

Adsorption and catalytic properties of Pd/SiO₂, Cu/SiO₂, and Pd–Cu/SiO₂ systems

III. Carbon monoxide and benzene hydrogenation over Pd–Cu/SiO₂ catalysts

Carlos A. Leon y Leon and M. Albert Vannice*

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802 (USA), tel. (+1-814) 8634803, fax. (+1-814) 8657846

(Received 2 July 1990, revised manuscript received 19 September 1990)

Abstract

The addition of copper to a well dispersed 2.48% Pd/SiO₂ catalyst gave reasonably homogeneous, stable bimetallic systems under mild reaction conditions. Benzene hydrogenation exhibited a relatively constant activation energy around 11.5 kcal mol⁻¹ (1 cal = 4.1868 J) and a reversible activity maximum with temperature which shifted to higher values with increasing copper content. The turnover frequency (TOF) decreased non-linearly with copper content and implied the active site was an ensemble of three surface palladium atoms. Activation energies for methane did not vary with copper content when palladium was present, and TOFs at 0.1 MPa changed little as copper was added although a weak maximum was obtained with 42% Cu. This behavior showed that methanation is a structure-insensitive reaction over palladium. At 1.5 MPa, another weak maximum was observed for methane formation and a sharper maximum for methanol synthesis was obtained near a composition of 59% Cu. Selectivity to methanol increased with increasing copper content. At 1.5 MPa and 548K these SiO₂-supported catalysts sintered significantly during the first 24 h on stream. This tended to increase methanol selectivity, but it made the determination of actual metal surface compositions much more difficult.

Keywords: palladium/silica, copper/silica, palladium–copper/silica, carbon monoxide hydrogenation, benzene hydrogenation, adsorption, selectivity, methanol, methanation.

INTRODUCTION

The catalytic behavior of bimetallic systems has been frequently investigated, and the combination of Group VIII–Group IB metals has been the most thoroughly studied, primarily because of the influence of the latter metal on structure-sensitive reactions and the utilization of these catalysts in petroleum reforming reactions [1]. However, reactions over Pd–Cu catalysts have been mentioned only twice – De Jongste and Ponc [2] conducted pentane hydrogenolysis over a Pd–Cu/SiO₂ catalyst, and Elliott and Pennella [3] conducted methanol synthesis over a palladium-doped commercial Cu/ZnO catalyst. A

study of carbon monoxide hydrogenation over Pd–Cu catalysts is of interest not only because of the commercial use of copper-based catalysts and the discovery that methanol can also be selectively produced over palladium [4], but also because palladium has much higher sulfur tolerance than copper under reaction conditions [5,6]. The influence of copper on benzene hydrogenation over some Group VIII metals has been determined [1], but not over palladium surfaces. This paper describes methanation at 0.1 MPa (1 atm), methanol synthesis at 1.5 Pa (15 atm), and benzene hydrogenation over a series of Pd–Cu/SiO₂ catalysts that was thoroughly characterized by hydrogen, carbon monoxide and oxygen chemisorption and X-ray diffraction [7,8].

EXPERIMENTAL

Kinetic data for carbon monoxide hydrogenation were collected in a stainless steel reactor system capable of operating at pressures from 0.1 to 4 MPa (1–40 atm) [5,6]. The fixed-bed, plug-flow microreactor was made of 316 stainless steel and coated with an electroplated gold film on the inner surface to make it nonreactive. Pressure was measured with a digital pressure transducer (Validyne), and the reactor temperature was kept constant to within ± 1 K by using a TECAM Model SBS-4 fluidized sandbath and a West Model 400 temperature controller. UHP Grade helium and hydrogen (Linde) were flowed through 5A molecular sieve traps (Supelco), and the hydrogen was also flowed through an Engelhard Deoxo purifier, whereas carbon monoxide (Matheson Grade) was flowed through a preheated trap to decompose any carbonyls. Gas flow rates were regulated by Brooks mass flow controllers. Reactor effluent gases were analyzed using a Perkin-Elmer Sigma 2B gas chromatograph equipped with a thermal conductivity detector, temperature programming, and Chromosorb 106 columns (2 mm \times 2.1 m). All effluent gas lines and the gas sampling valve were constantly heated above 373 K to prevent product condensation. Response peak areas were determined using either a H-P 3390A integrator or a P-E LCI-100 integrator. Product compositions were determined by normalizing the peak areas after correction using the response factors reported by Dietz [9].

The family of catalysts studied contained 2.48% Pd on SiO₂ and copper was added by the subsequent impregnation of a Cu(NO₃)₂ solution [7]. This constitutes the B series of catalysts characterized in the preceding paper [8].

Carbon monoxide hydrogenation runs at 0.1 MPa consisted of: (a) loading the reactor with 0.5–0.6 g of catalyst; (b) flowing hydrogen (50 cm³ min^{−1}) at 300 K for 30 min; (c) heating to 393 K (ca. 5 K min^{−1}) and holding for 30 min; (d) heating to 533 K (ca. 4 K min^{−1}) and holding for 30 min; (e) heating to 673 K (ca. 3 K min^{−1}) and holding for 1 h; (f) cooling to 493 K (ca. 2 K min^{−1}) and then introducing carbon monoxide. Unless otherwise noted, a total flow of 24 cm³ min^{−1} of feed gas (H₂/CO = 3) was employed. Conversions were

kept below 5% (typically below 1%) to minimize heat and mass transfer effects. Steady-state reaction conditions were achieved by allowing the reaction to proceed for 20 min prior to analyzing the reactor effluent stream; however, a slow catalyst deactivation process occurred whose influence on the data was minimized by flowing only hydrogen for 20 min between each kinetic run [10]. Between 493 and 593 K, six data points were taken with increasing temperature and four with decreasing temperature to check for irreversible deactivation. Extreme care was taken to minimize the differences in time-on-stream and in maximum temperature among the samples because both parameters could influence the resulting Arrhenius plots. After each run the reactor was cooled to 300 K in flowing hydrogen and the catalyst was characterized by chemisorption and X-ray diffraction. These results were reported and discussed in the preceding paper [8].

