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Ester Hydrogenation over Pd–Zn/SiO_2

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The activity of bimetallic Pd–Zn/SiO_2 catalysts have been measured for a series of samples prepared by either impregnation or ion-exchange techniques. Catalysts prepared by ion-exchange of $Pd(NH_3)_4^+$ onto SiO_2 followed by reduction and subsequent impregnation of Zn exhibited the highest activity for methyl acetate hydrogenation. Both catalyst activity and selectivity to ethanol were dependent on the Pd : Zn ratio. The presence of PdZn bimetallics was confirmed using controlled atmosphere XRD, XPS, and STEM/EDS analysis. Oxidation at ambient temperatures did not disrupt the bulk Pd–Zn interaction, but did result in changes in the reversible oxidation of the surface.

INTRODUCTION

When Pd and other noble metals are supported on ZnO and reduced in hydrogen, significant reduction of the ZnO support material has been observed (*1–7*). In the case of Pd, strong evidence exists that the reduced Zn component interacts with the Pd metal particles to form well defined bimetallic particles (*2, 3, 6*). This interaction is distinctly separate from the well known "SMSI" phenomenon, where oxides such as TiO_2 have been shown to modify the activity of supported metal particles by migration under high-temperature treatments. In the case of Pd/ZnO, reduction of the Zn has been observed with formation of PdZn and Pd_2Zn_3 phases identified by XRD (*3*).

It has also been demonstrated that the catalytic behavior of Pd can be significantly modified by using ZnO as the support material. Pd/ZnO catalysts have been studied for the hydrogenation of isoprene (*3*), crotonaldehyde (*4*), and esters of carboxylic acids (*1, 8*). In all of these cases, the use of ZnO has been found to modify the activity of Pd for hydrogenation reactions. The use of Pd/ZnO for hydrogenation of esters is of particular interest because Pd/ZnO has been shown to be active for this reaction at much lower hydrogen pressure than that required by conventional catalysts and may have some commercial merit. It should be noted that Pd supported on other supports such as Al_2O_3 or SiO_2 are poor catalysts for the hydrogenation of esters. The activity of the Pd/ZnO catalysts for ester hydrogenation would appear to be directly related to the formation of the bimetallic Pd–Zn particles.

While Pd/ZnO exhibits interesting catalytic behavior, ZnO is not an ideal catalyst support material. ZnO typically exhibits low surface areas, is sensitive to acidic impurities, has a high density, and usually has poor crush strength. If the active component in the Pd/ZnO catalyst is Pd–Zn bimetallic particles, it should be possible to achieve similar catalytic performance by preparing supported Pd–Zn bimetallics on higher surface area materials such as SiO_2. Supporting the Pd and Zn components should also result in improved activity if the Pd dispersion can be increased and may also minimize the other problems noted above that are associated with using bulk ZnO as a support.

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In this study, a variety of palladium–zinc bimetallic catalysts were prepared on silica and evaluated for ester hydrogenation activity. The model system chosen to evaluate the catalytic activity of these supported bimetallics was the vapor phase hydrogenolysis of methyl acetate to methanol and ethanol.

EXPERIMENTAL

All catalysts were prepared by palladium addition to silica, followed by subsequent impregnation of zinc. Preparation variables altered in developing the Pd/Zn catalyst family include the palladium addition technique, the atomic ratios of Pd to Zn, and the catalyst treatment prior to the impregnation of zinc. The palladium addition techniques are outlined below. In all cases, the metal loadings were determined using atomic absorption spectroscopy. The following convention will be used throughout the text to distinguish between the various samples. The Pd metal loading is expressed as a wt%, whereas the Zn loading is based on the atomic ratio of Pd : Zn. Thus, 1% Pd–Zn (1 : 2)/SiO$_2$ denotes a sample with 1 wt% Pd loading and a 1 : 2 atomic ratio of Pd : Zn.

Incipient Wetness Preparation

All catalysts prepared by aqueous impregnation contained 1 wt% Pd. For a typical sample, 0.48g of Pd(NO$_3$)$_2$ (Alpha Products) were dissolved in 29.4 ml of distilled, deionized (D-D) H$_2$O and the resulting solution was added to 20 g of the SiO$_2$ support (Davison 59 SiO$_2$, 14–40 mesh). The resulting solid was dried in air at 90°C for 30 min and then calcined in air at 350°C for 12 hr. In one of these samples (noted later in the text), the intermediate calcination step was excluded.

The same Pd/SiO$_2$ sample was used to prepare several samples with different Pd : Zn ratios. Following Pd addition, the sample was split into separate fractions for Zn addition. Zinc impregnation was accomplished by using the same procedure as for Pd addition, except the final calcination temperature was 200°C and the amount of Zn was adjusted to give the desired Pd : Zn ratio. Zinc nitrate (Zn(NO$_3$)$_2$ · 6H$_2$O) was used as the source of Zn. Metal loading levels for all samples were confirmed by atomic absorption spectroscopy.

