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increase with the decrease in the micropore size. However, our limited data are insufficient to support the merits of one over the other.

Conclusion

We have shown that low-temperature ^{129}Xe NMR together with xenon adsorption isotherms provides valuable information about changes in H–Y zeolite resulting from steaming. In particular, we find that (1) in dealuminated zeolites, the number of micropores with pore size similar to the supercage can be estimated by associating the ^{129}Xe NMR line-width minimum and the chemical shift at the minimum with a definite physical state of the xenon in the supercage, (2) changes in the supercage size can be determined from σ_e, the chemical shift at the NMR end point, and (3) the chemical shift at the limit of zero xenon loading, σ_0, is affected by changes in the micropore size as well as the distribution of the sizes.

Appendix

According to the rapid exchange model in ref 1, the ^{129}Xe NMR chemical shift at the limit of zero xenon loading can be written as

$$\sigma_0 = \sigma_s(N_s/V)(k_a/k_d)/[1 + (N_s/V)(k_a/k_d)] \qquad \text{(A1)}$$

At the limit of $(N_s/V)(k_a/k_d) \ll 1$, (A1) reduces to (3). Let us examine (A1) for the condition of a constant N_s. Then we have, using (5) and (6)

$$\begin{aligned}\sigma_0 &= \sigma_s\xi\langle(\lambda A + \xi)^{-1}\rangle \qquad \text{(A2)}\\ &= \sigma_s\xi\kappa\langle(V + \xi\kappa)^{-1}\rangle\end{aligned}$$

where $\xi = N_s d^2 v/k_d$ is a function of the temperature only. The second equality follows from $A\lambda = V/\kappa$, where κ^{-1} is a proportionality constant between $A\lambda$ and V. With $x = V - V_0$ and expanding $(V + \xi\kappa)^{-1}$ around $(V_0 + \xi\kappa)$

$$(V + \xi\kappa)^{-1} = (V_0 + \xi\kappa)^{-1}[1 - x/(V_0 + \xi\kappa) + x^2/(V_0 + \xi\kappa)^2 + ...]$$

we obtain, to second order

$$\sigma_0 = \sigma_s\xi\kappa(V_0 + \xi\kappa)^{-1}[1 + \Delta V^2/(V_0 + \xi\kappa)^2] \qquad \text{(A3)}$$

The ratio σ_0/σ_0(H–Y) calculated from (A3) differs from (12) by having V_0 renormalized to $V_0 + \xi\kappa$.

For the condition of constant N_s/A, we obtain

$$\sigma_0 = \sigma_s(\xi/A)\langle(\lambda + \xi/A)^{-1}\rangle \qquad \text{(A4)}$$

Equation A4 gives the identical relationship between σ_0 and λ as found by Demarquay and Fraissard.[14] The evaluation of (A4) can be performed in the same way as that of (A2).

Glossary

L_m	(mmol of Xe/g) loading corresponding to minimum line width in ^{129}Xe NMR. Locates just before pressure rise in adsorption isotherm. Corresponds to loading of 8.25 xenon atoms per supercage for H–Y zeolite
L_e	(mmol of Xe/g) loading at the NMR end point where solid xenon is first observed in ^{129}Xe NMR
L_s	(mmol of Xe/g) loading at saturation ($P = P_0$) in adsorption isotherm. Corresponds to total pore capacity accessible to xenon
L_{mi}	(mmol of Xe/g) total micropore (zeolite supercage) capacity. Equal to L_e for H–Y since pure H–Y has no mesopores
n	(mmol of micropores/g) total number of micropores in 1 g of sample.
V_m	(Xe atoms/micropore) number of xenon atoms in a micropore at loading L_m
V_e	(Xe atoms/micropore) total number of xenon atoms in a micropore at the NMR end point
V	free volume inside a micropore
σ_0	NMR chemical shift of adsorbed xenon at the limit of zero xenon loading
σ_e	NMR chemical shift of adsorbed xenon at the NMR end point
σ_{mi}	NMR chemical shift of xenon in a completely filled micropore

Registry No. ^{129}Xe, 13965-99-6.

Evidence for Migration of Palladium Species during Ethylene Dimerization on Palladium-Exchanged Na–Y and Ca–Y Zeolites Studied by Gas Chromatography Correlated with Electron Spin Resonance and Electron Spin-Echo Modulation Spectroscopies

Ashim K. Ghosh and Larry Kevan*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641 (Received: October 6, 1988)

Various palladium-exchanged Na–Y and Ca–Y zeolites (0–14 Pd^{2+}/unit cell) have been studied for ethylene dimerization. The reaction was found to occur on all O_2-pretreated Pd-exchanged Y zeolites at 25 °C after an induction period that is dependent on the palladium content, type of cocation used (Na^+ or Ca^{2+}), and reaction temperature. This induction period is apparently due in part to formation of active Pd^+ species and their migration toward the zeolite supercage. The generation of Pd^+ species during catalyst pretreatment in H_2 ether eliminates or greatly shortens the induction period. This together with electron spin resonance (ESR) and electron spin-echo modulation (ESEM) results confirms that monovalent palladium cations are active for the dimerization reaction. ESR spectra of NaPd–Y and CaPd–Y zeolites recorded at various reaction times show that various Pd^+ species ($g_\parallel = 2.88$–2.33, $g_\perp = 2.10$) are coordinated to ethylene during the reaction. These can be detected by ESEM methods and confirm that a Pd^+–ethylene complex is formed during the dimerization reaction. The results are discussed in terms of a mechanism for ethylene dimerization on zeolites. The results are also compared to previously obtained data on palladium-exchanged Na–X and Ca–X zeolites to examine the effect of the Si/Al ratio in the generation and migration of palladium species in the zeolites.

Introduction

Palladium-exchanged zeolites are used as catalysts for ethylene dimerization.[1-8] It is generally accepted that palladium species directly participate in the formation of catalytically active sites. However, the oxidation state of the active palladium species is

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uncertain. Lapidus et al.[3,4] reported that when samples of Na–Y and Ca–Y exchanged with $[Pd(NH_3)_4]^{2+}$ were pretreated in argon or hydrogen at 380 °C, 95% of the Pd^{2+} cations were converted to Pd^0 and the catalysts were found to be almost inactive for ethylene dimerization. However, if the catalysts were heated in flowing air at 380 °C to decompose the $[Pd(NH_3)_4]^{2+}$ and generate Pd^{2+} and Pd^+, the catalysts were found to be highly active for ethylene dimerization. The results suggest that Pd^0 is inactive but that Pd^{2+} and/or Pd^+ species are catalytically active for the reaction. In previous studies,[7,8] we have reported that various paramagnetic Pd^+ species showing ESR signals with $g_{\parallel}$ = 2.88–2.33 all with the same $g_{\perp}$ = 2.10 are observed prior to dimerization of ethylene on palladium-exchanged Na–X and Ca–X zeolites. Electron spin-echo modulation (ESEM) studies[8] confirmed that ethylene is complexed with the Pd^+ species, and consequently monovalent palladium cations are considered to be catalytically active sites.