Each high pressure carbon monoxide hydrogenation run consisted of: (a) loading the reactor with 0.5–0.6 g catalyst; (b) using the previous pretreatment and repeating the run at 0.1 MPa to check for consistency; (c) re-reducing by heating in flowing hydrogen ($50 \text{ cm}^3 \text{ min}^{-1}$) to 673 K and holding for 1 h; (d) cooling to 493 K; (e) pressurizing the system to 1.46 MPa (200 psig) and then introducing carbon monoxide. Again a total feed gas flow of $24 \text{ cm}^3 \text{ min}^{-1}$ STP ($\text{H}_2/\text{CO}=3$) was used. The catalytic activity was monitored by periodically analyzing effluent gas samples until steady-state conditions were reached, and only then was the temperature increased (ca. 15 K per data point) for another set of data. No bracketing technique was required since each point was reproducible after 30 to 45 min of steady-state operation, and about 12–16 sets of data points were obtained during both ascending and descending temperature sequences. Finally, the effect of total pressure on activity was monitored at a chosen temperature while gradually lowering the system pressure to 0.1 MPa. Five to six sets of data were taken in this fashion, allowing an hour between points for stabilization. After this the catalyst was again characterized by chemisorption and X-ray diffraction. These results were also given previously [8].

Special safety precautions were used with benzene, and the reactor system designed for that purpose has been described elsewhere [11]. Liquid benzene (Baker analyzed) was kept inside a plastic glove bag constantly flushed with helium. Prior to each kinetic run, the benzene was degassed in helium by first heating then cooling to room temperature before it was admitted into the reactor preheater using a calibrated Rainin peristaltic pump. The benzene feed-rate was simultaneously measured using a calibrated 1 cm^3 pipette inside the glove bag as a temporary reservoir and timing the decrease in liquid volume. Small indentations in the glass reactor walls allowed thermocouples to be placed in the catalyst bed. In each run, 0.05–0.2 g catalyst was chosen to keep conversions near or below 10% in the desired temperature regime to minimize heat and mass transfer effects. To maintain low conversions at higher temperatures

at the same flow-rates, a smaller amount of the catalyst was used so that the entire range of 363–583 K could be covered. Constant reactor temperatures (± 1 K) were achieved using a fluidized sandbath connected to a temperature controller. The reactor effluent line was heated above 353 K to prevent product condensation, and the products were analyzed by a Hewlett-Packard Model 700-00 gas chromatograph equipped with Carbowax 20M columns (2 mm \times 2 m). When held isothermally at 338 K, these columns gave excellent cyclohexane–benzene separation and represented an improvement over previous conditions [11,12].

A typical pretreatment consisted of: (a) flowing helium (50 cm³ min⁻¹) at 300 K for 30 min; (b) heating to 393 K (ca. 5 K min⁻¹) and holding for 30 min; (c) heating to 533 K (ca. 4 K min⁻¹) and holding for 30 min; (d) switching the gas to hydrogen (50 cm³ min⁻¹), heating to 673 K (ca. 3 K min⁻¹) and holding for 1 h; (e) cooling to 363 K (ca. 3 K min⁻¹) and then introducing benzene. Activity data were taken during both ascending and descending temperature sequences and a bracketing technique was again employed, allowing 25 min for steady-state operation conditions, 2 to 6 min for sampling, and 25 min for catalyst regeneration in flowing hydrogen. Standard reaction conditions were 0.9 KPa (680 Torr) hydrogen and 0.07 KPa (50 Torr) benzene.

RESULTS

Benzene hydrogenation

The kinetic behavior of this series of catalysts for benzene hydrogenation with increasing copper content is shown in Fig. 1. As shown previously, irreversible hydrogen and carbon monoxide adsorption agrees well and either appears to be a good measure of the number of Pd_s atoms. As copper is added, both the rate per gram catalyst and the turnover frequency (TOF) based on surface palladium atoms (Pd_s) decrease and the maximum in activity shifts to higher temperatures, but the activation energy below 423 K is relatively constant and exhibits no trend, as indicated in Table 1. This reversible maximum has been observed before for palladium and other Group VIII metals [12], and it is not due to poisoning or thermodynamic constraints. None of the catalysts in this series showed any significant deactivation. Because of their high activity, the very small reactor sample sizes made accurate chemisorption measurements difficult; therefore, TOF values and surface compositions were based on results obtained on the fresh catalysts [8]. Neither the 4.32% Cu/SiO₂ sample nor the 15% Cu/SiO₂ sample possessed any detectable activity up to 673 K.

Methanation (0.1 MPa)

At atmospheric pressure and the temperatures used here, only methane and

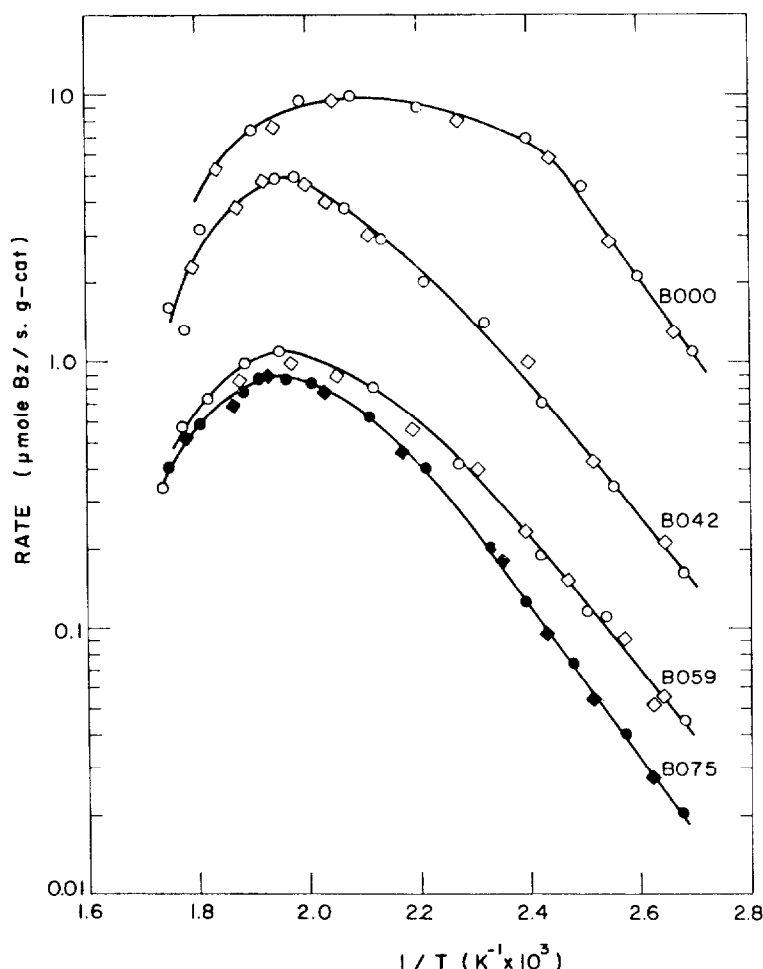


Fig. 1. Activities of Pd-Cu/SiO₂ catalysts for benzene hydrogenation at 50 Torr benzene and 680 Torr hydrogen, B000, 2.48% Pd/SiO₂; B042, 42 atom-% copper; B059, 59 atm-% copper; B075, 75 atom-% copper: ascending temperature (○); descending temperature (◇). Some symbols are filled for clarity only.