Ion-Exchange Preparation

All samples prepared by ion exchange were supported on Davison 59 SiO$_2$ sieved to 14–40 mesh. For a typical preparation, 100 g of SiO$_2$ was placed into 2000 ml of D-D H$_2$O and NH$_4$OH added until the pH was 11.0. [Pd(NH$_3$)$_4$]Cl$_2$ (7.0 g, Alpha Products) was dissolved in 20 ml of D-D H$_2$O and the resulting solution was added dropwise to the SiO$_2$ containing solution while stirring. Following 80 min of contact, the SiO$_2$ was removed from solution by filtration and then rinsed with 400 ml of D-D H$_2$O. The sample was then dried in air at 120°C for 24 hr. At this point some of the samples were reduced by heating to 260°C in Ar and then heating to 400°C in H$_2$. The reduction was continued at 400°C for 1.5 hr. Following Pd addition (and in some cases Pd reduction), zinc was added by standard incipient wetness techniques as outlined above. Finally, the samples were calcined at 200°C for 3 hr.

Hydrogen and CO chemisorption are typically used to measure the amount of exposed Pd metal. The successful application of chemisorption to measure metal dispersions requires assumptions regarding the adsorption stoichiometry of H$_2$ and CO. While the stoichiometry is well known for Pd on supports such as SiO$_2$ or Al$_2$O$_3$, the stoichiometry can be altered by the presence of additional components such as Zn. In fact, H$_2$ and CO chemisorption were attempted in this study, but because of a strong suppression of CO and H$_2$ adsorption capacity in the presence of Zn, chemisorption was not useful for the measurement of metal dispersion.

For the series of samples prepared by Pd reduction prior to Zn addition, the Pd metal particle sizes and compositions were measured using a scanning transmission electron microscope (STEM). The Pd–Zn/SiO_2 catalysts were ground and dispersed onto holey carbon-coated Cu grids. The size, morphology, and elemental composition of nanometer-size catalyst clusters were determined by using a Vacuum Generators, HB501 STEM. This microscope is equipped with a cold-field emission source and energy dispersive spectrometer (EDS) consisting of a Link AN10000 and Link LZ5 series E (30 mm^2) windowless X-ray detector, and was operated at 100 kV. One-hundred-micrometer virtual objective and selected area apertures (SA) were used. The second condensor (C2) lens was focused at SA and C1 was set to 16. This electron optical configuration effectively reduced the hole count to zero.

Nanometer-size Pd–Zn particles were localized in images using annular dark field (ADF) imaging with a high angle, dark-field detector. Metal particle sizes were measured directly from the cathode ray tube (CRT) display prior to recording the particle's composition. Since particles on the order of a few nanometers in diameter are relatively unstable under the electron beam and can undergo significant migration during the 50 sec required to collect an X-ray spectrum, the area under analysis was imaged at high magnification (20×10^6 X) and the particle motion was compensated for electronically. The CRT was calibrated using a 0.34-nm graphite fringes, while quantitative X-ray analysis employed the standard RTS2 programs for thin specimens.

Nitrogen BET surface areas were measured for all catalysts using a Quanta-Chrome Corporation Quantasorb surface area analyzer. All samples were outgassed on the QuantaChrome Corporation Monotector for at least 1 hr at 200°C, or until drying was complete as determined by the TC detector on this instrument, before conducting surface area measurements.

Variable temperature, hydrogen atmosphere XRD experiments were performed on a Scintag theta–theta diffractometer equipped with a Huber high-temperature furnace at the High Temperature Materials Laboratory of Oak Ridge National Laboratory. Samples were prepared by slurring the catalyst with acetone and then using this slurry to deposit the catalyst on either an off-axis Si single-crystal zero-background plate or a polycrystalline corundum plate. Correction for displacement errors in the measured peak positions was performed by using the corundum lines as the reference in the corundum-mounted samples and a polycrystalline Si internal standard in the samples mounted on the zero-background plate. Measurements were made with Cu $K\alpha$ radiation and a liquid-nitrogen-cooled Ge energy dispersive detector. Data points were collected in 0.01° steps at speeds ranging from 0.1–1.0 deg/min. *In situ* reductions were performed by flowing 99.99% hydrogen at 1 atm over the heated sample. All patterns of the reduced catalysts were recorded with the sample chamber filled with hydrogen. Samples were reoxidized by exposure to air at room temperature.

Crystallite sizes were determined by using the Scherrer equation. Instrumental broadening data were not available for the diffractometers at ORNL, therefore in this study no correction was made for instrumental broadening. Furthermore, because of the small crystallite sizes involved in this study, instrumental broadening should be a minor contribution to the measured peak width and, therefore, should have a negligible effect on the calculated crystallite size.