It is known that the catalytic efficiency of a cation-exchanged zeolite for nonacid catalysis is dependent on the type, amount, and location of active cations in the zeolite structure.[9–12] Previous studies[13,14] in this laboratory have shown that the location of transition-metal cations in zeolites can be controlled by several parameters including (a) the charge and size of the coexchanged cation, (b) the Si/Al ratio, (c) the structural type of the zeolite, (d) the thermal pretreatment, and (e) the presence of various adsorbates. We have previously observed the formation of paramagnetic Pd^+–ethylene complexes and dimerized products (butenes) after an induction period that is dependent on the concentration of palladium, coexchanged cation (Na^+ or Ca^{2+}), and reaction temperature.[7,8] These results are explained by different locations of the catalytically active palladium species within the zeolite structure.

Zeolites X and Y are structurally identical with different Si/Al ratios of 1.2 and 2.4, respectively. Accordingly, Y zeolites contain fewer charge-balancing cations. A comparison of the results of ethylene dimerization on palladium-exchanged X and Y zeolites provides a better understanding of the factors controlling the generation and location of paramagnetic species in X and Y zeolites.

The present work describes the results of ethylene dimerization on Pd-exchanged Na–Y and Ca–Y zeolites with use of a static reactor. With electron spin resonance (ESR) spectroscopy, the generation and migration of paramagnetic species are monitored before and during the ethylene reaction. In order to obtain information on the immediate environment of the active catalytic site, ESEM spectra of the Pd^+ species in the zeolite are recorded with adsorbed C_2D_4. In this paper, these results will also be compared to previously obtained data on palladium-exchanged Na–X and Ca–X zeolites.

Experimental Section

Linde Na–Y zeolite was obtained from the Union Carbide Corp. Ca–Y zeolite was prepared from Na–Y by ion exchange with 0.1 M $CaCl_2$ solution at 80 °C for 1 week. Palladium was introduced into the zeolite as $Pd(NH_3)_4{}^{2+}$ cation by ion exchange with various amounts of 0.01 M palladium tetraammine chloride (Alfa) solution at room temperature for 24 h. Commercial atomic absorption was used to determine the palladium content. In this work, ethylene dimerization was studied with use of samples of Na–Y, $NdPd_2$–Y, $NaPd_5$–Y, $NaPd_{10}$–Y, $NaPd_{14}$–Y, Ca–Y, $CaPd_2$–Y, $CaPd_5$–Y, $CaPd_{10}$–Y, and $CaPd_{14}$–Y zeolites where the subscript refers to the number of palladium ions per unit cell. Ethylene and deuterated ethylene were obtained from the Linde Division of Union Carbide and MSD Isotopes, respectively.

TABLE I: Ethylene Dimerization on Various Palladium-Exchanged Na–Y and Ca–Y Zeolites at 25 °C with Use of a Static Reactor

catalyst	pretreatment	induction period/ min	rate of dimerization[a]/ mmol g^{-1} h^{-1}
Na–Y[b]	O_2/500 °C/16 h		
$NaPd_2$–Y	O_2/500 °C/16 h	150	0.03 (0.1%, not obs)
$NaPd_5$–Y	O_2/500 °C/16 h	90	0.4 (10%, not obs)
	O_2/500 °C/16 h/H_2/ 25 °C/24 h	50	4.1 (84%, not obs)
$NaPd_{10}$–Y	O_2/500 °C/16 h	45	6.9 (91%, not obs)
	O_2/500 °C/16 h/evac/ 500 °C/46 h	40	8.4 (99%, not obs)
	O_2/500 °C/16 h/H_2/ 25 °C/24 h	0	8.3 (98%, not obs)
$NaPd_{14}$–Y	O_2/500 °C/16 h	25	9.6 (56%, 1 h)
Ca–X[b]	O_2/500 °C/16 h		
$CaPd_2$–Y	O_2/500 °C/16 h	40	2.2 (21%, not obs)
$CaPd_5$–Y	$O_2$0500 °C/16 h	20	3.7 (67%, not obs)
	O_2/500 °C/16 h/H_2/ 25 °C/1 h[c]	0	5.0 (37%, 1 h)
$CaPd_{10}$–Y	O_2/500 °C/16 h	10	5.1 (55%, 1 h)
	O_2/500 °C/16 h/H_2/ 25 °C/1 h[c]	0	7.0 (14%, 10 m)
$CaPd_{14}$–Y	O_2/500 °C/16 h	5	7.1 (37%, 30 m)

[a] In parentheses are given the percent ethylene converted in 3 h and the period of reaction at which the catalyst started deactivating. Not obs means deactivation was not observed in 3 h. [b] Reaction studied also at 50, 65, and 85 °C. [c] Sample became brown to gray immediately on exposure to H_2.

Experiments were carried out with a fixed bed type reactor made of glass with a closed, static reactor system of total internal volume of about 58 cm^3. A zeolite sample of 0.05 g was placed on a sintered glass disk inside the reactor. The zeolite was heated in oxygen flow (30 cm^3/min) while the temperature was slowly increased to 500 °C at which heating was continued for 16 h. In most cases, the O_2-pretreated sample was cooled to room temperature and O_2 was briefly pumped before the sample was subjected to ethylene dimerization. In some cases, the O_2-pretreated sample was either subsequently evacuated at 500 °C for 46 h or exposed to H_2 (5 Torr) at 25 °C for a period followed by pumping off unreacted H_2 before the samples were used for ethylene dimerization.

Ethylene dimerization was studied on pretreated zeolite samples by introducing a measured quantity of ethylene (0.65 mmol) into the reactor containing pretreated zeolite at a specific reaction temperature. The reaction products were analyzed at different reaction times by withdrawing aliquots for analysis by an on-line gas chromatograph (Varian Model 3300 equipped with an electronic integrator with a thermal conductivity detector with a 6-ft column (i.d. 0.085 in.) packed with 0.19 wt % picric acid on 80/100-mesh Graphic GC support at 35 °C). The rate of ethylene dimerization was calculated from the initial slope of product formation.