small amounts of ethane were detected during gas chromatographic (GC) analysis, as listed in Table 2. No detectable activity for the 4.32% Cu/SiO₂ sample was observed, so the kinetic data for the copper-only catalyst was obtained with 15% Cu/SiO₂, which had measurable activity only above 630 K; consequently, the rates in Table 2 are those extrapolated to the lower temperatures. Initial and final TOFs were obtained by dividing the initial and final activities by irreversible hydrogen and carbon monoxide uptakes on the fresh and used samples [8], respectively, and the influence of copper content on these values is illustrated in Figs. 2a and b. The uncertainty in the TOF values

TABLE 1

Kinetic behavior of Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) in benzene hydrogenation (number following B designates percent copper in metal fraction)

$T = 413$ K, $P_{\text{H}_2} = 680$ Torr, $P_{\text{C}_6\text{H}_6} = 50$ Torr

Catalyst (Series B)	Copper loading (wt.-%)	Activity ($\mu\text{mol s}^{-1} \text{ g cat}^{-1}$)	TOF ($\text{s}^{-1} \times 10^3$)		E_{act}^{γ} (kcal mol^{-1})	T_{max}^{δ} (K)
			Based on $\text{H}_{\text{ad}}^{\alpha}$	Based on $\text{CO}_{\text{ad}}^{\beta}$		
B000 (2.48% Pd/SiO ₂)	0	6.95	40.9	43.3	11.6	481
B042	1.07	0.91	7.24	7.87	10.0	506
B059	2.11	0.26	3.60	3.60	10.6	513
B075	4.14	0.10	2.17	2.06	12.5	519
B100 (4.32% Cu/SiO ₂)	100	N.D. ^ε	(0.003) ^ζ		(-5.8) ^ζ	(345) ^ζ

^αMolecule·s⁻¹·Pd_s⁻¹ on fresh catalyst.

^βMolecule·s⁻¹·Pd_s⁻¹ on fresh catalyst.

^γBelow 423 K.

^δTemperature of maximum benzene conversion.

^εNot detectable.

^ζFrom Schoenmaker-Stolk et al. (ref. 16).

TABLE 2

Kinetic behavior of Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) for carbon monoxide hydrogenation at 0.1 MPa ($\text{H}_2/\text{CO} = 3$)

Catalyst ^α	Product	E_{act} (kcal mol^{-1})	Activity ($\text{nmol s}^{-1} \text{ g cat}^{-1}$)			
			$T = 523$ K		$T = 548$ K	
			Initial	Final	Initial	Final
B000 (2.48% Pd/SiO ₂)	CH ₄	28.6	3.30	1.72	10.3	7.08
	C ₂ H ₆	26.2	0.54	0.20	1.42	0.88
B042	CH ₄	28.2	3.45	1.91	10.8	7.60
	C ₂ H ₆	26.2	0.38	0.18	1.07	0.69
B059	CH ₄	30.0	1.81	1.05	6.16	4.60
	C ₂ H ₆	28.4	0.29	0.09	0.82	0.50
B075	CH ₄	29.8	0.82	0.58	3.00	2.18
	C ₂ H ₆	28.3	0.09	0.03	0.29	0.09
B100' (15% Cu/SiO ₂)	CH ₄	20.6	0.01	0.005	0.024	0.012
	C ₂ H ₆	-	0	0	0	0

^αNumber following B gives the metal percentage of copper.

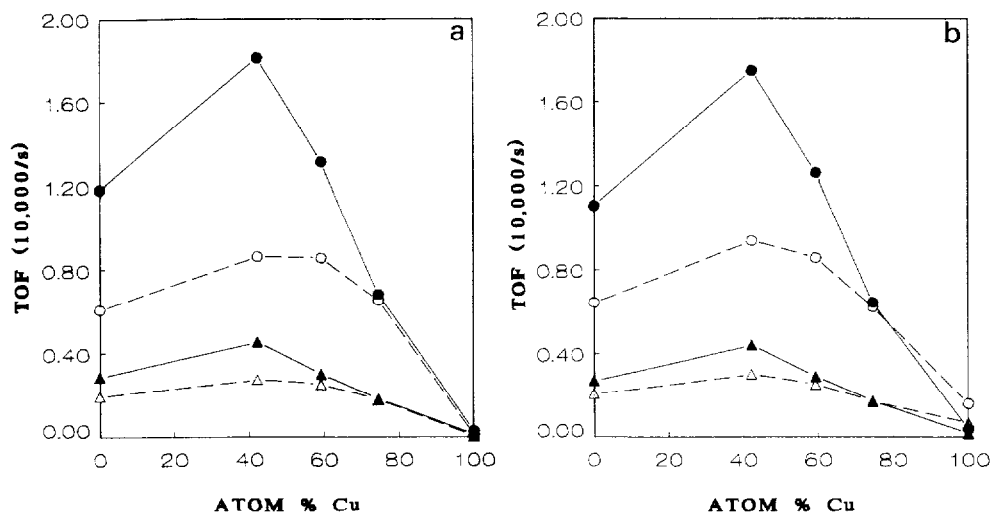


Fig. 2. Influence of copper content on methane turnover frequency on Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) at 0.1 MPa, H₂/CO=3, and $T=523$ K (Δ , \blacktriangle) or $T=548$ K (\circ , \bullet): (a) Initial activity based on H_{irr} adsorption on fresh samples; open symbols, final activity based on H_{irr} on used samples; filled symbols; (b) as in (a) but based on CO_{irr} adsorption on fresh and used samples, respectively.

is approximately $\pm 0.1 \cdot 10^{-4} \text{ s}^{-1}$. The trends are independent of the adsorbate chosen to titrate Pd_s atoms and the somewhat lower initial TOF values for the copper-poor surfaces may well be due to the loss of palladium surface area that occurred after the first carbon monoxide exposure [8]. Some carbon dioxide formation was observed over the palladium-containing catalysts, but activities or activation energies are not reported because a change in the slope of the carbon dioxide Arrhenius plots made extrapolation uncertain [13].