The XPS experiments were performed on a Perkin–Elmer PHI Model 5400 ESCA Spectrometer using monochromated Al $K\alpha$ radiation. The spectrometer was equipped with a spherical capacitor energy analyzer and a resistive anode position sensitive detector. The analysis area was 1 × 1 mm. Charge neutralization of the samples was accomplished by flooding with low-energy (1–5 eV) electrons. All binding energies were referenced to the Si 2*p* peak, which was assigned a binding energy at 103.4 eV. Samples were reduced in a reaction chamber attached to the analysis chamber. Reductions were performed by flowing a mixture of 10% hydrogen in argon over the heated sample at atmospheric pressure. Following reduction the reaction chamber was evacuated to 10^{-5} Torr and the sample was transferred to the analysis chamber. Samples were oxidized by exposing to air at room temperature.

Kinetic evaluations were conducted in a high pressure microreactor constructed from $\frac{3}{8}$" high-pressure tubing. All samples were prereduced at 300°C and 500 psig in H_2 gas (452 sccm) for 2.5 hr. The system pressure was raised to 750 psig after H_2 pretreatment. Liquid methyl acetate was fed to a vaporizer (0.4 ml/min) which was flushed with the H_2 feed gas. The resulting feed mixture was passed over a 1.0-cc catalyst bed at 300°C. Product vapors were condensed in a trap at −5.0°C. The relative molar product ratios in both the gas exiting the trapping system and the liquid samples were analyzed by using a Hewlett–Packard HP 5890 gas chromatographs. For the liquid samples, a capillary column (30 M DB5) was used while gas analysis was accomplished on a Chromosorb 102 packed column. Total conversions were kept low (<10%) to ensure differential conditions in the reactor.

The methyl acetate feed used in this study was obtained from Kodak. Methyl acetate usually contains small amounts of H_2O and alcohols (primarily methanol) which were removed by drying over molecular sieves followed by distillation from P_2O_5.

RESULTS AND DISCUSSION

Kinetic Studies

Results obtained with the Pd–Zn/SiO_2 catalysts prepared by impregnation are presented in Table 1. While these catalysts were active for the hydrogenation of methyl acetate, the predominant products observed with all of these catalysts were methanol and ethyl acetate, not methanol and ethanol as might be expected. Ethyl acetate can be formed by the transesterification reaction between methyl acetate and ethanol:

$$\mathrm{EtOH} + \mathrm{MeOAc} \rightarrow \mathrm{EtOAc} + \mathrm{MeOH}. \quad (1)$$

TABLE 1

Methyl Acetate Hydrogenation over 1 wt% Pd : Zn/SiO_2 Prepared by Impregnation (300°C, 750 psig, H_2/MeOAc = 4.5)

Pd : ZN[a]	Treatment[b]	S.A.[c]	Rate (μmole/g sec)			
			MeOH	EtOH	EtOAc	Adjusted[d] rate
1 : 1	None	241	2.91	0.01	0.61	0.62
1 : 1	Calcined	268	2.30	0.03	0.60	0.63
1 : 2	Calcined	234	6.52	0.10	2.43	2.53
1 : 5	Calcined	236	2.80	0.0	0.85	0.85
1 : 10	Calcined	223	2.28	0.02	0.73	0.75
1 : 0	Calcined	229	1.07	0.02	0.08	0.10
0 : 1	—	0.0	0.0	0.0	0.0	—

[a] Expressed as atomic ratio of Pd : Zn.

[b] None—no intervening calcination prior to addition of Zn; calcined—calcined prior to Zn addition.

[c] N_2 BET surface area in $m^2\,g^{-1}$.

[d] Adjusted rate = rate of EtOH + EtOAc.

This reaction has previously been observed over Pd/ZnO and is thought to be catalyzed by $Zn^{\delta+}$ formed during ZnO reduction (*8*). Because this reaction decreases the observed rate of ethanol formation, the measured rates of ethanol production are lower than the true rate of methyl acetate hydrogenation. The actual rate of methyl acetate hydrogenation should be equal to the sum of the observed rate of ethanol and ethyl acetate production. For this reason, an adjusted rate ($Rate_{EtOH} + Rate_{EtOAc}$) has been used in this study as the measure of catalyst performance.

It should be noted that the transesterification reaction also results in an increase in the observed rate of methanol formation. If ester hydrogenation and transesterification reactions were the only two reactions that occurred, the true reaction rate should also be equal to an adjusted rate of methanol formation ($Rate_{adj}$ = Observed $Rate_{MeOH}$ − Observed $Rate_{EtOAc}$). As can be seen from the data in Table 1, in almost all cases this is not true.

