

CO Poisoning of Pt/Al₂O₃: Structural Effects on the Hydrogenolysis of Methylcyclopropane

D. E. DAMIANI¹ AND J. B. BUTT²

Ipatieff Laboratory and Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60201

Received October 10, 1984; revised January 28, 1985

The hydrogenolysis of methylcyclopropane has been used as a probe reaction to investigate the structure sensitivity of the deactivation of a series of well-characterized Pt/Al₂O₃ catalysts by carbon monoxide.

After a standardized reduction procedure, the catalysts were prepoisoned by pulse chemisorption of carbon monoxide at 298 K to varying levels of surface coverage, then the hydrogenolysis was carried out under differential conversion conditions at 273 K. Results were obtained in terms of reaction turnover frequency and selectivity as a function of percentage of metal exposed (D_h) and surface coverage of carbon monoxide. The general pattern of structure sensitivity for this reaction on Pt/Al₂O₃ was not altered substantially upon progressive poisoning, although the change in absolute magnitude of turnover frequency was larger for low- D_h catalysts than for high- D_h catalysts. Product selectivity between isobutane and *n*-butane was not affected. A comparison with prior results obtained for a similar series of Pt/SiO₂ (Önal, I., and Butt, J. B., *J. Chem. Soc. Faraday Trans. 1* **78**, 1887, 1982) is given. Comparison of prepoisoning from CO-Ar pulses with that from CO-H₂ pulses indicate differences for high- D_h catalysts. Thus there may be differences in apparent poisoning behavior as indicated by prepoisoning experiments compared to continuous introduction of poison with the reactants. Comparison of the mode of prepoisoning, pulse chemisorption vs thermal desorption from a monolayer, indicated generally similar results for the two methods. Some discrepancies appearing at low coverages of CO may be due to reordering of the adlayer in the thermal desorption treatment. © 1985 Academic Press, Inc.

INTRODUCTION

There are many instances of reactions carried out on supported metal catalysts in which the reaction turnover frequency is sensitive to the morphology of the metal (structure sensitive). Similarly, the chemisorption stoichiometry of small molecules in some cases is also structure sensitive. Combination of these two observations leads to the conclusion that the deactivation of catalysts, particularly by poisoning, may itself be a structure-sensitive process in certain instances, and further, that it might be possible to tailor catalyst morphology in such cases to induce a preferential resistance to poisoning.

¹ Present address: PLAPIQUI-UNS, 8000-Bahia Blanca, Argentina.

² To whom correspondence should be addressed.

Mitrofanova *et al.* (1) correlated the activity in various hydrogenation and dehydrogenation reactions on several Pt/SiO₂ catalysts with metal particle size. Although hydrogenation reactions are generally regarded to be structure insensitive, it was concluded that deactivation processes could induce an appreciable variation of activity as one goes from one type of surface to another. Ostermaier and co-workers (2) looked at the effect of crystallite size on the specific activity of supported Pt in ammonia oxidation with molecular oxygen. The catalysts had average crystallite dimensions of 2.0, 2.7, and 15.5 nm, and all showed deactivation in the first 6 h of reaction. However, smaller crystallites were more severely poisoned than larger ones. This effect was explained in terms of the change of the surface concentration of active

dioxygen with particle size. In a study of the isomerization of *n*-hexane on Pt/zeolite catalysts, Rabo *et al.* (3) found that catalysts prepared by ion exchange, presumed to be atomically dispersed, were unaffected by 10 ppm of thiophene in the feed. On the contrary, a catalyst prepared by impregnation rapidly lost activity in the presence of thiophene.

Structure-sensitive deactivation on single crystal surfaces has been reported by Davis and Somorjai (4), who investigated hydrogenolysis and hydrogenation of cyclohexane on various Pt surfaces at low pressures. The formation of carbonaceous deposits was monitored by AES; it was found that the carbon deposit deactivated the most reactive surface (kinked) at the slowest rate and the least active surface (111) at the fastest rate. The strong hydrogen bonding capability of kinked surfaces as demonstrated by TPD was apparently the reason for the preferential resistance to deactivation. Similar observations were recently reported by Ponc (5). In studies at atmospheric pressures, however, Hertz *et al.* (6) found that a complex carbonaceous overlayer was rapidly formed on all surfaces and there was no well-defined trend with surface structure.

Maurel, Barbier, and co-workers (7, 8) introduced the designation of "demanding poison" for those chemicals that are selective poisons, and have considered several possible explanations for selective poisoning. In order to choose from the various possibilities, they studied the effect of several poisons on a number of reactions over a series of Pt/Al₂O₃ catalysts with percentage exposed ranging from 5 to 65%. The toxicity of the poisons was defined as the relative number of Pt atoms made unavailable by the poison for the reaction. It was observed that some poisons (nonselective) affected a number of different reactions, while others affected only specific reactions. Some of the poisons, although selective, modified the same reaction to a different extent on different catalysts. The results were explained generally in terms of

surface heterogeneity in which some reactions take place on the whole surface while others occur only on part of the surface. Obviously, the active part of the surface might not be the same for all structure-sensitive reactions. Selective poisoning therefore takes place when the poison is adsorbed nonuniformly and implies that the same poison must have the same toxicity for all reactions occurring on the same site. A more detailed review of these concepts has recently been given by Hegedus and McCabe (9).