The generation and migration of paramagnetic palladium species in the system were examined by ESR. The reactor was connected to a small quartz tube (3-mm o.d.) so that the ESR spectrum could be recorded without exposure of the sample to air. Both before and after various amounts of ethylene reaction, the sample was quenched to room temperature and transferred in situ to the ESR tube. ESR spectra were immediately recorded at 77 K with a Varian E-4 spectrometer. Electron spin-echo spectra were recorded at 4.2 K with a home-built spectrometer.[15,16] Deuterated ethylene was used for ESEM measurements in order to detect and analyze deuterium modulation.

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TABLE II: Comparison of Ethylene Dimerization on O_2-Pretreated Palladium-Exchanged X and Y Zeolites

zeolite	reactn, temp/°C	induction period/min	rate of dimerization/ mmol g^{-1} h^{-1}	deactivation[a]	ref
$NaPd_{1.6}$-X	25	*b*			7.8
	50	*b*			7, 8
$NaPd_2$-Y	25	150	0.03	not obs	this work
	50	30	3.9	not obs	this work
$NaPd_{12.5}$-X	25	*c*			7, 8
	50	60	5.6	not obs	7, 8
$NaPd_{10}$-Y	25	45	6.9	not obs	this work
	50	0	14.6	1 h	this work
$CaPd_{1.7}$-X	25	30	2.0	not obs	7, 8
$CaPd_2$-Y	25	40	2.2	not obs	this work
$CaPd_{9.6}$-X	25	15	2.9	2.5 h	7, 8
	50	0	9.3	50 min	7, 8
$CaPd_{10}$-Y	25	10	5.1	1	this work
	50	0	15.6	20 min	this work

[a] Period of reaction at which the catalyst started deactivating. Not obs means deactivation was not observed in 3 h. [b] No reaction was found to occur at 25, 50, and 65 °C, but it occurs at 85 °C. [c] Only a trace amount of butenes was detected after 4 h reaction period.

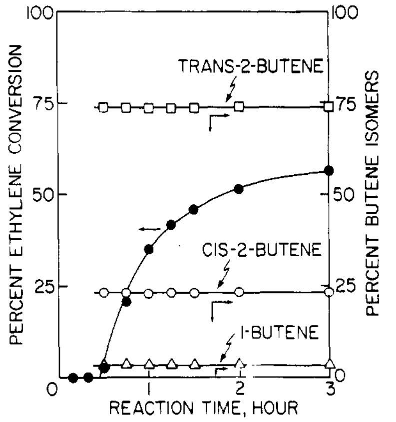

Figure 1. Ethylene dimerization on O_2-pretreated $NaPd_{14}$-Y zeolite. Reaction conditions: 0.05 g, catalyst; 400 Torr, C_2H_4; reaction temperature, 25 °C.

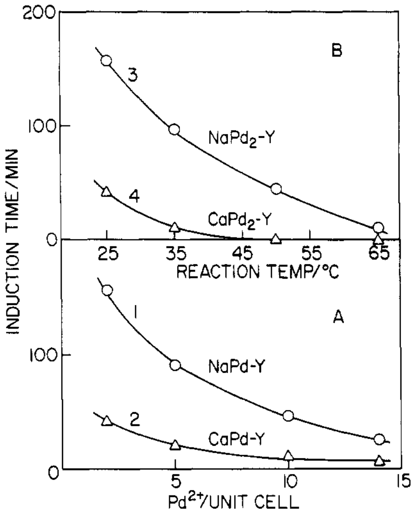

Figure 2. Effect of (A) Pd concentration and (B) reaction temperature on induction time for ethylene dimerization on Pd-Y zeolites. Reaction conditions are the same as in Figure 1.

Results

Catalytic Studies. All catalytic data of ethylene dimerization on various Y zeolites are summarized in Table I. No reaction was found to occur when Na-Y and Ca-Y zeolites were exposed to ethylene. However, the dimerization reaction was found to occur on all palladium-exchanged Y zeolites, confirming that palladium directly participates in the formation of catalytically active sites.[1-8]

In most cases, ethylene dimerization was studied on O_2-pretreated zeolite samples at a reaction temperature of 25 °C. All palladium-exchanged Na-Y and Ca-Y zeolites are shown to be active for ethylene dimerization. As expected, the rate of ethylene dimerization increases with decreasing induction time due to an increase of palladium content in the zeolite. A typical catalytic run of ethylene dimerization with a static reactor is shown in Figure 1. The *n*-butene reaction products were detected in the gas phase after an induction period of about 25 min. The isomers of *n*-butenes reach an equilibrium quite rapidly, as was previously observed in the case of Pd-exchanged Na-X and Ca-X zeolites.[8] It is noted that the percent ethylene converted in 3 h increases with increasing palladium content at low palladium exchange (e.g., $NaPd_2$-Y, $NaPd_5$-Y, $NaPd_{10}$-Y, $CaPd_2$-Y, and $CaPd_5$-Y) but decreases at high cation exchange (e.g., $NaPd_{14}$-Y, $CaPd_{10}$-Y, and $CaPd_{14}$-Y) due to catalyst deactivation. This catalyst deactivation is presumably due to reduction of active palladium cations to Pd^0 that occurs more rapidly if the cations occupy relatively more accessible sites, which is the case in higher palladium-exchanged zeolites. It is important to note that the samples slowly became buff or light brown in color during the reaction at 25 °C.

Figure 2 shows the effect of the palladium content in the zeolite and of the reaction temperature on the induction period. The induction time decreases slowly with an increase of palladium concentration or reaction temperature in both palladium-exchanged Na-Y or Ca-Y zeolites. It is important to note that a shorter induction period is required in CaPd-Y zeolite in comparison to NaPd-Y zeolite (compare curves 1 and 2 in Figure 2a and curves 3 and 4 in Figure 2b).

In Table I are included results of ethylene dimerization on samples of $NaPd_{10}$-Y zeolite pretreated in O_2 with and without subsequent evacuation at 500 °C for 46 h. In both cases, the dimerization reaction occurs after an induction period that is slightly shorter in the "evacuated" sample. The rates of dimerization do not show an appreciable change with the pretreatment. As will be seen later, the evacuated sample possesses a small amount of Pd^+ ions, in addition to Pd^{3+} and Pd^{2+} ions. The shorter induction period observed in the evacuated samples seems due to the presence of catalytically active Pd^+ species.