Carbon monoxide hydrogenation (1.5 MPa)

The activities of these catalysts for methane and methanol formation at 1.5 MPa after the Arrhenius runs were completed are listed in Table 3. Based upon irreversible hydrogen and carbon monoxide uptakes (and oxygen adsorption on the used Cu/SiO₂ samples), which are given in the preceding paper [8], TOF values again based only on Pd_s atoms were calculated for methane and methanol formation on these Pd-Cu catalysts, and they are depicted in Figs. 3 and 4, respectively. The uncertainty in these TOFs is also $\pm 0.1 \cdot 10^{-4} \text{ s}^{-1}$. The influence of copper addition on selectivity is shown in Fig. 5. The activity maintenance of these catalysts was monitored over a 24-hour period to obtain plots such as those in Fig. 6, and the remaining deactivation plots are shown elsewhere [13]. The results are summarized in Fig. 7, which shows the changes

TABLE 3

Kinetic behavior of Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) for carbon monoxide hydrogenation at 1.5 MPa (H₂/CO=3): Data taken after 1 h on stream

Catalyst ^α	Product	Activity (nmol s ⁻¹ g cat ⁻¹)		
		<i>E</i> _{act} (kcal mol ⁻¹)	523 K	548 K
B000	CH ₄	34.3	0.33	1.75
	CH ₃ OH	21.7	0.21	0.59
	C ₂ H ₆	25.1	0.02	0.11
B042	CH ₄	33.6	0.57	2.48
	CH ₃ OH	22.1	0.76	2.00
	C ₂ H ₆	31.1	0.02	0.09
B059	CH ₄	36.3	0.62	3.05
	CH ₃ OH	17.4	1.05	2.26
	C ₂ H ₆	28.4	0.03	0.11
B075	CH ₄	33.8	0.45	2.01
	CH ₃ OH	12.7	1.11	1.96
	C ₂ H ₆	25.8	0.06	0.15
B100	CH ₄	42.1	0.03	0.16
	CH ₃ OH	12.4	0.09	0.26
	C ₂ H ₆	27.5	0.03	0.10
	CO ₂	20.7	1.11	2.75

^αNumber following B gives the metal percentage of copper.

in activity for methane, methanol, and total carbon monoxide converted (including carbon dioxide) with time-on-stream.

Using power rate laws of the form $r_{\text{CH}_4} = kP_{\text{H}_2}^x P_{\text{CO}}^y$ and $r_{\text{CH}_4} = k_T P_T^z$ at 0.1 MPa and 548 K, where P_T is the total pressure, values of $x=0.74$, $y=0.22$ and $x=0.70$, $y=0.13$ were obtained for methane formation over 2.48% Pd/SiO₂ and 2.48% Pd-2.11% Cu/SiO₂ (B059) samples, respectively. Upon decreasing P_T following the high pressure runs from 1.5 to 0.1 MPa (with H₂/CO=3), z values of 0.72 ± 0.03 were obtained for all palladium-containing catalysts. Methanol formation at 548 K was not quantitatively measurable below 1 MPa.

DISCUSSION

Benzene hydrogenation

An analysis of the results in Table 1 and Fig. 1 allows several effects of copper addition to be established: (1) both the activity and the TOF decrease as copper content increases, (2) the reversible activity maximum shifts to higher

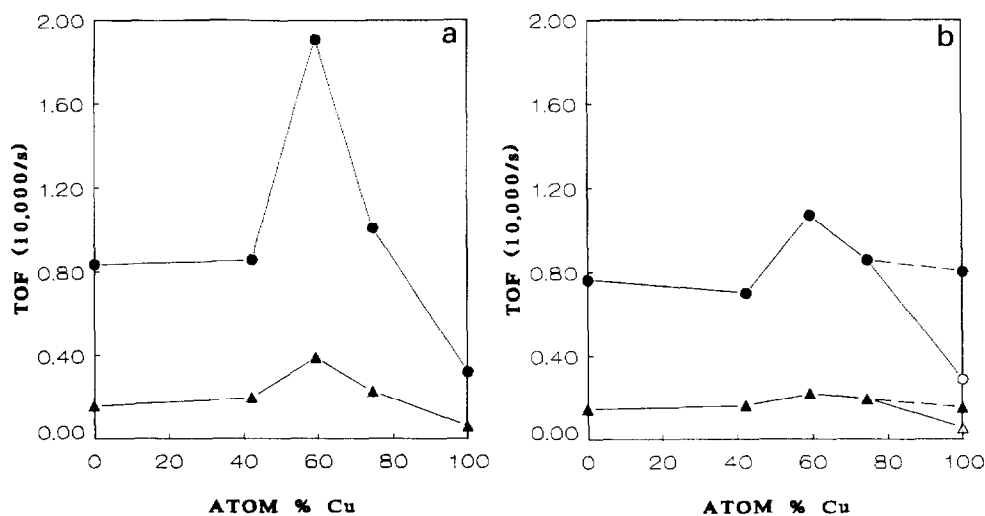


Fig. 3. Influence of copper content on methane turnover frequency over Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) at 15 atm, H₂/CO=3, 548 K (●), 523 K (▲): (a) Based on H_{irr} uptake on used catalyst; (b) based on CO_{irr} uptake on used catalyst. Open symbols represent values as molecules s⁻¹ Cu_s⁻¹ based on oxygen chemisorption on copper at 143 K.

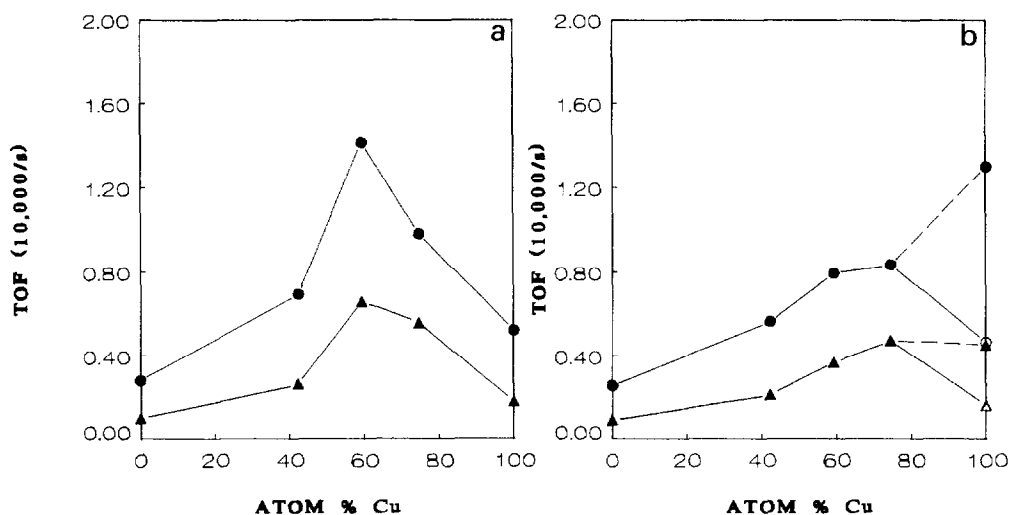


Fig. 4. Influence of copper content on methanol turnover frequency over Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) at 15 atm, H₂/CO=3, 548 K (●), 523 K (▲): (a) Based on irreversible hydrogen uptake on used catalyst; (b) based on irreversible carbon monoxide uptake on used catalyst. Open symbols represent values as molecule s⁻¹ Cu_s⁻¹ based on oxygen chemisorption at 143 K.