In this laboratory, Önal (10, 11) used methylcyclopropane hydrogenolysis as a probe reaction in the investigation of the promotion/poisoning effects of oxygen and carbon monoxide on a series of Pt/SiO₂ catalysts varying in percentage metal exposed from ca. 6 to 80%. Oxygen, pulsed before reaction, enhanced the activity of those catalysts and the increase in activity was structure sensitive. The selectivity was also changed. When the same series of catalysts was poisoned with carbon monoxide, a structure-sensitive effect was noted in the deactivation, with the selectivity remaining unchanged. The structure sensitivity of the methylcyclopropane reaction varied as a function of the carbon monoxide coverage and exhibited a maximum resistance to deactivation for a catalyst with 63.5% exposed when the carbon monoxide coverages were greater than 40%. Such results are very interesting because they imply that an optimum particle size may exist for which the deactivation process is inhibited. From a technological point of view, it may be more important to have a catalyst with a longer lifetime, although less active, than to have one initially very active which deactivates rapidly.

The present work presents additional information on possible structure sensitivity of CO poisoning of methylcyclopropane hydrogenolysis for a series of Pt/Al₂O₃ catalysts similar to the Pt/SiO₂ series of Önal. Since the chemical reaction and the supported metal remain the same as in (10, 11),

the study should give information directly comparable to that obtained with Pt/SiO₂.

With respect to the nature of adsorption, for metals such as Pt and Pd the ratio of linear- to bridge-bonded CO is an important factor. Komers *et al.* (12) found that the CO TPD spectra were broad and flat over the range 50 to 600°C. This was attributed to interconversion of different adsorption modes during desorption. Interconversion of such species may be kinetically controlled; Norton *et al.* (13) concluded that linear and bridged species are not in thermodynamic equilibrium at temperatures as high as 320 K. By monitoring the work function change of a Pt (111) plane upon heating and cooling after adsorption of carbon monoxide they found that the work function corresponding to the final temperature was different from that obtained when carbon monoxide was adsorbed at that temperature. The results showed that the carbon monoxide layer produced by warming the carbon monoxide adsorbed at 95 up to 298 K and by adsorbing at 298 K, were not identical, and it was estimated that equilibrium between both adsorbed modes is not reached below about 400 K.

EXPERIMENTAL

Catalysts. The catalysts are from a series prepared in this laboratory about 5 years ago. They were prepared by impregnation of alumina to incipient wetness with [Pt(NH₃)₃(NO₂)]NO₂. The support was γ -Al₂O₃ (Cyanamid, Aero-1000), reported 99.99% pure. The major impurity, Fe, was determined via neutron activation as 30 \pm 10 ppm. Specific surface area was 160 m²/g and the average pore diameter was 120 Å.

The samples used in the present study were of D_h (percentage exposed measured by hydrogen-pulse chemisorption at 25°C) 26.1, 39.4, 72.4, and 96.7%. They are designated here and in prior work (14–16) as 26.1-Al₂O₃-PtNN, 39.4-Al₂O₃-PtNN, etc. and information pertinent to the present study is given in Table 1.

TABLE 1

The Preparation of Alumina-PtNN Catalysts (16)

D_h (%) ^e	26.1 ^d	39.4	72.4	96.7
Pt (wt%)	0.82	0.21	0.28	0.29
T_{calc}	85 ^b	90 ^b	85 ^b	400 ^a
Time (h)	12	18	12	1
T_{red} ^c	300	300	200	300
Time (h)	2	2	2.5	2

^a Calcination at temperature listed in pure oxygen, °C.

^b Calcination at temperature listed in air in oven, °C.

^c Temperature of reduction in hydrogen, °C.

^d Catalyst obtained by reimpregnation after reduction of a 36.1% dispersion catalyst. After reduction, treatment was as indicated in the table.

^e Percentage exposed by hydrogen adsorption after preparation.

Apparatus. Rate measurements were made in an experimental system that is a combination of a differential flow reactor and a chemisorption unit (10, 11, 17). Two types of reactors were used: a $\frac{1}{4}$ -in. Pyrex glass tube with the catalyst maintained in a fixed-bed configuration by glass-wool plugs, or a $\frac{1}{2}$ -in. tube with a fine fritted glass support on top of which the catalyst bed could be maintained in a contained fluidized-bed configuration. The reactor and an upstream temperature equilibration coil were maintained in the same thermostatic bath during reaction experiments.

Procedure. The primary experiments consisted of determination of the activity (turnover frequency) of prepoisoned catalysts for the hydrogenolysis of methycyclopropane under fixed conditions, generally under differential conversion (<10%) and 0°C with 19/1 H₂/MCP feed.