Several other reactions can also effect the observed rate of methanol formation. Methanol can be formed from the direct hydrolysis of methyl acetate to produce acetic acid and methanol. While the methyl acetate used in this study was distilled from P_2O_5 to remove H_2O impurities, it is difficult to remove all H_2O from methyl acetate, and it is probable that, at low conversions, the observed rate of methanol formation was significantly perturbed by this side reaction. In addition, methanol can undergo catalytic decomposition to carbon monoxide and hydrogen over Pd catalysts and, if this reaction was occurring under our reaction conditions, would result in a decrease in the apparent rate of methanol formation. Because these side reactions alter the amount of methanol produced, the adjusted rate of methanol formation is not a good indicator of the true rate of hydrogenation and therefore not used in this study to monitor catalyst activity.

When comparing the results for the samples prepared by impregnation, it is evident that the Pd : Zn ratio has a profound effect on the catalyst activity. The sample with a Pd : Zn ratio of 1 : 2 was found to be four times as active as the catalyst with a Pd : Zn ratio of 1 : 1. Further addition of Zn to ratios of 1 : 5 and 1 : 10 resulted in a decrease in catalyst activity compared to the catalyst with a 1 : 2 ratio. It is also apparent that calcination of the sample prior to Zn addition had little effect on the catalytic activity of the resulting sample.

To verify that the catalytic activity observed with these samples is related to the presence of both Pd and Zn, monometallic samples were also evaluated for ester hydrogenation activity (Table 1). While the Pd/SiO_2 sample exhibited some baseline activity for this reaction, the samples containing both Pd and Zn are at least six times as active as the Pd/SiO_2 sample. The sample which contained Zn only is not active for methyl acetate hydrogenation.

While the activity of the Pd–Zn bimetallic catalysts is clearly greater than that of the monometallic catalysts, the overall activity for methyl acetate hydrogenation is lower than that on Pd/ZnO catalysts previously studied (*1*, *8*). In an effort to improve the catalytic activity of the SiO_2-supported Pd–Zn bimetallics, the preparative procedure was modified to incorporate an ion-exchange procedure for Pd addition. It has been shown that ion-exchange of $Pd(NH_3)_4^{+2}$ onto SiO_2 supports results in higher Pd dispersions than can be achieved by conventional impregnation techniques (*9*). Assuming that the subsequent addition of Zn would not alter the Pd dispersion, it was postulated that the greater dispersions should increase the activity of the catalysts. The results obtained using catalysts prepared by ion-exchange of the Pd component, followed by Zn impregnation, are given in Tables 2 and 3.

The results presented in Table 2 clearly show that the activity of these catalysts for methyl acetate hydrogenation is directly related to the Pd metal content. For a series

TABLE 2

Methyl Acetate Hydrogenation with Pd : Zn/SiO_2 Prepared by Ion-Exchange of $Pd(NH_3)_4Cl_2$ (Davison Grade 59 SiO_2, Pd : Zn = 1 : 2, 300°C, 730 psig, H_2/MeOAc = 4.0)

Wt% Pd	Rate (μmole/g sec)				EtOH
	MeOH	EtOH	EtOAc	Adjusted[a] rate	EtOH + EtOAc
1% Pd	4.1	0.8	1.7	2.5	0.32
2.8% Pd	8.4	3.6	2.9	6.5	0.55
5% Pd	30.	6.0	14.6	20.	0.30

[a] Adjusted rate = rate of EtOH + EtOAc.

of Pd–Zn/SiO_2 samples with a Pd : Zn ratio of 1 : 2, increasing the Pd metal content by a factor of 5 resulted in almost an order of magnitude increase in the rate of methyl acetate hydrogenation. While the selectivity (i.e., ethanol/ethanol + ethyl acetate) to ethanol is higher for the catalysts prepared by ion exchange than that found with the impregnated catalysts, significant levels of ethyl acetate were observed for all ion exchanged catalysts. This result most likely indicates that excess Zn is present on the surface of these catalysts; Zn is an active catalyst for the transesterification reaction.

If the transesterification reaction is catalyzed by excess Zn on the surface (i.e., Zn not associated with Pd), one should be able to control the extent of this reaction by varying the Pd–Zn ratio. To test this hypothesis, a series of 2.8% Pd–Zn/SiO_2 samples were prepared using the ion-exchange technique for Pd addition in which the Pd : Zn ratio was varied from 1 : 1 up to 1 : 5. Results obtained with these catalysts are given in Table 3. A significant trend in selectivity to ethanol is evident with changing Pd : Zn ratios. At a Pd : Zn ratio of 1 : 1, the catalyst activity is almost equivalent to the catalyst with a ratio of 1 : 2, but the selectivity to ethanol is much higher (73 vs 55%). As the Zn loading is increased to a Pd : Zn ratio of 1 : 5 the selectivity to ethanol de-