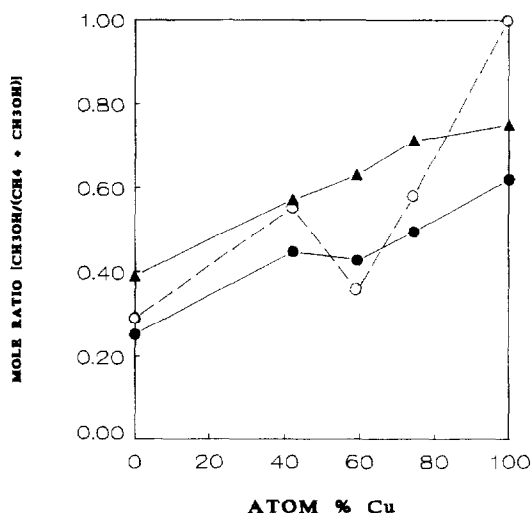


Fig. 5. Methanol selectivity over Pd-Cu/SiO₂ catalysts (based on 2.48% Pd/SiO₂) as a function of copper content: $P=1.5$ MPa, $H_2/CO=3$, $T=548$ K (●, ○); 523 K (▼). Filled symbols, selectivity after 1 h on stream (from Table 3); Open symbols, selectivity after 24 h on stream (from ref. 13).

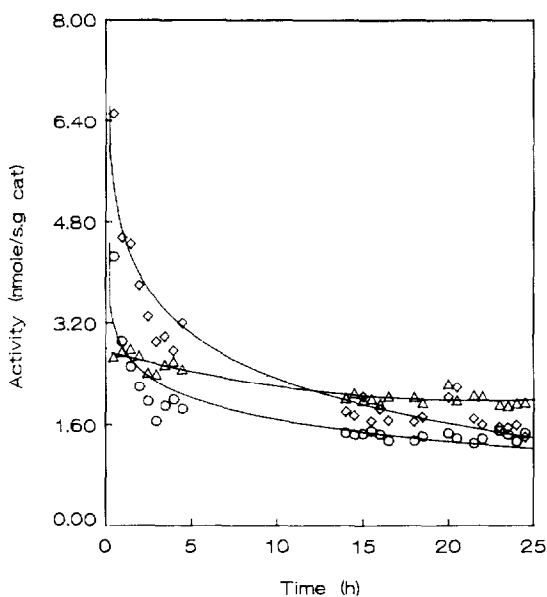


Fig. 6. Activity maintenance for carbon monoxide hydrogenation over 2.48% Pd-1.07% Cu/SiO₂ (B042), $P=1.5$ MPa, $T=548$ K, $H_2/CO=3$, $24 \text{ cm}^3 \text{ (STP) min}^{-1}$: Methane (◇); Methanol (△); carbon dioxide (○).

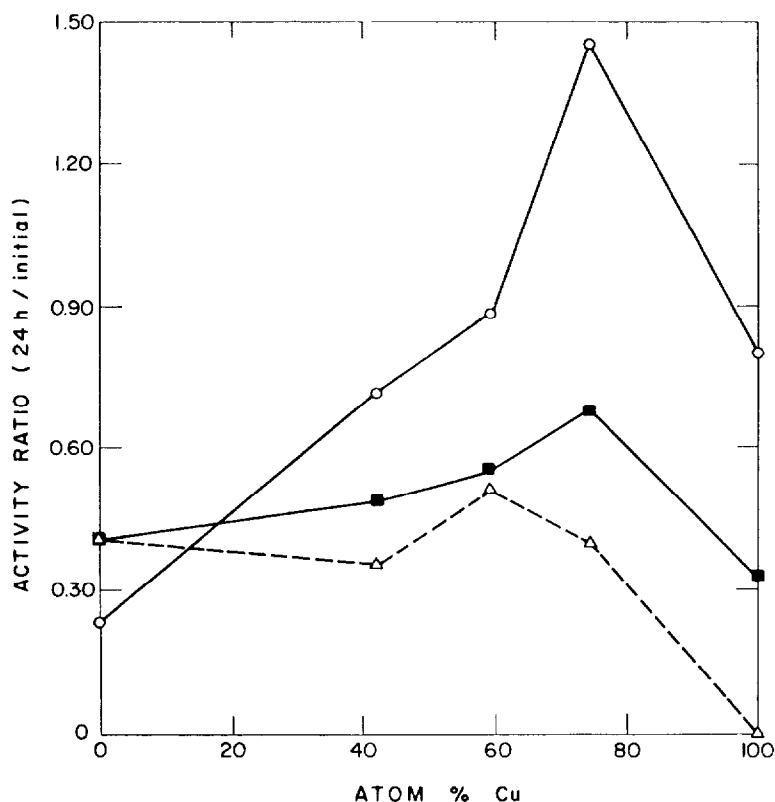


Fig. 7. Carbon monoxide hydrogenation activity maintenance over Pd-Cu/SiO₂ catalysts (Series B) after 24 h on stream ($P=1.5$ MPa; $T=548$ K, $H_2/CO=3$): Methane (Δ); Methanol (\circ); all products formed (\blacksquare).

temperatures as copper is added, (3) the activation energy at lower temperatures is approximately constant at 11.5 ± 1.0 kcal mol⁻¹ for all catalysts containing palladium, and (4) the copper-only catalysts are inactive for benzene hydrogenation. These results are in excellent agreement with previous work on palladium-only and copper-only catalysts. The TOF on the 2.48% Pd/SiO₂ catalyst is consistent with earlier values of 0.060 ± 0.025 s⁻¹ at these conditions, and the activation energies for all the catalysts containing palladium are near those of 8–12 kcal mol⁻¹ reported by others [12,14,15]. A reversible maximum in activity vs. temperature has been found previously for palladium as well as other group VIII metals [11,12 and references therein], and it even occurs for copper but at a much lower temperature [16,17]. Schoenmaker-Stolk et al. also found that TOFs were extremely low on an ion-exchanged Cu/SiO₂ catalyst, as anticipated for Group IB metals [16–19], and the negative apparent activation energy above 350 K would further decrease its contribu-

tion above 413 K [16,17]. This maximum can be straightforwardly explained by the equilibrium adsorption constant for benzene which is contained in the Langmuir-Hinshelwood rate expressions describing this reaction [11,20]. Physically the maximum implies that a decrease with increasing temperature in the initial, near-saturation coverages of benzene at lower temperatures is substantial enough to decrease rates of reaction. The shift to higher temperatures upon copper addition indicates a smaller coverage dependence on temperature, hence a lower heat of adsorption for benzene on copper [20].