Prior to the poisoning/reaction experiments a standard pretreatment procedure was used, with oxidation in flowing O₂ at 300°C for 0.5 h followed by reduction in H₂ at 300°C, 1 h, and purge with Ar, 480°C for an additional hour. (This will be designated subsequently by the code O₂,300°,0.5; H₂, 300°,1; Ar,480°,1). After the Ar treatment the catalyst was cooled to 25°C and CO

pulsed onto the surface from a 1.5% mixture of CO in Ar. Immediately after the poison adsorption the catalyst temperature was adjusted to the desired level ($-17 \leq T \leq 37^\circ\text{C}$) and the feed mixture that bypassed the reactor during CO adsorption was admitted. Products were sampled via a TCD to monitor conversion for calculation of the rate of reaction; conversions reached a steady state in a few minutes with a slow deactivation rate. The same procedure was employed for each catalyst sample in the series and for CO coverages up to 80% monolayer. Reaction conditions were such that diffusional intrusions were unimportant (17).

Both pulsed and thermal desorption modes were used for prepoisoning. In the pulsed mode the 1.5% CO-Ar mixture was injected in pulses of known volume with the catalyst maintained in a contained fluidized-bed configuration to ensure uniform coverage. Extent of coverages was determined by the material balance. In the desorption mode of poisoning, the catalyst was saturated with carbon monoxide at room temperature after completion of the pretreatment. Saturation was accomplished by successive injection of CO pulses until no additional uptake was detected. After this the catalyst bed was slowly heated in flowing Ar to a predetermined temperature to desorb part of the initial CO monolayer, maintained at this temperature for 0.5 h, then brought to reaction temperature (always under Ar flow).

In the desorption mode of poisoning the relationship between final desorption temperature and fractional coverage, θ , was determined in a separate series of experiments using the following procedure:

(i) Pretreating the catalyst using the normal sequence of $\text{O}_2, 300^\circ, 0.5; \text{H}_2, 300^\circ, 1; \text{Ar}, 480^\circ 1$.

(ii) Saturating the sample at room temperature with repeated pulses of CO in an Ar stream (contained fluidized bed).

(iii) Heating the catalyst slowly (normally 30 to 40 min to final temperature) in flowing Ar.

(iv) Maintaining the catalyst at that temperature under argon flow for another 30 min.

(v) Cooling the sample to room temperature under argon.

(vi) Injecting carbon monoxide pulses to determine the fraction of bare surface.

Separate experiments were required to determine the CO to Pt (surface) stoichiometry. Under the conditions employed here this was essentially 1 : 1 for all catalysts. A standard pulse method was employed; details are given in Ref. (17).

Product analysis. The composition of reactants and products was determined by means of a Gow-Mac Model 9454 thermal conductivity detector. The current, set at 250 mA, was provided by a Gow-Mac power supply control unit Model 40-001. The detector was kept at room temperature.

High-purity He was used as carrier gas for chromatographic analysis. The mixture of reactants and products was separated in a two-column train: a $\frac{1}{4}$ -diameter \times 12-foot-long column packed with 25% dimethylsulfolane on Chromosorb kept in an ice bath at 0°C , and a $\frac{1}{4}$ -in.-diameter \times 1-foot-long silica gel column submerged in an agitated water bath at 57°C . Hydrogen, *n*-butane, isobutane, and methylcyclopropane had retention times of 4.2, 6.6, 7.8, and 11.4 min, respectively.

Reagents. Argon, oxygen, and hydrogen were ultrahigh-purity quality. The oxygen was used in the pretreatment without further purification; the other gases were further treated by passing them through a Dexo unit followed by a molecular sieve 3A column, a silica-gel trap at liquid-nitrogen temperature, and a MnO/SiO₂ bed. Helium for chromatographic analysis was high purity and circulated through a molecular sieve 3A column only. Carbon monoxide, 99.99% minimum purity, was used without further treatment.

The methylcyclopropane (K & K Co.) purity ranged from 98 to 99% as supplied; purification consisted of olefin elimination (primarily butene) in a copper tetraamine

on silica column and demethanation in a molecular sieve 4A column before the preparation of the mixture of reaction. The MnO/SiO₂ and copper tetraamine/SiO₂ columns were prepared following the procedure of Önal (11).

RESULTS AND DISCUSSION

Surface coverage of poison. Determination of poison surface coverage requires knowledge of the carbon monoxide-to-platinum surface atom stoichiometry and the percentage of metal exposed before poisoning. The CO and H₂ uptakes at room temperature were determined in a pulse chemisorption unit. On the basis of H₂ chemisorption experiments (16), a hydrogen-to-surface Pt ratio value of one was used in the calculations ($H/Pt_s = 1$). The samples used in the chemisorption experiments were exposed to the same pretreatment as the samples used in rate measurement experiments (O₂, 300°, 0.5; H₂, 300°, 1; Ar, 480°, 1). Modifying the pretreatment to (O₂, 300°, 0.5; H₂, 480°, 1; Ar, 480°, 1) did not alter significantly the uptakes or the catalyst activity level for the probe reaction (17).

The CO/Pt_s ratios were determined at full CO coverage but it was verified that these did not change at lower coverages. The thermal desorption of CO from Pt in various forms has been reported in the literature and a number of binding states reported (18). There is some variation in the lowest temperature of desorption reported, but for the strongly bound states that one would associate with poisoning there does not appear to be significant desorption below 100°C. Further, there is no evidence of reaction between H₂ and CO or disproportionation of CO up to 200°C (17), in accord with the results of Fujimoto *et al.* (19) and Fogar and Anderson (20).

