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Catalytic Hydrogenation of Esters over Pd/ZnO

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The vapor phase hydrogenation of methyl acetate has been studied using Pd/ZnO catalysts. This catalyst system is active for the conversion of methyl acetate to methanol and ethanol at pressures below 1000 psig (ca. 68 bar). The addition of small amounts of H_2O to the liquid feed significantly lowers the rate of by-product formation. This catalyst has also been used for the hydrogenation of methyl propionate, methyl butyrates, and ethyl acetate.

INTRODUCTION

The catalytic hydrogenation of carboxylic acid esters to the corresponding alcohols has been practiced commercially for many years. Of particular interest is the reduction of diesters to diols (e.g., butanediol, hexanediol, cyclohexanedimethanol), which are incorporated into the production of many polyesters. The current commercial catalyst for this reaction is copper chromite, which is frequently promoted with Ba or Mn (*1*). Unfortunately, using copper chromite for this reaction requires the use of high hydrogen pressure to achieve commercially attractive rates (*2*).

Over the past several years new catalysts have been developed as replacements for the existing catalyst system. Several promising catalysts based on copper have been identified, but these catalysts have found limited use (*3–6*). Copper catalyst are generally not thermally stable and can rapidly deactivate if the reaction temperature is not carefully controlled.

Basset and co-workers (*7*) reported that supported Rh catalysts can be used for the low-pressure hydrogenation of esters. While this catalyst is interesting from a scientific view, the high cost of Rh (>$5000/oz) precludes serious development of this catalyst system. Other group VIII transition metals such as Ru are also active for this reaction (*8*).

It is interesting to note that copper chromite and CuO–ZnO are active for both methanol synthesis from CO and H_2 and ester hydrogenation. When considering the types of surface species proposed in the synthesis of methanol such as formyls and formates, it would appear that related species could also be proposed for ester hydrogenation. Based on this assumption, the search for new ester hydrogenation catalysts should include catalysts known to be active for the methanol synthesis reaction.

Pd/ZnO has been reported as a catalyst for methanol synthesis (*9*) and would appear to be a good candidate for ester hydrogenation. In this study we report on the use of Pd/ZnO for the vapor phase hydrogenation of methyl acetate and other low-molecular-weight fatty acid esters.

EXPERIMENTAL

Catalyst samples used in this study were prepared by aqueous impregnation of Pd salts on to ZnO (Alpha Products Ultrapure 99.999%, 3–7 $m^2\ g^{-1}$). An aqueous solution of $Pd(NO_3)_2$ (Alpha) was prepared in a minimum volume of H_2O and slowly added to the ZnO support to form a tan paste-like material. Other salts of Pd such as the chloride can also be used to prepare these catalysts, but we have found that catalysts produced with Pd acetate are inactive. All samples prepared in this study contained 1 wt% Pd as determined by atomic absorption

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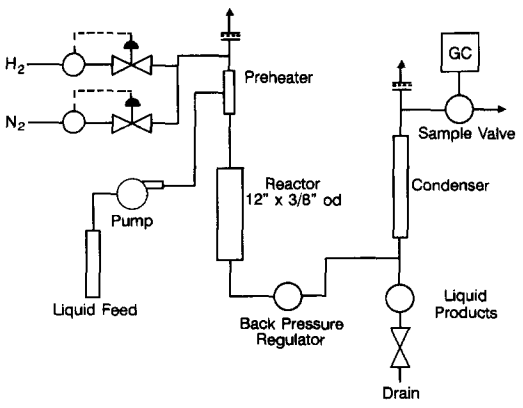


FIG. 1. Simplified drawing of the microreactor system.

spectroscopy. Following impregnation, the samples were dried in air at 90°C and then calcined in air 250°C for 2–4 h.

A $Pd/ZnO–Al_2O_3$ catalyst was prepared by impregnation of $Pd(NO_3)_2$ onto a $ZnO–Al_2O_3$ support. This support was made by precipitation of ZnO from zinc nitrate with sodium carbonate followed by addition of hydrated alumina (*10*). The resulting support material had a BET surface area of 79 $m^2\ g^{-1}$.