The effect of prereduction of palladium cations in zeolite on ethylene dimerization was studied by exposing O_2-pretreated samples of $NaPd_5$-Y, $NaPd_{10}$-Y, $CaPd_5$-Y, and $CaPd_{10}$-Y to H_2 (see Table I). The samples turned rapidly from brown to gray in CaPd-Y and slowly to light brown in NaPd-Y on exposure to H_2. The reaction induction period is eliminated or greatly shortened due to catalyst pretreatment in H_2. As will be shown later, a significant amount of Pd^+ species is present in H_2-reduced samples in comparison to O_2-pretreated samples that do not show any Pd^+ species. Apparently, the induction period is eliminated or shortened due to the presence of Pd^+ ions, confirming that Pd^+ species are catalytically active for ethylene dimerization.

In Table II, comparison is made between results of ethylene dimerization on palladium-exchanged X and Y zeolites with similar Pd exchange levels. As mentioned earlier, all NaPd-Y

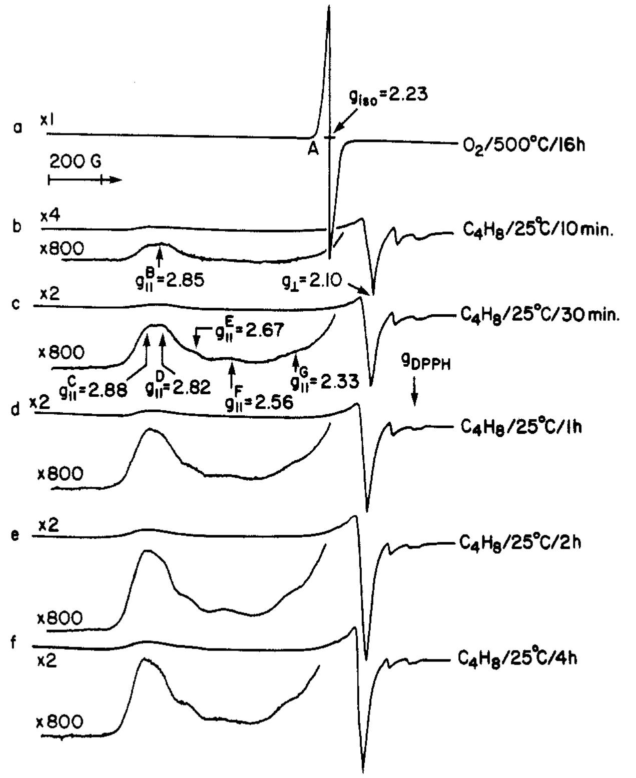

Figure 3. ESR spectra at 77 K of $NaPd_{10}$–Y: (a) after pretreatment under O_2 flow at 500 °C, (b–f) at different contact times with *cis*-2-butene in a static reactor at 25 °C.

zeolites are found to be catalytically active for ethylene dimerization at 25 °C. In contrast, palladium-exchanged Na–X zeolites are shown to be inactive for this reaction at 25, 50, and 65 °C for $NaPd_{1.7}$–X and at 25 °C for $NaPd_{12.5}$–X. However, the dimerization reaction was found to occur over these catalysts at higher reaction temperature after a longer induction period in comparison to NaPd–Y zeolites.

All Pd-exchanged Ca–X and Ca–Y zeolites are shown to be active for the dimerization reaction. The reaction occurs at a faster rate in CaPd–Y zeolites. However, little effect on the induction period was observed. In CaPd–Y zeolites catalyst deactivation occurs more rapidly than in CaPd–X zeolites.

Electron Spin Resonance Studies. Na–Y and Ca–Y zeolites pretreated in O_2 are white and do not show any ESR signal. Palladium-exchanged Na–Y or Ca–Y zeolites became white to buff or brown when pretreated in O_2 flow at 500 °,C. All O_2-pretreated NaPd–Y zeolites show an ESR isotropic signal at g = 2.23. This ESR peak has been previously seen in Pd–X zeolite and has been assigned to Pd^{3+} ions.[6–8,17,18] In contrast to NaPd–Y, the O_2-pretreated CaPd–Y zeolites at low palladium exchange [e.g., 2 Pd^{2+}/unit cell (UC)] do not show signal A attributed to Pd^{3+} ions. However, this signal A is present in higher palladium-exchanged Ca–Y zeolites (e.g., >5 Pd^{2+}/UC).

The absorption of 1-butene, and *cis*- and *trans*-2-butene was studied on a palladium-exchanged Na–Y zeolite. No appreciable difference was observed in the ESR spectra of the zeolite samples with adsorbed butene isomers. Figure 3 shows ESR spectra of $NaPd_{10}$–Y zeolite at various stages of adsorption of *cis*-2-butene at 25 °C. Signal A, attributed to Pd^{3+} ions, disappeared on exposure of the zeolite sample to butene, and a signal designated as B appeared at $g_{\parallel}$ = 2.85 and $g_{\perp}$ = 2.10. The signal intensity increases with time, and it seems that this peak resolves into peaks C and D at $g_{\parallel}$ = 2.88 and $g_{\parallel}$ = 2.82, respectively, with the same $g_{\perp}$ = 2.10. Additional peaks designated as E–G are observed at $g_{\parallel}$ = 2.68, 2.56, and = 2.33, respectively, all with the same $g_{\perp}$ = 2.10.

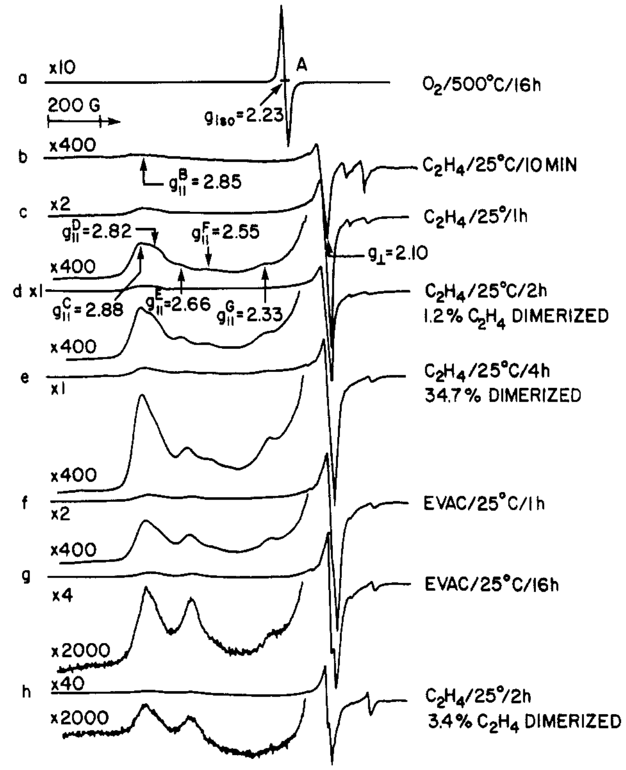

Figure 4. ESR spectra at 77 K of $NaPd_5$–Y: (a) after pretreatment under O_2 flow at 500 °C, (b–h) at different reaction times with ethylene in a static reactor at 25 °C.