During the activity experiments using the pulse mode of prepoisoning progressive poisoning was obtained by increasing the amount of CO injected to a fresh sample each time rather than by injecting succes-

sive equal-size pulses to the same sample. Therefore each experiment involved the use of a new charge of catalyst. An exception was 26.1-Al₂O₃-PtNN. This was a re-impregnated material (16), and sufficient variation was seen from sample to sample that it was preferable to complete the whole deactivation study on the same reactor charge.

The surface coverage resulting from the thermal desorption mode of prepoisoning did not correlate well with the behavior predicted by standard isotherm equations such as those by Langmuir or Freundlich. Hence to obtain a θ - T relationship, a second-order polynomial was fitted to the data for individual cases to provide a reliable interpolation model. An example of such a fit is given in Fig. 1 for 26.1-Al₂O₃-PtNN.

Activity for each catalyst is reported as initial isobutane turnover frequency vs D_h at different poison levels or as the ratio of the turnover frequency for isobutane formation on the poisoned sample to that on the fresh sample (N/N_0). The reaction rate on fresh and deactivated catalysts was measured at temperatures ranging from -17 to 37°C.

Relationship of activity to surface coverage. In Fig. 2, the relative activity of the series of catalysts (pulse-mode prepoisoning) is shown as a function of the extent of poisoning. A general pattern of nonlinear deactivation is seen in all cases. If it is assumed that diffusional gradients are absent in the chemisorption of poison, then the nonlinearity can be attributed either to a nonuniformity of the strength of chemisorption as a function of surface coverage, per Maxted (21), or to the requirement of site ensembles involved in the poison/reaction sequence, per Herington and Rideal (22). However, the results of Verma and Ruthven (23, 24) and Clay and Petersen (25) on the poisoning of the hydrogenolysis of cyclopropane on Pt indicate a linear decay of activity with the extent of poisoning. Thus, the nonlinearity indicated in Fig. 2 could possibly be due to diffusional gradients encountered in the deposition of poi-

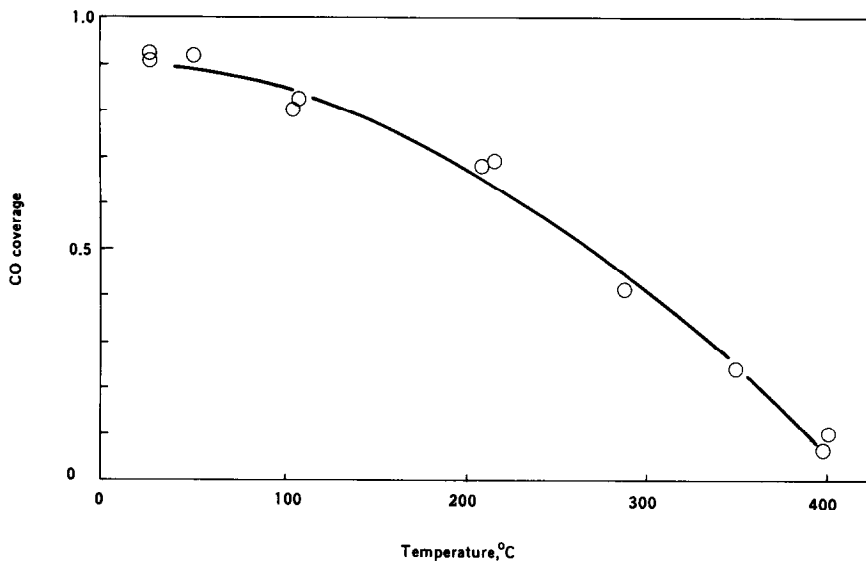


FIG. 1. Example of correlation for CO coverage vs temperature. Thermal desorption experiments for 26.1-Al₂O₃-Pt/NN.

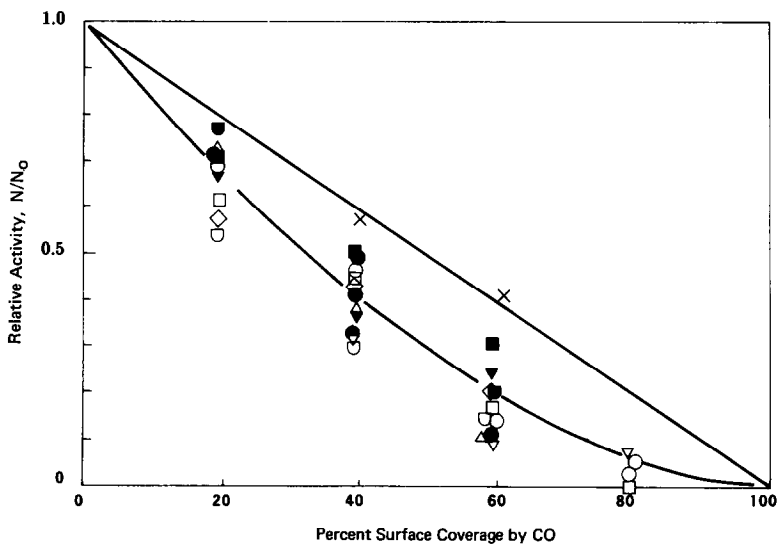


FIG. 2. Relative activity, N/N_0 , vs extent of poisoning at several temperatures of reaction. (x) Fixed-bed experiments.

