H_5\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3} \xrightarrow{H_2} \underset{\text{X}}{C_6H_{11}\text{—}\overset{\overset{OH}{|}}{C}H\text{—}CH_3}$$

$$\underset{\text{IX}}{C_6H_5\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3} \xrightarrow{H_2} \underset{\text{XI}}{C_6H_{11}\text{—}CH_2\text{—}\overset{\overset{OH}{|}}{C}H\text{—}CH_3}$$

Only minor amounts of hydrocarbons, formed from hydrogenolysis of the alcohol function, were found. In these respects the gel catalyst is similar to Rh/C and Rh/Al_2O_3. The course of reduction of these substrates over Rh/C and Rh/Al_2O_3 has been followed quantitatively (*9*). The formation of the saturated alcohol product was found to proceed through the intermediacy of the saturated ketone (path A,

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[1] A first order dependence of reaction rate on H_2 solubility is assumed in the normalization. Normalized rates are computed in order that the diffusional effects of various solvents on reaction rate can be examined independently of the effect of hydrogen solubility.

TABLE 2

HYDROGENATION OF MESITYL OXIDE IN VARIOUS SOLVENTS[a]

Solvent	Vol% swelling[b]	H_2 Solubility (ml H_2/ml solvent)[c]	Initial rate ($\times 10^6$, M sec^{-1})	Relative rates with Pd/C[d]
Methanol	65	0.068	34.0	1.2
Acetic acid	70	0.053	93.0	1
Ethyl acetate	<10	0.070	0.3	1.5

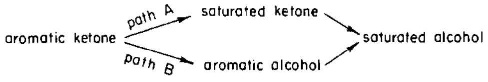
[a] 30 mg 1.7 wt% Pd in poly(HEMA) gel, 0.1 ml (0.87 mmole) mesityl oxide, 4.9 ml solvent, 30°C, 70 cm Hg total pressure.

[b] Ref. (5).

[c] Estimated for conditions of this work from data given in Ref. (9).

[d] Rates relative to rate reported for hydrogenation in acetic acid at room temperature; Ref. (9).

initial ring reduction) and aromatic alcohol (path B, initial carbonyl reduction):



We have made no such detailed study with the Rh/poly(HEMA) catalyst but note only that analysis of a number of reaction mixtures at early stages of reduction revealed relatively high ratios of saturated ketone/aromatic alcohol (path A over path B) were present. Once again, internal diffusional effects dominate the relative rates of reduction with the gel catalyst.

The metal/poly(HEMA) gels described above are reasonably efficient and stable catalysts when employed in a reduction solvent capable of swelling the polymeric matrix and exhibit moderate selectivity differences in relation to standard supported catalysts. In this preliminary investigation no attempts were made to optimize their selectivity patterns via the use of additives or promoters. Presumably it should be also possible to change the microenvironment and hence selectivity towards reduction of a particular substrate by the incorporation of an appropriate amount of comonomer of desired functionality.

In conclusion, it has been demonstrated that the selective reduction of a substrate to a desired product at the expense of another may be accomplished by taking advantage of conditions of hydrogen transport control (*10*). In many cases this is best accomplished by locating the transport control within the catalyst particle

TABLE 3

HYDROGENATION OF ACETOPHENONE IN VARIOUS SOLVENTS[a]

Solvent	Initial rate ($\times 10^6$, M sec^{-1})	Relative rates with Rh/C[b]
Methanol	36.0	1.0
Ethanol	20.5	—
n-Propanol	3.5	—
Acetic acid	38.0	2.4
Ethyl acetate	~0.2	2.0

[a] 43 mg 0.6 wt% Rh in poly(HEMA) gel, 0.1 ml (0.86 mmole) acetophenone, 4.9 ml solvent, 30°C, 70.2 cm Hg total pressure.

[b] Rates relative to rate reported for hydrogenation in methanol at room temperature; Ref. (9).

TABLE 4

HYDROGENATION OF PHENYLACETONE IN VARIOUS SOLVENTS[a]

Solvent	Initial rate ($\times 10^6$, M sec^{-1})	Relative rates with Rh/Al_2O_3[b]
Methanol	20.4	1.5
Ethanol	9.7	1.0
n-Propanol	1.6	1.0
Acetic acid	23.4	—
Ethyl acetate	~0.1	1.3

[a] 90 mg 0.6 wt% Rh in poly(HEMA) gel, 0.1 ml (0.75 mmole) phenylacetone, 4.9 ml solvent, 30°C, 70.2 cm Hg total pressure.

[b] Rates relative to rate reported for hydrogenation in ethanol at room temperature; Ref (9).

rather than relying on gas–liquid or bulk-liquid control of the reactor (*11*). Our data suggest that the metal/poly(HEMA) catalysts are suitable for this method of obtaining selectivity.

Further work in this laboratory is directed toward a better understanding of the nature of these catalysts (e.g., the Ni, Co and Ru gels may very well contain some boride of the metal as well as the metal itself). Reactions other than hydrogenation are also being studied.

ACKNOWLEDGMENT

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