This reaction is typically considered to be structure insensitive, thus implying that the number of metal atoms constituting an "active site" is small [21]. Cadenhead and Masse [22] examined benzene hydrogenation over Pd-Au alloys and proposed that the number of Pd_s atoms in an active site varied from 6 on bulk palladium to 2 on the alloy surface. As copper and the Group VIII metal retain their band structure in bimetallic systems to a large extent [23,24],

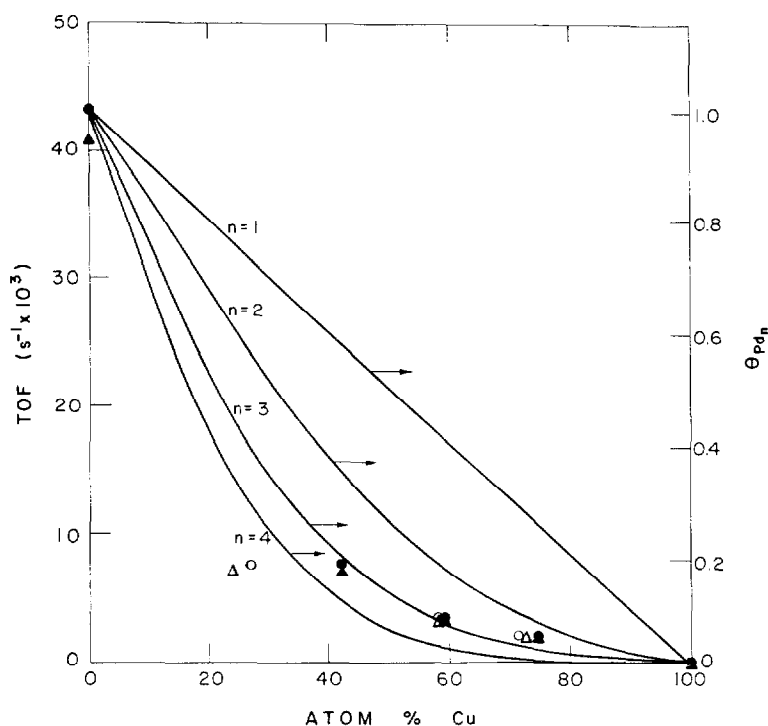


Fig. 8. Predicted dependence of turnover frequency on surface composition assuming n Pd_s atoms in an ensemble constituting an active site. Experimental values are from Table 1, with TOFs based on hydrogen chemisorption (Δ, \blacktriangle); TOFs based on carbon monoxide chemisorption (\circ, \bullet). Filled symbols, assuming complete homogeneity in mixing; open symbols, assuming surface compositions based on chemisorption from ref. 8.

geometric factors play the predominant role in altering adsorption and catalytic behavior [25–29]. Thus Pd–Cu systems would be expected to behave similarly to Ni–Cu systems once the awareness is acknowledged that there is a stronger driving force for surface segregation of copper in the latter system [30–34]. The effect of an inert diluent on specific activity can be statistically predicted once the size of the ensemble of palladium atoms constituting an active site is chosen [25,26,35]. Fig. 8 depicts the expected decrease in TOF based on an ensemble containing n Pd_s atoms, as well as the corresponding experimental points taken from Table 1. Assuming completely homogeneous particles with equal surface and bulk compositions, an ensemble size of three Pd_s atoms is indicated, and the assumption that surface compositions are equal to those calculated from chemisorption on the fresh reduced catalysts [8] does not change this conclusion significantly. This result is in excellent agreement with the value of $n = 3 \pm 1$ reported by others for the Ni–Cu system [25–29]. Thus our conclusion is the same as theirs and others [1,22,30,36]; the addition of copper to palladium is primarily that of an inert diluent exerting a geometric effect by breaking up ensembles of palladium atoms which constitute active sites. However, the small shift in the activity maximum as copper is added could imply a small electronic effect on the adsorption bond strength of benzene, one result of which could be a reduction in hydrogen-deficient adsorbed species which can inhibit activity [20].

Methanation at 0.1 MPa

The final TOF on the 2.48% Pd/SiO₂ catalyst at 548 K ($1.2 \cdot 10^{-4} \text{ s}^{-1}$), shown in Fig. 2, was equal to that on palladium powder [37] and within the range of $1\text{--}10 \cdot 10^{-4} \text{ s}^{-1}$ reported for SiO₂-supported palladium [6,10,38–41]. The activation energy was constant within experimental uncertainty at $29.0 \pm 0.7 \text{ kcal mol}^{-1}$ for all the catalysts containing palladium, and it is very consistent with previous values for many palladium catalysts [10,38,42]. Copper is known to have very low methanation activity at this pressure [43], and both the TOF values and the activation energy for the 15% Cu/SiO₂ catalyst are in good agreement with previous values ($3.0 \cdot 10^{-6} \text{ s}^{-1}$ vs. $1.8 \cdot 10^{-6} \text{ s}^{-1}$ based on irreversible hydrogen adsorption, and $20.6 \text{ kcal mol}^{-1}$ vs. $15.2 \text{ kcal mol}^{-1}$, respectively) reported by Vannice [43]. However, the TOFs are somewhat lower than the value of $20 \cdot 10^{-6} \text{ s}^{-1}$ found by Chen et al. [44].