-17°C	0°C	23°C	37°C	D_h (%)
—	○	—	—	26.1
—	□	■	◇	39.4
—	▽	▼	△	72.8
●	◻	■	—	96.7

son (26). However, plausible mechanistic proposals for the hydrogenolysis of cyclopropanes on metals (27, 28) require an ensemble of more than two atoms that, under poisoning conditions, should lead to a nonlinear decay, as shown in Fig. 2, even in the absence of diffusion.

It would appear these apparent discrepancies between those reporting linear and nonlinear deactivation relationships for this system may be the result of either the deactivation mechanism or experimental procedure. In the case of Clay and Petersen, Pt thin films were poisoned by AsH₃, and a type of "reactive sintering" of the film under reaction conditions was reported; we do not feel that situation is analogous to the present case. Verma and Ruthven used the procedure of injecting the poison in a flow system with a fixed catalyst bed, producing a front of poison that deactivated the catalyst from entrance to exit. This will produce an apparent linear decay of the catalyst when the reactor is operated under differential conversion conditions. In separate experiments here, when pure carbon monoxide was injected into a fixed bed (crosses in Fig. 2), higher activities were obtained than for fluid-bed poisoning and apparent linear decay resulted.

In summary, we feel that the fluid-bed poisoning procedure used here results in poison uniformly distributed on the catalyst and the data reported subsequently are representative of uniform poison distributions within the particles. Further evidence of the absence of intraparticle gradients of poison is obtained by comparing results obtained by prepoisoning via pulse and thermal desorption methods, as discussed below.

Relationships of activity to percentage exposed. Figure 3 shows the turnover frequency for isobutane formation at 0°C as a function of D_h at different extents of deactivation after prepoisoning by pulse chemisorption. Two factors are of importance here. First is the mild structure sensitivity apparent from the curve at the 0% level of

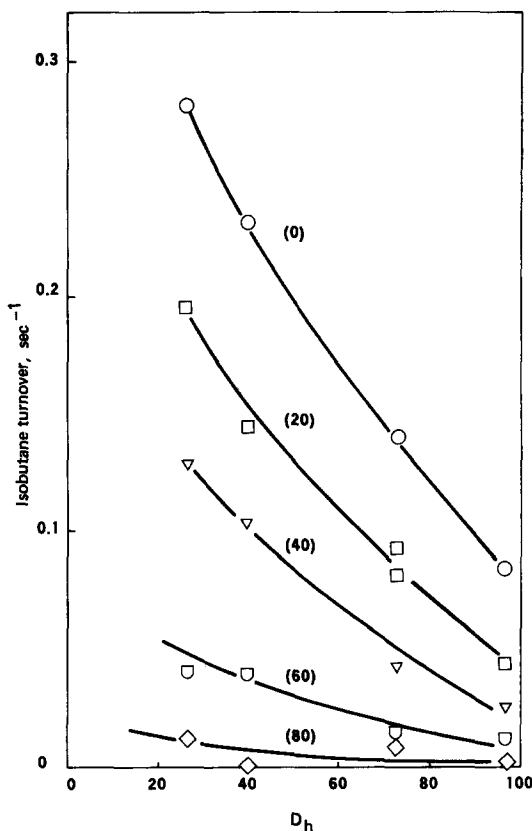


FIG. 3. Isobutane turnover frequency at 0°C vs percentage exposed. Parameter: percentage surface coverage by CO.

poisoning. Methylcyclopropane hydrogenolysis on Pt/Al₂O₃ catalysts was regarded as essentially structure insensitive by Wong *et al.* (29); however, they employed higher pretreatment temperatures in hydrogen than the ones used in this work (370 or 480 vs 300°C) and the reaction is known to be sensitive to this variable. The range of values of turnover frequencies in the two cases (ca. 0.2 sec⁻¹ for isobutane) and the selectivities, though, are similar.

Second, the activity vs percentage exposed falls with increasing carbon monoxide coverage without developing a maximum as was observed by Önal (10, 11) for the same reaction on Pt/SiO₂. Önal observed a maximum in activity upon increasing the severity of the poisoning for a cata-

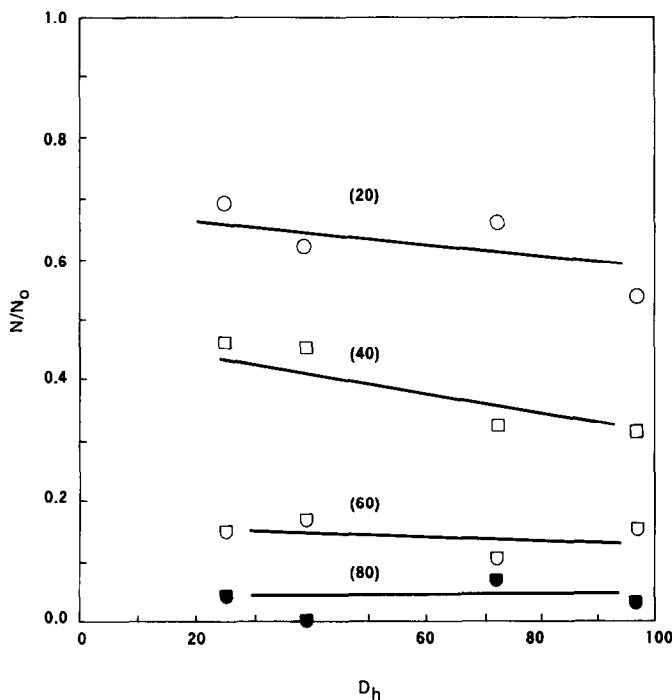


FIG. 4. Relative activity vs percentage exposed. Parameter: percentage surface coverage by CO.