TABLE 3

Methyl Acetate Hydrogenation over 2.8 wt% Pd : Zn/SiO_2 Prepared by Ion Exchange of $Pd(NH_3)_4Cl_2$ (Davison Grade 59 SiO_2, 300°C, 750 psig, H_2/MeOAc = 4.5)

Pd : Zn[a]	S.A.[b]	Rate (μmole/g sec)				EtOH
		MeOH	EtOH	EtOAc	Adjusted[c] rate	EtOH + EtOAc
1 : 0	216	3.17	0.02	0.86	0.88	0.02
1 : 1	—	5.70	3.64	1.35	5.00	0.73
1 : 2	193	8.72	3.73	3.05	6.78	0.55
1 : 5	226	4.60	0.41	2.18	2.59	0.16

[a] Expressed as atomic ratio of Pd : Zn.

[b] N_2 BET surface area in m^2 g^{-1}

[c] Adjusted rate = rate of EtOH + EtOAc.

creases further; see Table 3. This would be the predicted trend if the transesterification reaction is catalyzed by Zn which is not associated with the Pd component, because it is reasonable to assume that more isolated Zn should be present as the Zn loading is increased.

It is also evident from the data in Table 1 and Table 3 that there is an optimum Pd : Zn ratio which should be employed to maximize the catalyst activity. Increasing the Zn loading above a Pd : Zn ratio of 1 : 2 results in a dramatic decrease in activity. It would appear that, for this series of catalysts, a trade-off exists between overall activity and selectivity to ethanol and that the Pd : Zn loading levels can be adjusted to maximize either activity or selectivity.

It is interesting to note that the apparent activation energy for methyl acetate hydrogenation is dependent on the Pd : Zn ratio in the catalyst. As shown in Table 4, increasing the Pd : Zn ratio from 1 : 1 to 1 : 5 resulted in an increase in the apparent activation energy from 16 to 30 kcal/mole. The change in activation energy is most likely due to a change in the Pd : Zn stoichiometry within the Pd–Zn bimetallic particles. It has been reported that in Pd/ZnO catalysts both PdZn and Pd_2Zn_3 are present following reduction in hydrogen (*3*). In their study on isoprene hydrogenation, Zakumbaeva *et al.* postulated that a small number of pure Pd particles are required to activate H_2 and that PdZn bimetallics are not effective for H_2 activation. If their theory is true, the change in activation energy with Pd : Zn ratios may be indicative of the relative distribution of PdZn, Pd_2Zn_3, and pure Pd particles on the SiO_2 support. As the Zn loading increases (i.e., lower Pd : Zn ratios), one would expect fewer pure Pd particles to be present and a corresponding increase in the number of PdZn and Pd_2Zn_3 particles. This shift in particle composition may also explain the decrease in activity that was observed as the loading of Zn was increased (see Tables 1 and 3).

TABLE 4

Methyl Acetate Hydrogenation with 2.8% Pd : Zn/SiO_2 Apparent Activation Energies (Davison Grade 59 SiO_2, 280–300°C, 700 psig, H_2/MeOAc = 3.0)

Pd : Zn ratio	Apparent E_a (Kcal/mol)
1 : 1	16.2
1 : 2	23.3
1 : 5	29.9

While the results obtained using the catalysts prepared by ion-exchange exhibit interesting trends with metal loading and Pd : Zn ratios, the overall activity of the 1% Pd–Zn/SiO_2 and the 2.8% Pd–Zn/SiO_2 samples are not significantly different from the samples prepared by wet impregnation (when adjusted for Pd metal loading). This was somewhat surprising, as the ion-exchange technique should result in highly dispersed Pd and thus increased activity relative to catalysts prepared by impregnation.

When impregnating the Zn component onto the Pd/SiO_2 precursor, it was noted that the pH of the impregnating solution was very low (<1). It is plausible that addition of the Zn at such low pH results in a dissolution of unreduced Pd from the support surface and a subsequent coimpregnation of both Pd and Zn. Given that the ion-exchange procedure was employed to fix the Pd dispersion prior to addition of the Zn component, redistribution of the Pd component is undesirable and the preparative procedure was once again altered in an attempt to stabilize the Pd component prior to Zn addition.

While there are several methods which may stabilize the Pd component prior to Zn addition (e.g., raise the pH of the Zn solution, change the Pd or Zn precursor, etc.), one of the simplest methods is reduction of the Pd after ion-exchange. Metallic Pd should be stable under the acidic conditions encountered during impregnation. A series of 2.8% Pd–Zn/SiO_2 samples were prepared in which the Pd was reduced in H_2 at 200°C prior to impregnation of Zn.