Reactions were conducted in a microcatalytic reactor system capable of operating at 1500 psig at 350°C (Fig. 1). Liquid feeds were introduced by pumping into a heated chamber with an Eldex micrometering pump. Hydrogen feed gas also flowed through this chamber to ensure adequate mixing and feed gas preheating prior to exposure to the catalyst. Hydrogen gas flow rates were controlled using Brooks Instruments Model 5810B mass flow controllers. The reactor portion of this system consisted of a $\frac{3}{8} \times$ 12-in. (ca. 1 × 30.5 cm) medium pressure nipple (316ss, Autoclave Engineers). The catalyst was held in place using quartz wool. Typical catalyst charges in this unit were approximately 1 g. Reactor pressure was controlled using a dome loaded back pressure regulator (Circle Seal) downstream from the reactor. The product gas stream exiting the reactor system was passed through a trap at −5°C to separate liquid and gaseous products. Gaseous products were analyzed using an on-line gas chromatograph (HP 5890A) with a Chromosorb 102 column. Liquid samples were analyzed on a HP5890A capillary gas chromatography using a 30M DB5 column. In all cases the conversion of methyl acetate was kept below 10% to ensure differential conditions.

For a typical evaluation, the Pd/ZnO was charged to the reactor and heated to the desired reaction temperature under H_2 flow. Once the reaction temperature had been reached, the reaction was initiated by addition of the liquid feed to the vaporizor. Prolonged reduction of the catalyst was not required to achieve acceptable activity.

Nitrogen BET surface area measurements were made using a Quantasorb surface area analyzer. Pd particle size estimates based on hydrogen and carbon monoxide chemisorption studies were not feasible because the presence of Zn significantly alters the chemisorption properties for the reduced catalysts. Pd particle sizes were estimated using TEM (Hitachi-HU-11).

Except where noted in the text, the methyl acetate (Kodak) feed was purified before use by first drying over molecular sieves and then distilling from P_2O_5 prior to use. The distillation step was required to remove trace amounts of water as well as alcohol impurities (e.g., methanol), which would make data analysis more difficult at low conversions. All other esters were used without further purification.

RESULTS AND DISCUSSION

While the hydrogenation of methyl acetate is expected to give methanol and ethanol, a significant amount of ethyl acetate is also observed in the product. In fact, at low conversions, ethyl acetate is sometimes the only product observed. The overall reaction scheme can be written as follows:

$$MeOAc + H_2 \rightarrow MeOH + EtOH \quad (1)$$

$$MeOAc + EtOH \rightarrow EtOAc + MeOH. \quad (2)$$

The transesterification reaction (Eq. (2)) is known to be catalyzed by acidic sites (e.g., Zn^{2+}, Al^{3+}) and is an expected side reaction if oxide vacancies are present. Because of the secondary side reaction producing ethyl acetate, the apparent rates of methanol or ethanol production do not represent the true rate of methyl acetate hydrogenation. For this reason, the rate of ester hydrogenation is expressed as an adjusted ethanol rate, which is equal to the sum of the observed rates of ethanol and ethyl acetate formation. If the reactions shown in Eqs. (1) and (2) were the only reactions of importance, the difference between the observed rate of methanol and ethyl acetate production could also be used as a indication of the rate of methyl acetate hydrogenolysis:

$$\text{Rate}_{\text{EtOH}} + \text{Rate}_{\text{EtOAc}} = \text{Rate}_{\text{MeOH}} - \text{Rate}_{\text{EtOAc}}. \quad (3)$$

However, methanol can also be produced by hydrolysis of methyl acetate to methanol and acetic acid or consumed by decomposition to CO and H_2:

$$\text{MeOAc} + H_2O \rightarrow \text{MeOH} + \text{HOAc} \quad (4)$$

$$\text{MeOH} \rightarrow \text{CO} + 2H_2. \quad (5)$$

While these reactions do not predominate and are difficult to quantify at low conversions, it is apparent that they occur to some degree because the observed rate of methanol formation is typically not equal to the adjusted rate of ethanol formation. No attempt was made in this study to quantify the significance of reactions (4) and (5) and, unless otherwise noted, all data reported are based on the adjusted rate of ethanol formation.

To initially optimize the adjusted rate of ethanol formation over these catalysts, a simplex optimization procedure was used (*11*). This procedure is useful for determining the optimum region for further catalyst evaluation. Four continuous variables (temperature, total pressure, H_2/MeOAc ratio, and total flow rate (W/F in g-min^{-1}-cm^{-3}) were chosen for optimization. The ranges for these variables used in this study are shown in Table 1. The methyl acetate feed used for the Simplex study was not purified by distillation and contained approximately 0.5 wt% H_2O.