As mentioned earlier, most of the catalytic studies were done with the O_2-pretreated samples. The ESR signal A at g_{iso} = 2.23, attributed to Pd^{3+} ions, in O_2-pretreated zeolite disappears completely on exposure of the sample to ethylene as can be seen in the spectrum recorded after 10 min of the reaction (Figure 4). A weak ESR signal B is observed at $g_{\parallel}$ = 2.85 and $g_{\perp}$ = 2.10, which is resolved into species C ($g_{\parallel}$ = 2.88, $g_{\perp}$ = 2.10) and D ($g_{\parallel}$ = 2.82, $g_{\perp}$ = 2.10) seen in spectra recorded at later stages. Additional species E ($g_{\parallel}$ = 2.66), F ($g_{\parallel}$ = 2.55), and G ($g_{\parallel}$ = 2.33) all with $g_{\perp}$ at 2.10 are observed. Simultaneously, ethylene dimerization products (*n*-butenes) are detected in the gas phase. All these ESR signals (B–G) have been previously assigned to Pd^+ species located at different sites.[7,8] When the sample is evacuated at 25 °C, signal intensities of all but species E and G decrease substantially. On further introduction of ethylene into the reactor, ethylene was dimerized to butene initially at a faster rate (compare conversion at 2 h), suggesting that Pd^+ species are catalytically active for the dimerization reaction. The features of the ESR spectrum do not change appreciably on further introduction of ethylene into the reactor. The intensities of the signals decrease gradually with time. The immediate disappearance of the ESR signal for Pd^{3+} ions and the gradual decrease of Pd^+ species imply that palladium cations are successively reduced to atomic Pd in the presence of ethylene and butenes.

When an O_2-pretreated sample was evacuated at 500 °C for 46 h, ESR signal A, attributed to Pd^{3+} ions, decreased by about 2 orders of magnitude and a new signal designated as B was observed at $g_{\parallel}$ = 2.85 and $g_{\perp}$ = 2.10 (Figure 5). Previously, under the same pretreatment conditions, Pd-exchanged Na–X and Ca–X zeolites showed ESR peaks at $g_{\parallel}$ = 3.01 and $g_{\perp}$ = 2.10 that were assigned to Pd^+ species.[6,7,17] On exposure of the evacuated sample to ethylene, signal A completely disappeared and signal B increased and later resolved into signals C and D with $g_{\parallel}$ = 2.88 and 2.82, respectively, both with $g_{\perp}$ = 2.10. The signals E–G are observed with the detection of butenes in the gas phase.

Ethylene dimerization was studied with use of samples of various Pd-exchanged Y zeolites pretreated in O_2 and subsequently reduced in H_2 at 25 °C. The O_2-pretreated samples became light brown in NaPd–Y and gray in CaPd–Y zeolites on exposure of the samples of H_2. However, ESR signal A, observed after O_2

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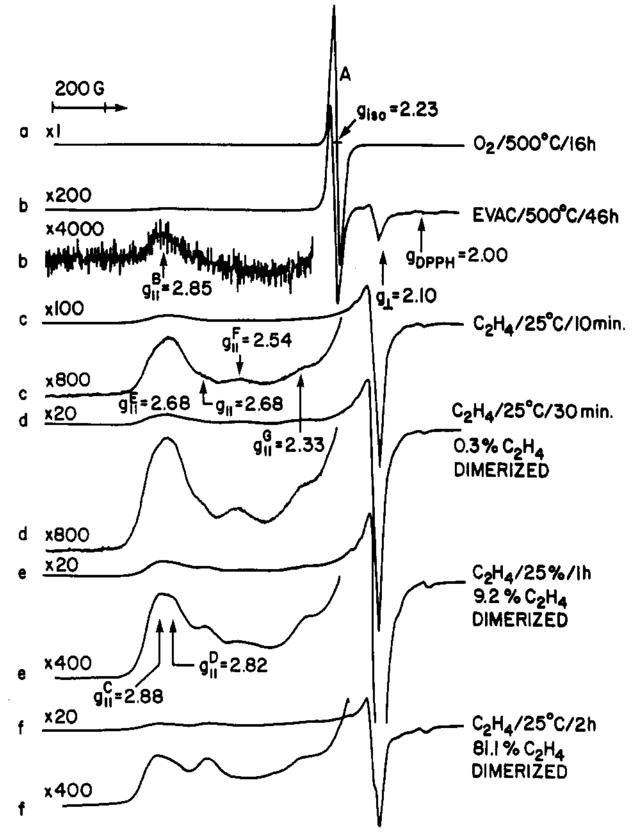

Figure 5. ESR spectra at 77 K of $NaPd_{10}$–Y: (a) after pretreatment under O_2 flow at 500 °C, (b) with subsequent evacuation at 500 °C for 46 h, (c–g) at different reaction times with ethylene in a static reactor at 25 °C.