The catalytic results obtained with these catalysts are presented in Table 5. A substantial increase in catalytic activity is evident for all catalysts when compared to the catalysts prepared by the other two procedures. Even the monometallic Pd/SiO_2 catalyst exhibited higher activity than the catalysts prepared without intervening H_2 reduction. However, addition of Zn still resulted in a sixfold increase in the rate of methyl acetate hydrogenation compared to the Pd/SiO_2 catalyst.

As in the case of the previous samples prepared without reduction of the Pd prior to Zn addition, the Pd : Zn ratio has a significant effect on the catalyst performance. Addition of Zn at an atomic Pd : Zn ratio of 1 : 1 results in improved activity and a selectivity to ethanol of 63%. Increasing the Pd : Zn ratio from 1 : 1 to 1 : 2 does not alter the activity of the catalyst, but the selectivity to ethanol drops from 63 to 46%. Increasing the Zn loading above a Pd : Zn ratio of 1 : 2 results in a further decrease in both the selectivity to ethanol and the overall activity of the catalyst. In fact, catalysts with Pd : Zn ratios of 1 : 5 and higher exhibited lower activity for methyl acetate hydrogenation than the Pd/SiO_2 sample.

TABLE 5

Methyl Acetate Hydrogenation with Pd : Zn/SiO_2 Prepared by Reduction of Pd Prior to Zn Addition (Davison Grade 59 SiO_2, 2.8% Pd, 300°C, 700 psig, H_2/MeOAc = 3.0)

Pd : Zn[a]	Rate (μmole/g sec)				EtOH
	MeOH	EtOH	EtOHc	Adjusted[b] rate	EtOH + EtOAc
1 : 0	21.	3.5	2.1	5.6	0.63
1 : 1	46.	24.	14.	38.	0.63
1 : 2	48.	16.	19.	35.	0.46
1 : 5	6.7	0.7	2.8	3.5	0.20
1 : 10	2.6	0.08	1.1	1.2	0.07

[a] Atomic ratio of Pd : Zn.

[b] Adjusted rate = rate of EtOH + EtOAc.

Based on these results, it is clear that the optimum preparative procedure for the formation of Pd–Zn bimetallics on SiO_2 requires stabilization of the Pd component prior to Zn addition. It is reasonable to assume that the active component in these catalysts are bimetallic Pd–Zn particles similar to those reported in Pd/ZnO and that the use of supported Pd–Zn bimetallics offer improved catalyst performance compared to Pd/ZnO.

Characterization Studies

As noted above, previous studies of Pd/ZnO have demonstrated that a strong interaction exists between reduced Pd and Zn and that the predominant phases may be PdZn and Pd_2Zn_3. XRD patterns were obtained for the 5% Pd–Zn (1 : 2)/SiO_2 sample which was prepared without prereduction of the Pd prior to Zn addition. This sample was chosen because of the high Pd loading level, which would result in better sensitivity. Prior to reduction, the XRD pattern consisted of a number of weak, broad peaks which correspond to PdO (Table 6). No peaks attributable to any Zn species could be identified in the pattern. The peak position of the most intense peak of PdO, the (101) reflection, is in agreement with the lit-

TABLE 6

XRD Results for 5% Pd–Zn (1 : 2)/SiO_2

Treatment	Phase	Reflection	2θ	d-Spacing
Literature	PdO	101	33.86	2.64
	Pd	111	40.11	2.25
Pd–Zn/SiO_2				
Fresh	PdO	101	33.86	2.64
Reduced at 200°C	(Pd)	111	41.52	2.17
Oxidized at 25°C	(Pd)	111	41.54	2.17
Rereduced at 200°C	(Pd)	111	41.51	2.17
Reoxidized at 25°C	(Pd)	111	41.51	2.17

Note. (Pd)—Strongly distorted.

erature value for PdO (*10*). The crystalline size of the PdO was estimated to be 40 Å.

Following reduction in hydrogen, the peak attributed to the PdO (101) reflection disappeared and a new peak was evident at a 2θ of 41.52° (d-spacing of 2.17 Å). This is significantly different from the Pd(111) reflection typically observed at 40.10°. The d-spacings for PdZn and Pd_2Zn_3 have been reported to be 2.19 (*11*) and 2.15 Å (*12*), respectively. The peak observed in this study was very broad and may actually consist of a mixture of the PdZn and Pd_2Zn_3 phases as reported by Zakumbaeva *et al.* (*3*). The apparent particle size calculated from line broadening is 28 Å, which is significantly smaller than the PdO particle size prior to reduction. The apparent reduction in particle size may be attributed to the presence of both PdZn and Pd_2Zn_3 which result in overlapping peaks and a broad peak in the XRD pattern.