TABLE 1

Continuous Process Variables for Simplex Optimization: Methyl Acetate Hydrogenation (1% Pd/ZnO)

Variable	Units	Range	Step size
Pressure	psig	100–1000	100
Temperature	°C	150–350	50
H_2/MeOAc	mol/mol	3–10	1
W/F (×100)	g min^{-1} cm^{-3}	0.20–1	0.1

While the complete details of this optimization study are not presented here, the results of this study showed that varying total pressure below 1000 psig, total flow rate, or the H_2/MeOAc ratio did not significantly alter the adjusted rate of ethanol formation over the ranges investigated (Table 2). Changing the reaction temperature did effect the adjusted rate of ethanol production and the apparent activation energy for methyl acetate hydrogenation was estimated to be 14.5 kcal mol^{-1}. Increasing the reaction temperature above 300°C resulted in the highest catalytic activity with adjusted rates of ethanol formation of up to 9–12 μmol g^{-1} s^{-1} at 330–350°C.

As mentioned above, attempts to characterize this catalyst system using conventional CO chemisorption techniques were unsuccessful. We believe that this is due to the strong Pd–Zn interaction present following reduction of these catalysts (*12*). In an attempt to characterize the Pd particle size for this catalyst we used TEM. The average Pd particle size measured by TEM for this catalyst was 40 Å. Assuming that the total particle surface was available for reaction, this corresponds to a turnover frequency of 4.1×10^{-1} s^{-1}.

On the basis of the results of the Simplex optimization, the following set of reaction

TABLE 2

Effect of Process Variables on Adjusted Rate of EtOH Formation with 1% Pd/ZnO (3 $m^2 g^{-1}$)

Pressure (psig)	Temperature (°C)	H_2/MeOAc	W/F ($\times 100$) (g min^{-1} cm^3)	Adjusted[a] rate EtOH	Selectivity[b]
700	250	5.0	0.20	0.41	98
800	250	5.0	0.20	0.41	100
700	300	5.0	0.20	3.20	96
700	250	6.0	0.20	0.40	98
700	250	5.0	0.30	0.39	100
740	330	4.0	0.22	9.0	91

[a] Rate in μmol g_{cat}^{-1} s.
[b] (Rate EtOH/adjusted rate EtOH) $\times$ 100.

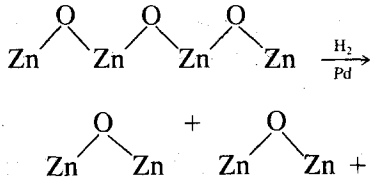
conditions were selected for all subsequent studies: reaction temperature of 300°C, total pressure of 720 psig, and a H_2/MeOAc equal to 4.0. The total flowrate was adjusted as necessary to maintain conversions below 10%.

While Pd/ZnO was active for hydrogenation of methyl acetate, the extent to which the secondary transesterification reaction proceeds is a major concern from a commercial standpoint. For higher molecular weight esters and diesters, this reaction can result in the formation of high molecular by-products and polymeric species. In previous studies on Pd/ZnO it was found that under reducing conditions some of the ZnO support is reduced (*12*, *13*). It is probable that a partial reduction of the ZnO would give rise to acidic sites (i.e., oxide vacancies) that could promote the transesterification reaction.

If this supposition is correct, controlled *in situ* reoxidation of Pd/ZnO should result in improved selectivity to ethanol. In an attempt to facilitate the reoxidation of reduced Zn species and to lower the acidity of the reduced ZnO surface under reaction conditions, a series of experiments was conducted in which H_2O was added to the dried MeOAc feed. As shown in Table 3, the addition of small amounts of H_2O to the feed significantly improves the selectivity to ethanol. When the MeOAc feed was dry, the selectivity for ethanol formation was only 37%. Addition of 1% H_2O to the feed resulted in an increase in selectivity to 92%. While this positive effect of H_2O addition to the MeOAc feed was observed at levels as high as 5%, the overall rate of MeOAc hydrogenation decreased with increasing H_2O concentrations. At H_2O levels above 1%, irreversible catalyst deactivation was observed.

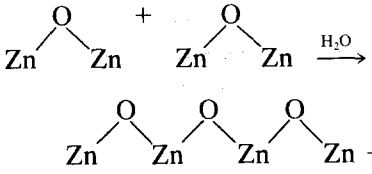
The effect of H_2O can be viewed in a simplistic fashion as shown below.