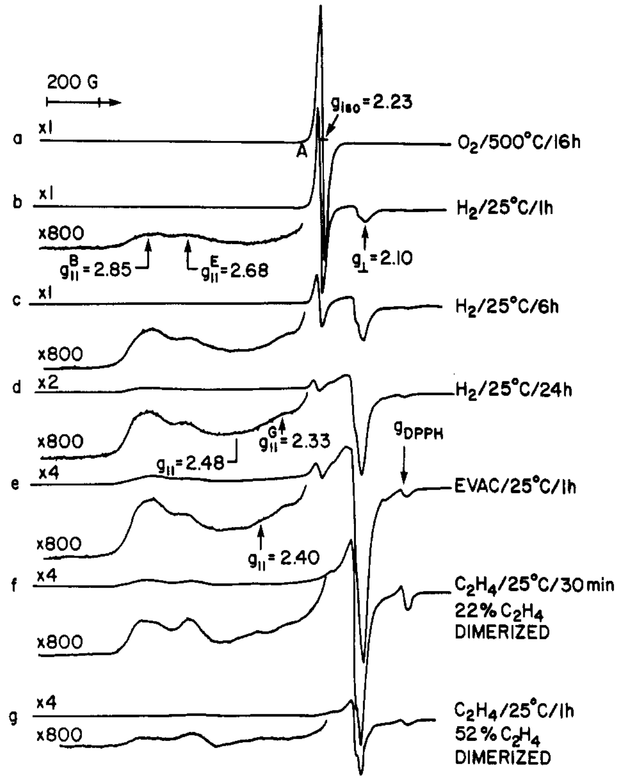

Figure 6. ESR spectra at 77 K of $NaPd_{10}$–Y: (a) after pretreatment under O_2 flow at 500 °C followed by brief evacuation at 25 °C, (b–d) at different contact times with H_2 (5 Torr) at 25 °C, (e) after subsequent evacuation at 25 °C for 1 h, (f–g) at different reaction times with ethylene in a static reactor at 25 °C.

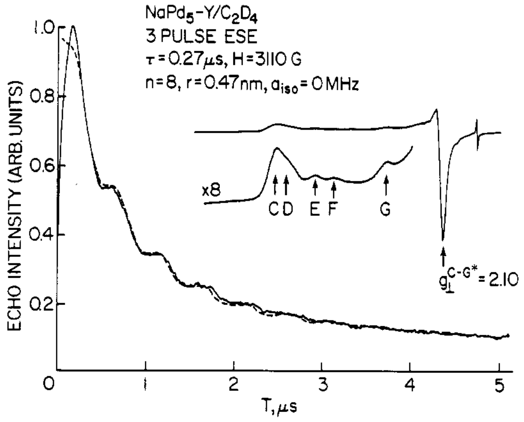

Figure 7. Experimental (—) and simulated (--) three-pulse ESEM spectra at 4 K of $NaPd_5$–Y with adsorbed C_2D_4 recorded at a magnetic field set at $g_{\perp}$(C–G) = 2.10 indicated by an asterisk on the inset at 77 K.

pretreatment, decreases slowly in the presence of H_2 in comparison to ethylene or butene. Various signals due to Pd^+ species are observed at $g_{\parallel}$ = 2.88–2.33 all with the same $g_{\perp}$ = 2.10 (Figure 6). When H_2 is pumped off at 25 °C, the ESR spectra do not change appreciably. On introduction of ethylene into the reactor containing the H_2-reduced sample, the intensity of the Pd^+ species decreases slightly and ethylene is dimerized with a shorter or no induction time, suggesting that Pd^+ species are involved in the dimerization reaction.

ESEM Studies. As mentioned earlier, species A in the O_2-pretreated zeolites, attributed to Pd^{3+} ions, diappears on exposure of the zeolite to ethylene and species B appears initially. No spin echo is observed for samples showing species B. However, when species E–G are observed, echo signals and deuterium modulation are observed with a maximum at a magnetic field set at $g_{\perp}$(B–G) = 2.10. In a previous study of C_2D_4 adsorbed on Pd–X zeolites,[8] field sweep experiments showed that species F and G have the major contribution to the modulation. In Pd–Y zeolites, the echo signal intensity is relatively weak and the echo was too small to record an ESE spectrum at $g_{\parallel}$(F) = 2.55. The three-pulse ESE spectrum recorded at $g_{\perp}$(B–G) = 2.10 and the simulated spectra are shown in Figure 7. The present results suggest that a Pd^+ ion is complexed with two ethylene molecules or one butene molecule with a Pd–D distance of 0.47 nm.

Discussion

Zeolite Y is composed of alternating AlO_2 and SiO_2 tetrahedra with a Si/Al ratio of 2.4. These units are linked to form truncated octahedra called sodalite cages or β-cages with an opening diameter of 0.22 nm. The unit cell of zeolite Y contains eight sodalite units (a total of 192 (Si,Al)O_4 tetrahedra) that are tetrahedrally bonded through a double six-ring unit called a hexagonal prism. This produces a larger cavity or supercage with a 12-ring opening of 0.74-nm diameter. Zeolite Y has a three-dimensional channel network with large pore openings that allow easy diffusion of molecules through the internal volume. Due to the excess negative charge present on the AlO_2 units, compensating cations are present to balance the charge in the zeolite framework. Various cation site locations are designated as follows:[12] Site SI is the center of the hexagonal prism, SI′ is a site displaced from SI into the β-cage, SII is the center of the hexagonal window between the β-cage and the α-cage, and SII′ and SII* correspond to displacement from site SII into the β-cage and into the α-cage, respectively, along an axis perpendicular to the hexagonal window.

Catalytically Active Species and the Induction Period. This work confirms previous studies[1-8] that palladium species are catalytically active for ethylene dimerization. In the present work, ethylene dimerized to *n*-butenes selectively, and the butenes reach an equilibrium ratio during the reaction time. It has been reported that ethylene is initially dimerized to 1-butene, which is subsequently isomerized to an equilibrium composition of *n*-butenes with predominant *trans*-2-butene over various transition metal cation exchanged zeolites.[19,20] In this work, isomerization of

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(19) Bonneviot, L.; Olivier, D.; Che, M. *J. Mol. Catal.* **1983**, *21*, 415.

1-butene, formed during ethylene dimerization, occurs very rapidly and reaches an equilibrium ratio at the reaction temperature. We have previously found that the isomerization of 1-butene is increased significantly when Pd^{2+} ions are exchanged for Na^+ or Ca^{2+} ions in Na–X and Ca–X zeolites, and the reaction was found to reach an equilibrium very rapidly.[8]

All palladium-exchanged Y zeolite used in this work showed catalytic activity for ethylene dimerization at a reaction temperature of 25 °C. The reaction products were detected after an induction period that is dependent on the palladium concentration, reaction temperature, and coexchanged cation used (Na^+ or Ca^{2+}). In both NaPd–Y and CaPd–Y zeolites, the induction period decreases with increasing palladium concentration. This may be attributed to preferential site location of the active palladium cation and/or ease of reduction of palladium cations. It is likely that, at low cation exchange, palladium cations preferentially occupy relatively inaccessible sites in the hexagonal prism or β-cage.[17,18] Since ethylene molecules with a kinetic diameter of 0.39 nm cannot enter the β-cage or hexagonal prism, the palladium cations must migrate toward the supercage in order to interact with ethylene. However, at higher cation exchange, palladium may occupy relatively accessible sites, e.g., SII or SII*, and reaction can occur with a shorter induction time. The migration of palladium cations toward an accessible site is expected to occur at a faster rate at higher temperature, resulting in a shorter induction time.