Surprisingly, repeated oxidation/reduction cycles did not alter the XRD pattern, indicating that the bulk Pd–Zn interaction is stable at room temperature. This is in contrast to the previous XPS studies on Pd/ZnO, where the Pd–Zn interaction was apparently disrupted by oxidation in air at room temperature (*2*).

The 5% Pd–Zn(1 : 2)/SiO_2 and the 2.8% Pd–Zn(1 : 2)/SiO_2 samples prepared without intervening Pd reduction were characterized with XPS; see Table 7 and Fig. 1.

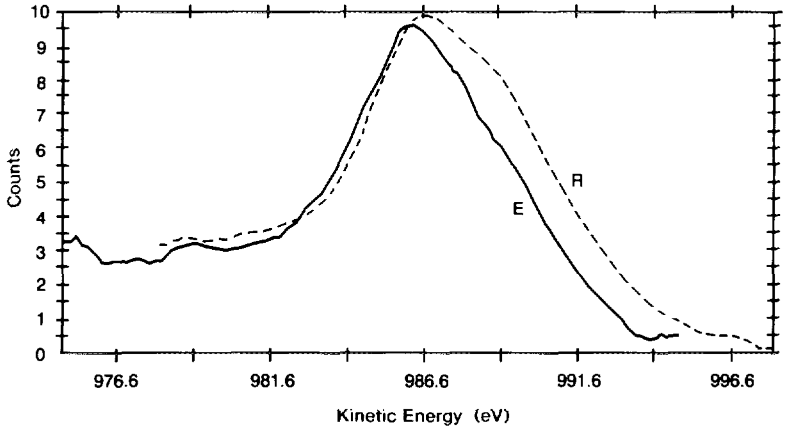

FIG. 1. Zn LMM Auger spectra obtained for the 5% Pd–Zn(1 : 2)/SiO_2 catalyst: (E) fresh sample and (R) reduced in hydrogen at 200°C.

TABLE 7

XPS Results for Pd–Zn/SiO$_2$ Catalysts Prepared without Pd Reduction prior to Zn Addition

Catalyst/treatment	Pd $3d_{5/2}$	Zn $2p_{3/2}$	Zn LMM
5% Pd–Zn(1 : 2)/SiO$_2$			
Fresh	336.8	1022.9	986.2
Reduced at 200°C	335.6	1022.6	986.2, 989.4
Oxidized at 25°C	335.5	1022.6	986.7
Rereduced at 200°C	335.6	1022.7	986.7, 990.1
Reoxidized at 25°C	335.7	1022.7	986.4
2.8% Pd–Zn(1 : 2)/SiO$_2$			
Fresh	336.9	1022.9	986.2
Reduced at 200°C	335.5	1022.6	986.2, 990.2
Oxidized at 25°C	335.5	1022.7	986.5
Rereduced at 200°C	335.6	1022.6	986.6, 989.8
Reoxidized at 25°C	335.6	1022.6	986.7

Note. All peaks referenced to the Si $2p$ peak assigned to be 103.4 eV.

Comparable results were obtained for samples prepared with intervening hydrogen reduction prior to Zn addition. On the freshly prepared catalysts, the XPS data are consistent with both Pd and Zn being present as the oxides, i.e., PdO and ZnO. Upon reduction at 200°C, the Zn $2p_{3/2}$ peak remains at ~1022.7 eV. The Pd $3d_{5/2}$ peak shifts to lower binding energy, indicating reduction of the Pd. In addition to the shift in the Pd $3d_{5/2}$ peak, the Zn LMM Auger peak broadens significantly toward lower binding energy and narrows upon exposure to air. This is similar to the results observed with Pd/ZnO (*2*) and is additional evidence for the formation of PdZn bimetallics following reduction in hydrogen.

The sensitivity of the Zn Auger peak to oxidation is in contrast to the XRD data reported above. This indicates that the Pd–Zn bimetallic particles are sensitive to surface oxidation, but that bulk oxidation does not readily occur at room temperature.

Results from CO chemisorption studies of the samples prepared by prereduction of the Pd prior to Zn addition are given in Table 8. The CO adsorption dramatically decreased as Zn was added to the catalyst. The apparent Pd particle size was calculated assuming a 1 : 1 CO/Pd stoichiometry. As noted above, the stoichiometry of CO adsorption is not known for Pd–Zn bimetallics and this assumption is highly questionable.