No added H_2O:



(6)

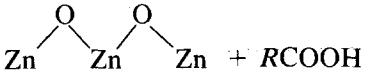
Low H_2O in feed:



(7)

High H_2O in feed:

$$R\text{COOR}' + H_2O \longrightarrow R\text{COOH} + R'\text{OH}$$



$$\longrightarrow \text{Zn}(\text{OOC}R)_2. \quad (8)$$

As mentioned above, under H_2 reducing conditions partial reduction of the ZnO can be observed by XPS (*12*) and could give rise

TABLE 3

Methyl Acetate Hydrogenolysis over 1% Pd/ZnO: Effect of Water Addition

H_2O in feed (%)	Rate (μmol g^{-1} cat s)			
	CH_3OH	CH_3CH_2OH	EtOAC	Total
0.0	7.3	2.1	3.6	5.7
0.1	4.3	2.4	1.8	4.2
0.5	2.8	1.5	0.33	1.8
1.0	1.5	1.1	0.06	1.2
5.0	1.4	0.5	0.02	0.5

Note. Temperature, 300°C; pressure H_2, 720 psig; H_2/ester, 4.0.

to Lewis acid sites on the catalyst surface (Eq. (6)). It is proposed that these sites are responsible for the transesterification reaction and that addition of H_2O converts these defects back to an oxidized surface (Eq. (7)). Under conditions of high H_2O concentrations in the feed, one would expect methyl acetate to undergo hydrolysis and form acetic acid, which would react with ZnO to give $Zn(OAc)_2$ (Eq. (8)). Zinc acetate readily sublimes above 200°C, which could result in severe migration of the Zn component of the catalyst. In fact, at high H_2O concentrations a water-soluble white solid, identified as $Zn(OAc)_2$, has periodically been observed in the product lines. If the Zn component migrates and covers the Pd, this mechanism would account for the irreversible catalyst deactivation observed at high H_2O feed rates. The lack of observable catalyst activity when samples are prepared from the acetate salt of Pd may also be related to formation of $Zn(OAc)_2$, which would be mobile above 200°C.

Under reducing conditions, Pd/ZnO is known to form bimetallic Pd–Zn particles on the surface of the ZnO support (*3*). Because Pd on other supports is not active for low-pressure ester hydrogenation, it is conceivable that the Pd–Zn bimetallic particles are the active component in these catalysts. While the addition of H_2O is targeted to keep the ZnO surface oxidized, it is also probable that H_2O perturbs the Pd–Zn bimetallic particles to some degree and results in the negative impact of H_2O on the overall rate of ester hydrogenation.

If the H_2O content is maintained at ≤ 1 wt%, excellent catalyst life can be achieved. As shown in Fig. 2, the catalyst has been evaluated for ~70 h at 330°C and a pressure of 700 psig using a MeOAc feed, which contained ~0.5 wt% H_2O. Following an initial decrease in activity of ~20% during the first 20 h of operation, the catalyst activity stabilized and no further deactivation was observed. The selectivity to ethanol also remained above 85–90% throughout the course of this evaluation.

In spite of the relatively high activity for ester hydrogenation observed with Pd/ZnO,

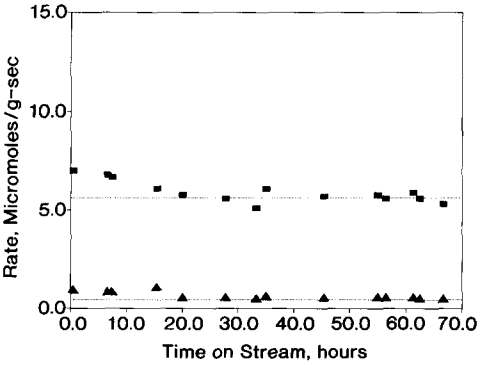


FIG. 2. Activity of 1% Pd/ZnO for the vapor phase hydrogenation of methyl acetate at 330°C, 700 psig, H_2/MeOAc = 4.0, and GHSV = 30,924 h^{-1}. The MeOAc feed contained approximately 0.5 wt% H_2O. (■) Ethanol, (▲) ethyl acetate.