lyst of 63.5% exposed; this maximum appeared at surface coverages greater than 40% and was clearly distinguishable at 50%. Figure 4 shows the change in the relative activity N/N_0 (ratio of turnover frequency for isobutane of poisoned sample to fresh catalyst), measured in this study for each catalyst upon increasing the level of poisoning. For a given concentration of poison on the surface, lower- D_h catalysts show a slightly better performance, however, all catalysts in the series lose activity to about the same extent. This conclusion is also reflected in Fig. 2.

The reason for the difference in the response to poisoning between Pt/SiO₂ and Pt/Al₂O₃ is not evident. In both cases during preparation, care was taken to avoid contamination so the support could be regarded as highly pure and effects induced by the presence of impurities in the support are unlikely. Chloride is absent from all catalysts of both series except for one Pt/SiO₂

sample, and the temperatures used are low enough to prevent formation of alloys (30, 31).

In the progressive poisoning experiments on the Pt/SiO₂ catalysts, it was assumed that the carbon monoxide-to-platinum surface atom ratio was 1 throughout the whole range of D_h . However, experimentally, values ranging from 0.85 to 1.12 were found. Since that ratio is essential in determining the fraction of poisoned surface area, calculation of the fraction covered with carbon monoxide using a ratio of 1 could lead to the observed discrepancy. However, reanalysis of the Pt/SiO₂ results using the experimentally determined carbon monoxide-to-platinum surface atom ratios for each catalyst still resulted in a maximum activity for coverages in excess of 50% at a percentage exposed of 63.5%, though, if the 63.6% catalyst is removed from the Pt/SiO₂ series examined by Önal, the trend of activity vs percentage exposed at increasing coverage

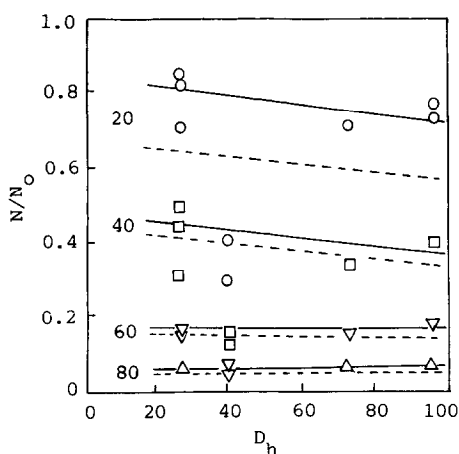


FIG. 5. Relative activity vs percentage exposed for all catalysts at different levels of CO surface coverage. Symbols and solid lines—desorption mode of poisoning; dotted lines—pulse mode of poisoning. (○) 20%, (□) 40%, (▽) 60%, (△) 80% CO coverage.

of carbon monoxide yields a result very similar to those presented here for Pt/Al₂O₃.

Although both silica and alumina are usually considered to produce only weak metal-support interactions, it is generally accepted that alumina interacts with the supported metal more strongly than silica. The possibility exists then that the differences in behavior of the two series is due to a stronger interaction between the alumina and the platinum particles, especially for high-percentage exposed catalysts. One can visualize the interaction as producing a stabilization of the properties of the particles supported on alumina. Those particles supported on silica are less influenced and probably retain characteristics that each particle acquired during preparation of the catalyst (for example, the planes exposed in the 63.5%-Pt/SiO₂ catalyst could be such that the carbon monoxide sticking coefficient is very low compared to that of the planes limiting the metal particles on the other catalysts). If the probability of adsorption is initially low and decreases further upon increasing CO coverage, it is pos-

sible to generate the observed maximum in the activity of the Pt/SiO₂ family when the severity of the poisoning is increased. Conversely, particles on alumina would tend to lose their history and have similar properties on all the catalysts.

The degree of consistency of the present results is indicated in Fig. 5, which compares the relative activities obtained in experiments after prepoisoning in the thermal desorption mode with those obtained after pulse chemisorption. The values of N/N_0 for 39.4-Al₂O₃-PtNN are anomalously low for all levels of surface coverage. At present we have no explanation for this but, since the magnitudes of (N/N_0) are comparable to the pulse results for all other catalysts, the following discussion omits consideration of this specific sample.