The variation in methane TOF with increasing copper content is illustrated in Fig. 2, and either hydrogen or carbon monoxide chemisorption to measure Pd_s atoms indicates that the TOF has little dependence on copper concentration but does exhibit a weak maximum at the lowest copper loading. This behavior, coupled with the invariant activation energy, is strong evidence in favor of a structure-insensitive reaction [21]. Whether methanation is such a reaction over palladium remains controversial. Ichikawa et al. [45] have reported

an increase in TOF at 548 K from $1.2 \cdot 10^{-4} \text{ s}^{-1}$ to $15 \cdot 10^{-4} \text{ s}^{-1}$ as palladium dispersion on SiO_2 increased from 0.2 to 1.0, whereas Rieck and Bell [39] have reported exactly the opposite behavior at 523 K for SiO_2 -supported palladium; i.e., the TOF decreased from $10.5 \cdot 10^{-4}$ to $3 \cdot 10^{-4}$ as dispersion increased from 0.2 to 0.85. Wang et al. [38] had originally found an essentially constant TOF at 548 K ($3 \cdot 10^{-3}$ to $6 \cdot 10^{-3} \text{ s}^{-1}$) on Al_2O_3 -supported palladium over a dispersion range of 0.05 to 0.44, and they obtained lower TOF values of $1 \cdot 10^{-4}$ to $3 \cdot 10^{-4} \text{ s}^{-1}$ for Pd/ SiO_2 catalysts that were near that for high purity palladium powder [37,38]. The behavior of these Pd–Cu catalysts is consistent with the latter results and indicates that methanation is a structure-insensitive reaction. In any case the TOF values reported elsewhere [39,45] vary by less than an order of magnitude and may reflect the influence of another component, such as chlorine. The small maximum in Figs. 2 and 3 could be a consequence of a weakened carbon monoxide adsorption bond [46,47], which might be expected to increase the TOF because of the volcano plot that exists for this reaction [43].

CO Hydrogenation at 1.5 MPa

As observed previously for methanation, an increase in pressure to 14.6 atm produces little or no increase in methane TOF values over palladium after continued high pressure use, and the value at 523 K for 2.48% Pd/ SiO_2 in Fig. 3 is the same as that reported for palladium powder [37] and other Pd/ SiO_2 catalysts [5]. The activation energy for all the palladium-containing catalysts was $34.9 \pm 1.4 \text{ kcal mol}^{-1}$, which is extremely consistent with that of many palladium catalysts at these reaction conditions [37,42]. The methane activation energy for the 4.32% Cu/ SiO_2 catalyst appears to be the first reported for copper at these conditions although Burch and Chappell have recently reported a steady-state TOF of $0.74 \cdot 10^{-6} \text{ s}^{-1}$ for methane formation under conditions (10 bar, $\text{H}_2/\text{CO}=3$, 523 K) similar to ours [48]. This value is 10 times lower than our TOF of $0.75 \cdot 10^{-5} \text{ s}^{-1}$ after 1 h on stream, but the latter decreases during the next 23 h to a nonmeasurable value, so the two values may actually be in better agreement than it would first appear.

As at 1 atm, the TOF for methane varied little with copper content but again exhibited a small maximum at intermediate loadings; however, because of the significant loss in metal surface area, especially that due to agglomeration of copper [8], the surface composition during reaction at 15 atm is less clear. The smaller relative decrease in chemisorption capacity with increasing copper content for the used samples compared to fresh ones [8] implies that a larger fraction of the palladium surface remains free; thus, the actual fractions of the surface that are composed of copper would be substantially smaller than those based on the nominal metal contents (representative of homogeneous mixing) shown in Fig. 3, and the maximum would coincide more closely with that shown

in Fig. 2. It should also be noted that at this pressure the TOF on copper has increased, even when normalized to Cu_s atoms counted by oxygen adsorption (see Fig. 3b), so it is much closer to that on palladium.

When examining the kinetic parameters for methanol formation over palladium, the activation energy of $21.7 \text{ kcal mol}^{-1}$ is on the high side of the range of $14\text{--}20 \text{ kcal mol}^{-1}$ found in the literature, while the methanol TOF value of $0.1 \cdot 10^{-4} \text{ s}^{-1}$ at 523 K is an order of magnitude lower than most values reported for Pd/SiO₂ [6,41,49,50]. This may perhaps be due to the absence of chlorine (or other promoters) in the palladium-only catalyst. Surprisingly, activation energies and specific activity values for methanol synthesis over copper have seldom been reported [50,51]. Activation energies of 26 and 34 kcal mol^{-1} at temperatures around 563 K and 523 K, respectively, have been reported for a Cu/ZnO/Al₂O₃ catalyst [51], and 10 kcal mol^{-1} has been reported for a Cu/ThO₂ catalyst [51]; thus our value of $12.4 \text{ kcal mol}^{-1}$ is quite similar to the latter. The recent study of Burch and Chappell contains a TOF of $0.56 \cdot 10^{-4} \text{ s}^{-1}$ for methanol formation on a 5% Cu/SiO₂ catalyst under conditions (10 bar, $\text{H}_2/\text{CO}=3$, 523 K) close to ours [48]. Our value of $0.23 \cdot 10^{-4} \text{ s}^{-1}$, which is also based on oxygen chemisorption to count Cu_s atoms (Fig. 4b), remained essentially constant during time-on-stream and is very similar to their value.

The addition of copper produces a maximum in the methanol TOF similar to but more pronounced than that found for methane, with the maximum again occurring at (or near) a composition of 59 atom-% copper catalyst. Because the trends for methane and methanol production parallel each other, the methanol selectivity at 548 K versus copper content exhibits a gradual increase as the copper concentration is increased, as shown in Fig. 5. These catalysts lose a significant amount of activity during a 24-h period on-stream, especially for methane formation, as indicated in Figs. 6 and 7. Consequently, the selectivity to methanol tends to increase, and for 4.32% Cu/SiO₂ no methane is produced after this period, as shown in Fig. 5. Thus the most pronounced problem with this bimetallic system is its tendency to sinter and lose activity when dispersed on this silica support. Both chemisorption and the activities in kinetic runs at 1 atm following those at 15 atm verified that large decreases in metal surface area had taken place [13].

SUMMARY

The addition of copper to a well dispersed Pd/SiO₂ catalyst appears to give a reasonably homogeneous bimetallic system under mild reaction conditions. Benzene hydrogenation over all palladium-containing catalysts exhibited a relatively constant activation energy around $11.5 \text{ kcal mol}^{-1}$ and a reversible activity maximum with temperature, as observed previously for Group VIII metals, which shifted to higher temperatures with increasing copper content. The TOF based on Pd_s atoms decreased non linearly and implied an active

site ensemble size of 3 Pd_s atoms. The copper-only catalysts had very low activity at 0.1 MPa. Methanation activation energies were insensitive to copper content when palladium was present, and TOFs changed little as copper was added although a weak maximum was obtained at 42 atom-% copper. This behavior is evidence that methanation is a structure-insensitive reaction over palladium, in agreement with recent results for SiO₂-supported platinum which also demonstrated structure insensitivity for this reaction [52]. At 1.5 MPa, another weak maximum for methane formation and a stronger one for methanol synthesis was obtained near a metal composition of 59 atom-% copper and selectivity to methanol increased with increasing copper content. Under these reaction conditions, these SiO₂-supported catalysts sinter significantly during the first 24 h on stream. This tends to increase methanol selectivity further, but makes the determination of actual metal surface compositions much more uncertain.