In an effort to obtain a better measurement of the particle sizes of the Pd–Zn bimetallics present on the samples prepared by prereduction of the Pd prior to Zn addition, STEM studies of this series of catalysts were conducted. Samples were reduced at 200°C in H$_2$, cooled, and then exposed to air at room temperature prior to transfer to the STEM. As discussed above, room temperature air exposure has been shown to disrupt the Pd–Zn interaction at the particle surface but does not affect the

TABLE 8

CO Chemisorption Results for 2.8% Pd–Zn/SiO$_2$

	(μmole/g ads)			
Pd : Zn ratio	CO$_{rev}$	CO$_{ir}$	CO$_{total}$	d (Å)
1 : 0	28	120	148	26
1 : 2	12	20	32	153
1 : 10	5.7	6.3	12	468

TABLE 9

STEM Data for 2.8% Pd–Zn/SiO_2 (Davison Grade 59 SiO_2, Reduced Prior to Zn Addition)

Pd : Zn	Particle size (Å)	Atomic % Zn
1 : 0	17 ± 7	0
1 : 1	32 ± 15	31 ± 13
1 : 2	26 ± 11	36 ± 9
1 : 5	33 ± 27	40 ± 13

bulk Pd–Zn interaction. While it would be preferable to measure particle sizes on samples which had not been exposed to air, the microscope used in this study did not have a pretreatment chamber and air exposure was unavoidable. The measured particle sizes for this series of catalysts are given in Table 9. Addition of Zn to the catalysts resulted in a slight increase in particle size when compared to the Pd/SiO_2 precursor, but the average particle size for all of the Zn samples was approximately 30 Å. Comparing the results in Tables 8 and 9, it is apparent that CO chemisorption is suppressed by the incorporation of Zn in these catalysts and cannot be used to effectively characterize these samples.

The STEM/EDS results gave direct confirmation of the presence of bimetallic Pd–Zn particles. As can be seen in the results presented in Table 9, the atomic percent of Zn in the particles increases slightly as the Zn loading is increased, but in all cases the Zn content of the bimetallics is below the ratio expected for either PdZn or Pd_2Zn_3 phases. It should be noted, however, that these samples were exposed to air prior to analysis and this may have altered the Pd–Zn ratio in the particles. In particular, exposure to air could have caused the precipitation of ZnO from the surface of the particles, thus increasing the Pd–Zn ratio.

The atomic composition of the particles as a function of particle size for the catalyst with a Pd/Zn ratio of 1 : 2 is shown in Fig. 2. As can be seen in this figure, the composition of the bimetallic particles is not dependent on the particle size. Similar results were obtained for the catalysts with Pd/Zn ratios of 1 : 1 and 1 : 5.

The results from the catalyst characterization studies support a model in which both Pd–Zn bimetallic particles and excess Zn^{2+} are present on the SiO_2 support. While the exact composition of the Pd–Zn bimetallics could not be unambiguously determined, the XRD results are consistent with the Pd–Zn being distributed between PdZn and Pd_2Zn_3 phases. The Zn Auger clearly shows that two forms of Zn are present following reduction in hydrogen; Zn on the surface and reduced Zn in the bimetallic particles. The improved methyl acetate hy-

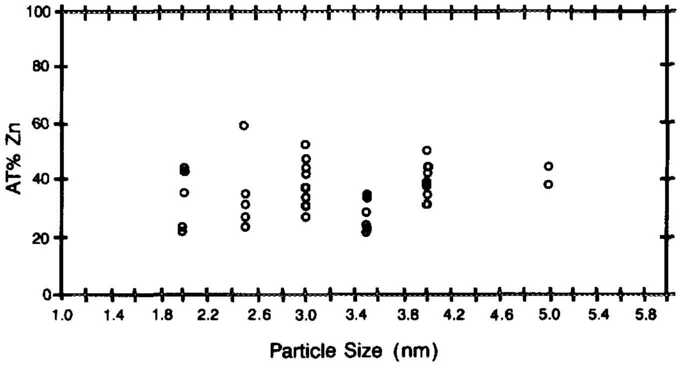

FIG. 2. Zn composition versus particle size as measured by EDS for 2.8% Pd–Zn(1 : 2)/SiO_2 prepared by prereduction of Pd prior to Zn addition.

drogenation activity obtained in this study can be attributed to the formation of the Pd–Zn bimetallic particles, while the secondary transesterification reaction resulting in the formation of ethyl acetate can be attributed to the excess Zn^{2+} on the SiO_2 support.

CONCLUSIONS

Supporting Pd–Zn bimetallic particles on SiO_2 results in catalysts which are active for the hydrogenation of methyl acetate to methanol and ethanol. The selectivity to ethanol (as opposed to ethyl acetate) can be modified by adjusting the Pd : Zn ratio. Pd : Zn ratios of 1 : 2 produce the most active catalysts, with higher Zn loading resulting in a decrease in activity. Catalyst characterization studies support the conclusion that addition of Zn to the supported Pd/SiO_2 catalysts result in the formation of Pd–Zn bimetallics. The Pd–Zn bimetallic particles are most likely distributed between PdZn and Pd_2Zn_3, although the exact distribution of these phases could not be measured. The optimum catalyst preparative procedure is one where the Pd is stabilized by reduction prior to addition of the Zn component.

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