It is seen in Fig. 5 that the relative activity for catalysts with low CO coverage (i.e., 20%) is somewhat higher than their counterparts prepared using pulse poisoning. This difference decreases substantially at 40% coverage and essentially disappears at higher coverages. We feel this difference can be generally explained in view of the observations of Crossley and King (32) and Bartok *et al.* (33). When desorption is initiated from a monolayer of CO, surface migration is limited since all surface sites are occupied and desorption occurs first from low Miller index planes. This is the situation at high surface coverages here, and the state of the surface is apparently similar to that produced by pulse chemisorption at high coverages. However, in the desorption mode of deactivation the adlayer must be heated up to fairly high temperatures to produce low coverages and by annealing the adsorbate layer surface reconstruction may result in desorption from states not present at the moment of adsorption (32, 33). Such rearrangements would not be expected in pulse poisoning at low coverages. Thus differences in the structure of the CO adlayer at low coverages are a possible explanation for the moderate differences in

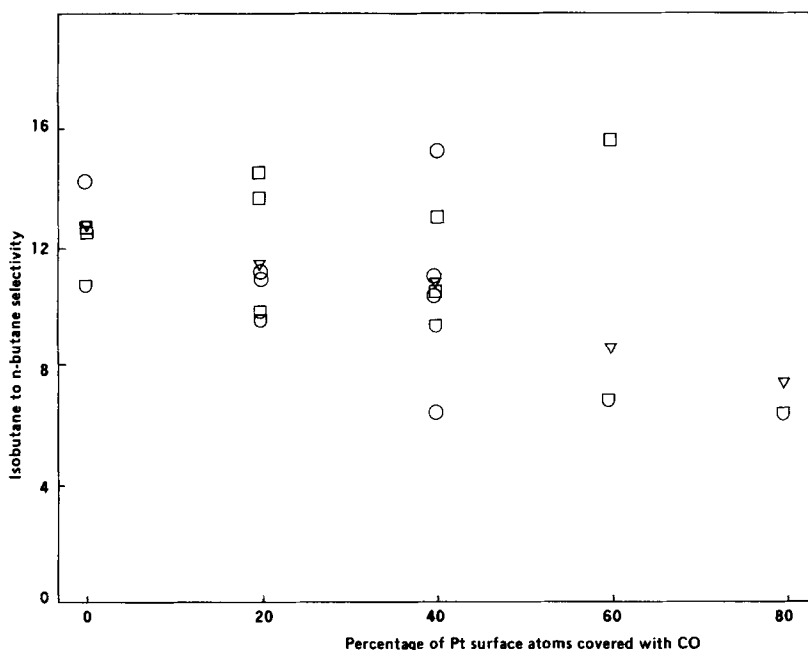


FIG. 6. Selectivity (N_{i-C_4}/N_{n-C_4}) as a function of extent of poisoning, reaction at 0°C. (□) 26.1-Al₂O₃-PtNN, (○) 39.4-Al₂O₃-PtNN, (▽) 72.4-Al₂O₃-PtNN, (◻) 96.7-Al₂O₃-PtNN.

activity observed at 20% coverage; such re-ordering leaves available more active surface in the desorption mode than the pulse mode although the apparent coverages are the same.

Selectivity. Figure 6 shows the selectivities measured for each catalyst as a function of the severity of the poisoning for reaction at 0°C after prepoisoning in the pulse mode. The scatter in the data reflects the error associated with the determination of the change in the mole fraction of *n*-butane from the inlet to the outlet of the reactor. No simple relation is evident. Normal butane is present to a small extent as an impurity in the feed and analysis of *n*-butane formation requires subtraction of two similar mole fractions. The smaller scatter at 0% coverage is due to a more accurate analysis because conversion is higher, and these data agree with those reported by Wong *et al.* (29). Essentially identical results were obtained after prepoisoning via thermal de-

sorption (17). Thus, selectivity appears invariant with increasing poisoning, as reported also for Pt/SiO₂ catalysts under poisoning conditions (10, 11). Since this indicates that isobutane and *n*-butane formation are similarly affected by the poison one would infer that, whatever the detailed mechanism of hydrogenolysis may be, the same site(s) are involved and are similarly affected for both products.

Apparent activation energies. The rate of reaction was measured on fresh and poisoned catalysts at three different temperatures (-17, 0, and 23°C or 0, 23, and 37°C) in order to obtain the corresponding Arrhenius plots. The results for isobutane formation are given in Table 2 while those for *n*-butane formation are given in Table 3. The apparent activation energies for the fresh catalysts are in very good agreement with the values reported earlier by Wong *et al.* (29) for catalysts of the same family. In that case the average activation energy of the

TABLE 2

Activation Energy for Isobutane Formation as a Function of Poisoning Severity

Catalyst and percentage of surface area poisoned	Activation energy (kJ/mole)
26.1-Al ₂ O ₃ -PtNN	
0	33.6
20	37.1
39.4-Al ₂ O ₃ -PtNN	
0	30.7
20	32.0
40	33.0
60	38.2
72.4-Al ₂ O ₃ -PtNN	
0	35.6
20	37.7
40	39.4
60	41.9
96.7-Al ₂ O ₃ -PtNN	
0	39.9
20	43.3
40	46.1
60	45.1
Average	34.9 ± 7.9

series for isobutane formation was found to be 36.4 ± 2.3 kJ/mole while for *n*-butane it was 42.3 ± 4.2 kJ/mole. In the present study the average activation energies for isobutane and *n*-butane formation are 35 and 40 kJ/mole, respectively.