If we compare NaPd–Y and CaPd–Y zeolites, a shorter induction period is observed for CaPd–Y. This has previously been interpreted[7,8] as being due to preferential occupancy of Ca ion at site SI′ that restricts the palladium cation from entering the more protected site SI (hexagonal prism) so that palladium must occupy the more accessible sites (SII′ or SII) in CaPd-Y in comparison to site SI in NaPd–Y zeolites. If monovalent cations (e.g., Na^+) are exchanged for divalent cations (e.g., Ca^{2+}) the number of cations is decreased by 50%. Consequently, this causes the zeolite cages to be less crowded. It is likely that migration of Pd species occurs more rapidly in CaPd–Y zeolites due to a smaller number of cocations in comparison to NaPd–Y zeolites.

It is likely that reduction of palladium cations in zeolite occurs gradually and smoothly to lower valences of Pd without populating a specific intermediate valence state. Depending on temperature, time, and adsorbate, Pd^{3+}, Pd^{2+}, Pd^+, Pd^0, and $Pd^0{}_n$ may exist. It is probable that, at any given degree of reduction, more than one valence of Pd is present. The O_2-pretreated zeolite sample, containing palladium mostly as Pd^{2+} and a small amount as Pd^{3+} ions, turned from brown to gray in H_2 for CaPd–Y zeolites and to light brown for NaPd–Y zeolites. In the former case, the formation of Pd^0 is most likely, and Pd^0 are inactive for olefin dimerization.[3,4] In both cases, the catalysts possess paramagnetic Pd^+ and Pd^{3+} as seen by ESR and diamagnetic Pd^{2+} species. So, the elimination of or shorter induction time after H_2 reduction is attributed to the presence of Pd^+ ions that are catalytically active for the reaction.

ESR Evidence of Formation and Migration of Pd^+ Species. The bulky $[Pd(NH_3)_4]^2$ ions, initially exchanged in Na–Y and Ca–Y zeolites, occupy sites in the zeolite supercage due to size considerations. This complex cation is decomposed to Pd^{2+} and NH_3 during thermal pretreatment, and the palladium cations so formed may undergo a rearrangement in the zeolite structure. The formation of Pd^{3+} ions (signal A) has been explained[18] by oxygen attack on Pd^{2+} by reaction 1. It is reported[21] that a small amount (~1%) of diamagnetic Pd^0 atoms or atom clusters (reaction 2) is produced due to thermal reduction of Pd^{2+} during pretreatment. It is assumed that Pd^0 species migrate in the zeolite during prolonged evacuation at high temperature and disproportionate with Pd^{2+} to form Pd^+ and with Pd^{3+} to decrease Pd^{3+} as shown in reactions 3 and 4. This mechanism explains the observed decrease of Pd^{3+} and the formation of Pd^+ after prolonged sample outgassing at 773 K. It is noted that not all Pd^{3+} cations disappear during prolonged evacuation at 773 K.

$$Pd^{2+} + O_2 \rightarrow Pd^{3+} + O_2^- \quad (1)$$

$$Pd^{2+} \xrightarrow{773\ K} Pd^0 \text{ cluster} \quad (2)$$

$$Pd^0 + Pd^{2+} \rightarrow 2Pd^+ \quad (3)$$

$$Pd^0 + Pd^{3+} \rightarrow Pd^+ + Pd^{2+} \quad (4)$$

In both NaPd–Y and CaPd–Y zeolites activated at 773 K both Pd^+ (signal B) and Pd^{3+} (signal A) are stabilized. Subsequent exposure of the O_2-pretreated sample to ethylene causes signal A to disappear immediately. This disappearance of signal A has been previously interpreted as due to reduction of Pd^{3+} ion by ethylene.[18] Since ethylene molecules are too bulky to reach palladium cations in the β-cage or hexagonal prism, this reduction is not clearly understood but is suggested[22,23] to occur via an indirect electron transfer from the adsorbate via zeolite lattice. This indirect reduction of Pd cation in NaPd–Y zeolite by bulkier benzene molecules was previously observed by other authors.[22,23]

The ESR signal B (at a later stage, C and D) appears simultaneously with the disappearance of signal A. This signal may be assigned to Pd^+ species at inaccessible sites in the β-cage or hexagonal prism.[8] Probably they are not coordinated to ethylene. This is supported by the fact that no ethylene dimerization product was detected when only species B was present. In a previous study of ethylene dimerization on palladium-exchanged Na–X and Ca–X zeolites,[8] we observed the formation of a similar ESR signal at $g_\parallel = 2.79–2.81$ with $g_\perp = 2.10$ without detection of butene formation. Subsequently, various paramagnetic species (E–G) are observed with butene formation. It is assumed that Pd^+ ion (signal B) so formed in the β-cage or hexagonal prism migrate towards the supercage to interact with ethylene. Previous ESEM studies have shown that species F and G are due to Pd^+ ion interacting with one and two molecules of ethylene, and they are considered to be precursors of butene formation. Species E has been assigned to Pd^+ ion interacting with one butene molecule. In this work, ESE spectra recorded for samples with adsorbed C_2D_4 at a magnetic field $g_\perp(B–G) = 2.10$ indicate that Pd^+ ion complexes with ethylene and butene. Due to a very weak spin-echo signal, it was not possible to record spectra at various fields to distinguish individual contributions of each of the species. We have proposed a reaction mechanism for ethylene dimerization involving an interaction of Pd^+ cation with one molecule of ethylene giving a π-complex identified as species F followed by the addition of another ethylene molecule to the same Pd^+ species giving a precursor identified as species G.[8] We assume that ethylene dimerization occurs on palladium-exchanged Y zeolites by the same mechanism as proposed for palladium-exchanged X zeolites.