TABLE 4

Methyl Acetate Hydrogenolysis over 1% Pd/ZnO: Effect of ZnO Surface Area

BET surface area ($m^2\ g^{-1}$)	Pd d(Å)[d]	Rate (μmol/g-cat s)				TOF (s^{-1}, $\times 10$)
		CH_3OH	CH_3CH_2OH	EtOAC	Total	
3	40	1.5	1.1	0.06	1.2	0.55
27[a]	—	6.0	5.8	0.4	6.2	—
79[b]	20	21.4	5.6	8.8	14.4	3.3
3[c]	40	10.1	8.1	0.7	8.8	4.0

Note. Temperature, 300°C; pressure H_2, 720 psig; H_2/ester, 4.0; 1.0 wt% H_2O.

[a] Catalyst prepared by Calsicat Div., Mallinckrodt, Inc.

[b] ZnO/Al_2O_3 support, reaction temperature 333°C, $H_2 < 0.1\%$.

[c] Temperature 333°C, $H_2O \approx 0.5\%$.

[d] Estimated using TEM particle size measurements.

the use of ZnO as a support material has some drawbacks from a practical standpoint. The bulk density of ZnO is high relative to conventional supports, but the physical strength is very low. In addition, the low surface areas of most common ZnO supports limit the Pd dispersion and loading levels. It is reasonable to assume that the activity of Pd/ZnO could be improved by use of a high-surface-area ZnO support.

In the case of other ZnO-based catalysts, such as CuO–ZnO for methanol synthesis, Al_2O_3 is sometimes incorporated into the catalyst composition to enhance the surface area and physical properties of the support. In this study a $ZnO–Al_2O_3$ support was prepared using a procedure developed for CuO–ZnO catalysts. When Pd was added to this ZnO/Al_2O_3 support (BET surface area 79 $m^2\ g^{-1}$) only a small increase in rate, from 9 to 14 μmol $g^{-1}\ s^{-1}$, was observed (see Table 4). This result is not surprising as the higher surface area for this catalyst is probably due to the Al_2O_3 component and not directly related to the ZnO. It should be noted that the $Pd/ZnO–Al_2O_3$ sample was evaluated with a dry MeOAc, which should have resulted in a further increase in rate when compared to the runs with Pd/ZnO that were performed with a small amount of H_2O in the feed. The absence of H_2O in the MeOAc used for the $Pd/ZnO–Al_2O_3$ evaluations was also the cause for the lower selectivity observed with the Al_2O_3 containing catalyst.

A second sample (Al_2O_3 free) prepared by Calsicat with ZnO having a BET surface area of 27 $m^2\ g^{-1}$ was much more active than the lower-surface-area material (Table 4). While little is known regarding the preparation of this catalyst, the data suggest that higher-surface-area ZnO supports are desirable for preparing Pd/ZnO catalysts.

Finally, the Pd/ZnO catalyst prepared on Alpha ZnO has been used in the vapor phase hydrogenation of other esters besides methyl acetate. It should be noted that the esters used in these runs were not dried prior to use and contained between 0.5 and 1 wt% H_2O. As a result, the selectivities to the desired alcohols were >95%. As shown in Table 5, relatively high activity is observed for a variety of esters. Surprisingly the hydrogenation activity does not dramatically change when changing from methyl acetate to ethyl acetate or methyl butyrates. This implies that this catalyst system may be useful for a variety of carboxylic acid esters and, with appropriate development, could ultimately replace the existing copper chrome-based high-pressure catalyst in commercial processes.

CONCLUSIONS

Pd/ZnO catalysts are active for the hydrogenation of methyl esters of carboxylic acids

TABLE 5

Pd/ZnO Catalyzed Hydrogenation of Esters at Low Pressures

Ester	Rate (μmol/g s)
Methyl acetate	9.0
Methyl propionate	9.0
Methyl-*n*-butyrate	6.0
Methyl-*i*-butyrate	6.0
Ethyl acetate	8.0

Note. Temperature 300°C; pressure, 700 psig; H_2/ester, 4.0; H_2O, 0.5–1.0%.

at pressures below 1000 psig. The major process variable effecting catalyst performance is the temperature of reaction. Secondary transesterification reactions can be minimized by the addition of small amounts of H_2O to the feed, but the overall reaction rate is lower when H_2O is present. This catalyst has been tested for a series of esters and the relative rate of hydrogenation is relatively insensitive to the chain length of the reactant. Pd/ZnO has promise as a replacement for the present copper chromite-based high-pressure catalyst system.

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