ACKNOWLEDGEMENT

This study was sponsored by a grant from the Eastman Chemicals Division, Eastman Kodak Co., Kingsport, TN.

REFERENCES

- 1 J.H. Sinfelt, *Catal. Rev. Sci. Eng.*, 9 (1974) 147.
- 2 H.C. de Jongste and V. Ponec, *J. Catal.*, 63 (1980) 389.
- 3 D.J. Elliott and F. Pennella, *J. Catal.*, 102 (1986) 464.
- 4 M.L. Poutsma, L.F. Elek, P.A. Ibarbia, A.P. Risch and J.A. Rabo, *J. Catal.*, 52 (1978) 157.
- 5 M.N. Berube, B. Sung and M.A. Vannice, *Appl. Catal.*, 31 (1987) 133.
- 6 L. Radovic and M.A. Vannice, *Appl. Catal.*, 29 (1987) 1.
- 7 C.A. Leon y Leon and M.A. Vannice, *Appl. Catal.*, 69 (1991) 269.
- 8 C.A. Leon y Leon and M.A. Vannice, *Appl. Catal.*, 69 (1991) 291.
- 9 W.A. Dietz, *J. Gas Chromatogr.*, 5 (1967) 68.
- 10 M.A. Vannice, *J. Catal.*, 37 (1975) 449.
- 11 K.J. Yoon and M.A. Vannice, *J. Catal.*, 82 (1983) 457.
- 12 P. Chou and M.A. Vannice, *J. Catal.*, 107 (1987) 129.
- 13 C.A. Leon y Leon, M.S. Thesis, The Pennsylvania State University (1988).
- 14 S. Fuentes and F. Figueras, *J. Chem. Soc. Faraday Trans. 1*, 74 (1978) 174.
- 15 R.L. Moss, D. Pope, B.J. Davis and D.H. Edwards, *J. Catal.*, 58 (1979) 206.
- 16 M.C. Schoenmaker-Stolk, J.W. Verwijs and J.J.F. Scholten, *Appl. Catal.*, 29 (1987) 91.
- 17 M.C. Schoenmaker-Stolk, J.W. Verwijs, J.A. Don and J.J.F. Scholten, *Appl. Catal.*, 29 (1987) 73.
- 18 R.G. James and R.B. Moyes, *J. Chem. Soc. Faraday Trans. 1*, 94 (1978) 1666.
- 19 L. Babernics, P. Tetenyi and L. Kortesz, *Z. Phys. Chem. NF*, 89 (1974) 237.
- 20 P. Chou and M.A. Vannice, *J. Catal.*, 107 (1987) 140.
- 21 M. Boudart, in G.C. Bond, P.B. Wells and F.C. Tompkins (Editors), *Proc. 6th Int. Congr. Catal.*, The Chemical Society, London, 1 (1976) 1.
- 22 D.A. Cadenhead and N.G. Masse, *J. Phys. Chem.*, 70 (1966) 3558.
- 23 V. Ponec, *Adv. Catal.*, 32 (1983) 149.

- 24 J.K.A. Clarke, *Chem. Rev.*, 75 (1975) 291.
- 25 C. Mirodatos, J.A. Dalmon and G.A. Martin, *J. Catal.*, 105 (1987) 405.
- 26 G.A. Martin and J.A. Dalmon, *J. Catal.*, 75 (1982) 233.
- 27 J.A. Dalmon, J.P. Candy and G.A. Martin, in G.C. Bond, P.B. Wells and F.C. Tompkins (Editors), *Proc. 6th Int. Congr. Catal.*, The Chemical Society, London, 2 (1977) 903.
- 28 M.V. Khotuleva, V.S. Gudkov, A.A. Slinkin and S.L. Kiperman, *Kinet. Katal.*, 27 (1986) 874.
- 29 J.P. Candy, P. Fouilloux and B. Imelik, *Nouveau J. Chim.*, 2 (1978) 45.
- 30 J.H. Sinfelt, *J. Catal.*, 29 (1973) 308.
- 31 A.D. van Langeveld, H.A.C.M. Hendrickx and B.E. Nieuwenhuys, *Thin Solid Films*, 109 (1983) 179.
- 32 A. Roberti, V. Ponec and W.M.H. Sachtler, *J. Catal.*, 28 (1973) 381.
- 33 P. van der Plank and W.M.H. Sachtler, *J. Catal.*, 12 (1968) 35.
- 34 J.A. Dalmon, *J. Catal.*, 60 (1979) 325.
- 35 J.A. Dalmon and G.A. Martin, *J. Catal.*, 66 (1980) 214.
- 36 W.A.A. van Barneveld and V. Ponec, *Rec. Trav. Chim.*, 93 (1974) 243.
- 37 C. Sudhakar and M.A. Vannice, *J. Catal.*, 95 (1985) 227.
- 38 S.Y. Wang, S.H. Moon and M.A. Vannice, *J. Catal.*, 71 (1981) 167.
- 39 J.S. Rieck and A.T. Bell, *J. Catal.*, 103 (1987) 46.
- 40 F. Fajula, R.G. Anthony and J.H. Lunsford, *J. Catal.*, 73 (1982) 237.
- 41 R.F. Hicks and A.T. Bell, *J. Catal.*, 91 (1985) 104.
- 42 M.A. Vannice, C. Sudhakar and M. Freeman, *J. Catal.*, 108 (1987) 97.
- 43 M.A. Vannice, *J. Catal.*, 50 (1977) 228.
- 44 H.W. Chen, J.M. White and J.G. Ekerdt, *J. Catal.*, 99 (1986) 293.
- 45 S. Ichikawa, H. Poppa and M. Boudart, *J. Catal.*, 91 (1985) 1.
- 46 A. Noordermeer, G.A. Kok and B.E. Nieuwenhuys, *Surf. Sci.*, 172 (1986) 349.
- 47 G.W. Graham, *Surf. Sci.*, 171 (1986) L432.
- 48 R. Burch and R.J. Chappell, *Appl. Catal.*, 45 (1988) 131.
- 49 K.P. Kelly, T. Tatsumi, T. Uematsu, D.J. Driscoll and J.H. Lunsford, *J. Catal.*, 101 (1986) 396.
- 50 G.C. Chinen, P.J. Denny, J.R. Jennings, M.S. Spencer and K.C. Waugh, *Appl. Catal.*, 36 (1988) 1.
- 51 K. Klier, *Adv. Catal.*, 31 (1982) 243.
- 52 B. Sen and M.A. Vannice, *J. Catal.*, in press.