Comparison between Zeolites X and Y. As mentioned earlier, Pd cations at a low-exchange level occupy sites in the β-cage and/or hexagonal prism that are inaccessible to ethylene. Hence, the cations must migrate toward the supercage in order to interact with ethylene. No ethylene dimerization was found to occur at reaction temperatures of 25, 50, and 65 °C on $NaPd_{1.7}$–X and at 25 °C on $NaPd_{12.5}$–X; however, reaction does occur at higher temperature. The paramagnetic species B, attributed to Pd^+ ions, was observed on exposure of the zeolite samples to ethylene at 25 °C, but no Pd–ethylene complexes (species F and G), butene precursors, were generated. In contrast, NaPd–Y zeolites at a similar Pd exchange level are shown to be catalytically active at 25 °C. It appears that the Si/Al ratio that controls the number of cations has a significant effect on the generation and migration of palladium species. It is assumed that palladium cations are successively reduced by an indirect mechanism as mentioned earlier. Subsequently, the Pd species migrate rapidly toward the supercage in NaPd–Y zeolites due to less cation crowding in the

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zeolite cage in comparison to NaPd–X zeolites.

The Si/Al ratio in both CaPd–X and CaPd–Y does not seem to have much effect on the generation of Pd species in comparison to that in NaPd–X and NaPd–Y zeolites. As mentioned, this may be due to the occupancy of Ca^{2+} ions at site SI′ forcing the Pd cations to occupy relatively accessible sites (SII′ or SiI). The dimerization reaction was found to occur on both CaPd–X and CaPd–Y zeolites at 25 °C. However, this reaction occurs on CaPd–Y zeolites at a faster rate in comparison to CaPd–X zeolites, suggesting that formation and migration of Pd^+ species occur more rapidly in CaPd–Y zeolites. This more rapid migration of Pd species can also be explained as due to a smaller number of cocations in the Y zeolites.

Conclusions

All palladium-exchanged Na–Y and Ca–Y zeolites pretreated under O_2 flow at 500 °C are shown to be active for ethylene dimerization at a reaction temperature of 25 °C. The reaction is found to occur after an induction period due in part to palladium reduction and migration toward the zeolite supercage. A decreased induction period is observed for higher palladium-exchanged zeolite, at a higher reaction temperature and for CaPd–Y zeolites. The decreased induction period is explained by different locations of Pd cations in the zeolite structure. The rate of dimerization increases with an increase of palladium content in the zeolite. However, catalyst deactivation occurs more rapidly at higher palladium exchange apparently due to formation of Pd^0 from palladiums at more accessible sites.

It is assumed that at low exchange the palladiums preferentially occupy inaccessible sites: at SI in the hexagonal prism for NaPd–Y and at SII′ in the β-cage for CaPd–Y. In the presence of ethylene, the cations are reduced and then migrate toward the supercage in order to interact with ethylene. At higher exchange, palladiums occupy relatively accessible sites in which case faster reduction and migration can occur giving a shorter induction period.

Subsequent pretreatment of O_2-pretreated palladium-exchanged zeolite samples with H_2 produces Pd^+ species. Ethylene dimerization was found to occur on the H_2-pretreated samples with a shorter induction period. This together with ESR and ESE results suggests that monovalent Pd cations are catalytically active for ethylene dimerization.

All palladium-exchanged zeolites after O_2 pretreatment possess Pd^{3+} (signal A). Signal A disappears with the simultaneous appearance of signal B assigned to Pd^+ ions in the β-cage or hexagonal prism. Pd^+ ions subsequently migrate toward the supercage in order to interact with ethylene, giving various ESR signals (E–G) with simultaneous detection of butene. ESE results suggest that at least a part of these species (E–G) are due to Pd^+ complexed with ethylene and butene. It appears that ethylene dimerization occurs in Pd-Y zeolites by the same mechanism as proposed for Pd–X zeolites involving interaction of Pd^+ ion with one ethylene molecule giving a π-complex followed by addition of another ethylene molecule to the same Pd^+ species giving a butene precursor.

A comparison of the results obtained on palladium-exchanged Na–X and Na–Y zeolites suggests that the Si/Al ratio, which controls the number of cations, has a significant effect on the generation and migration of palladium species during ethylene dimerization. This is mainly due to the fact that Na–X zeolite has about twice the number of cocations as does Na–Y zeolite, which causes the zeolite cages to be crowded. As a result, the migration of palladium species and hence ethylene dimerization require a longer induction period and the reaction does not occur at as low a temperature.

However, the Si/Al ratio has less effect on ethylene dimerization for CaPd–X and CaPd–Y zeolites. This is due to the decrease in the number of cations (divalent versus monovalent) as well as the preferential occupancy of Pd cations at accessible sites (SII′ or SII) to ethylene in comparison to NaPd–X and NaPd–Y zeolites.

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Registry No. Pd, 7440-05-3; Pd^+, 20561-55-1; ethylene, 74-85-1.

Surface-Enhanced Raman Spectroscopy as a Probe of Electroorganic Reaction Pathways. 2. Ring-Coupling Mechanisms during Aniline Oxidation

Ping Gao, David Gosztola, and Michael J. Weaver*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 *(Received: October 18, 1988)*

The adsorbed ring-coupling products formed during aniline electrooxidation at gold–aqueous interfaces have been identified by means of real-time surface-enhanced Raman spectroscopy (SERS) in conjunction with linear sweep voltammetry. In the absence of solution species, the electrooxidation of irreversibly adsorbed aniline yields predominantly adsorbed benzidine. In the presence of solution aniline, however, the "head-to-tail" dimer *N*-phenyl-1,4-phenylenediamine (PPDA) as well as benzidine is formed at the interface, the proportion of the former adsorbate increasing toward higher pH and larger aniline concentrations. A distinction between these interfacial reaction products can readily be made from the characteristic and intense SER spectra of the two-electron oxidation products formed from PPDA and benzidine. Markedly different ring-coupling product distributions were formed in solution (i.e., within the diffusion layer) as deduced voltammetrically, PPDA predominating except in strongly acidic media. Possible reasons for these observed differences are discussed. In alkaline media, azobenzene is observed to be the major ring-coupling product in both adsorbed and solution-phase environments.

The utilization of surface-enhanced Raman spectroscopy (SERS) as a surface mechanistic probe of multistep electrode processes involving adsorbed reactants and/or intermediates is a topic of continuing interest in our laboratory.[1] Several different classes of reaction and/or surfaces have proved amenable to this approach. These include the catalytic electrooxidation of carbon monoxide and small organic molecules on gold surfaces coated with transition-metal overlayers[2] as well as on unmodified gold[2c,3]

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