Careful examination of the data in Tables 2 and 3 reveals a mild increase in the apparent activation energy upon increasing the degree of poisoning. The actual meaning of this observation is obviously affected by the error associated with the determination of the activation energies, which we estimate as approximately 7.9 kJ/mole (17). This magnitude of error makes it difficult to decide whether there is a true change or not. However, the persistence of the trend throughout the whole series of catalysts and for both reaction products must have some significance and we feel it reflects the increasing influence of CO in progressively displacing the reaction to less-favorable sites. This would suggest that CO ad-

sorbs on the same sites where the reaction occurs, that there is a true competitive poisoning mechanism, and as poisoning progresses the reaction is displaced to higher activation energy sites. Since this explanation is consistent with the existence of a heterogeneous surface, it could be somewhat at odds with the view one could derive from the selectivity results, that indicate only the blocking of *n*-atom ensembles on a homogeneous surface. It is indeed possible, however, that the selectivity results also indicate that blocking of heterogeneous site distributions is similar over the distribution. Thus, in actuality both surface heterogeneity and ensemble effects could contribute to deactivation behavior, although the latter would presumably not affect the activation energy.

The simultaneous adsorption of carbon monoxide and hydrogen. Prepoisoning of the surface by carbon monoxide alone leads only to information concerning the CO-Pt interaction. It would be of interest to look at the competition, or at least cohabitation,

TABLE 3

Activation Energy for *n*-Butane Formation as a Function of Poisoning Severity

Catalyst and percentage of surface area poisoned	Activation energy (kJ/mole)
26.1-Al ₂ O ₃ -PtNN	
0	38.5
20	43.7
39.4-Al ₂ O ₃ -PtNN	
0	37.7
20	38.8
40	40.6
60	44.4
72.4-Al ₂ O ₃ -PtNN	
0	40.5
20	45.7
40	48.9
96.7-Al ₂ O ₃ -PtNN	
0	43.1
20	48.6
40	46.4
Average	39.9 ± 7.9

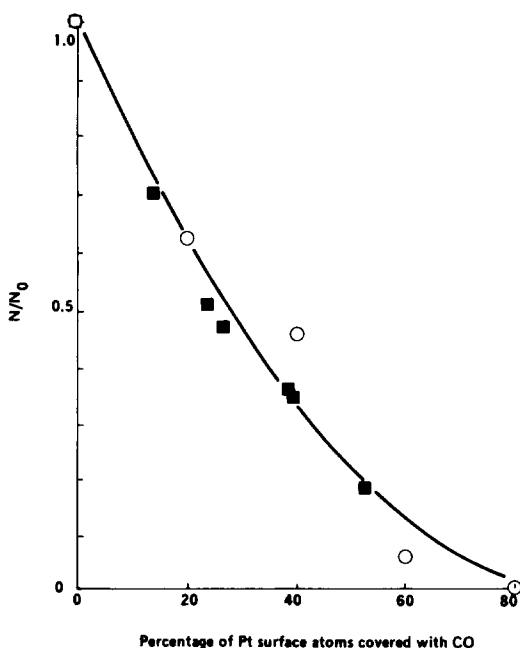


FIG. 7. Relative activity vs level of poisoning for 39.4- Al_2O_3 -PtNN. Reaction at 0°C . (○) Pulse poisoning, CO + Ar, (■) coadsorption, CO + H_2 .

of reactant and poison on the surface. Since methylcyclopropane is very strongly adsorbed on the surface the interesting pair here is carbon monoxide and hydrogen.

A mixture of ultrahigh-purity hydrogen and carbon monoxide having a CO mole fraction of 0.05734 was pulsed at room temperature over the 39.4- Al_2O_3 -PtNN and 96.7- Al_2O_3 -PtNN catalysts after the usual pretreatment and before reaction at 0°C . The fraction of the surface covered by the carbon monoxide was calculated assuming that all the carbon monoxide injected was adsorbed. Figures 7 and 8 show the results obtained. For the 39.4- Al_2O_3 -PtNN catalyst the relative activity change with coverage is similar to that observed in the case of the pure poisoning with CO-Ar. For the 96.7- Al_2O_3 -PtNN the relative activity is slightly higher than for similar conditions with CO-Ar. The selectivity is constant with the extent of the poisoning, similar to the results shown in Fig. 6.

There have been a number of studies of CO- H_2 coadsorption of Pt. In most cases it has been found that adsorption states of hydrogen are somewhat modified in the presence of CO (for example, the TPD results of Peebles *et al.* (34)) or, conversely, that CO IR spectra are not altered in the presence of hydrogen (35, 36). Both results suggest a stronger adsorption of CO than H_2 on Pt. The displacement of adsorbed hydrogen by CO has also been demonstrated (37, 38). On the basis of all this one would expect there to be no difference between CO-Ar and CO- H_2 prepoisoning.

The small increase in relative activity for 96.7- Al_2O_3 -PtNN here may be due to a modification of relative hydrogen and CO chemisorption with percentage exposed. Morgan and Somojai (39) have shown that hydrogen preferentially chemisorbs on high Miller index planes, and this result is consistent with the studies of Anderson *et al.* (40) on hydrogen TPD from Pt catalysts of varying particle size. Such high index planes should be more numerous on a relative basis for 96.7- Al_2O_3 -PtNN than for

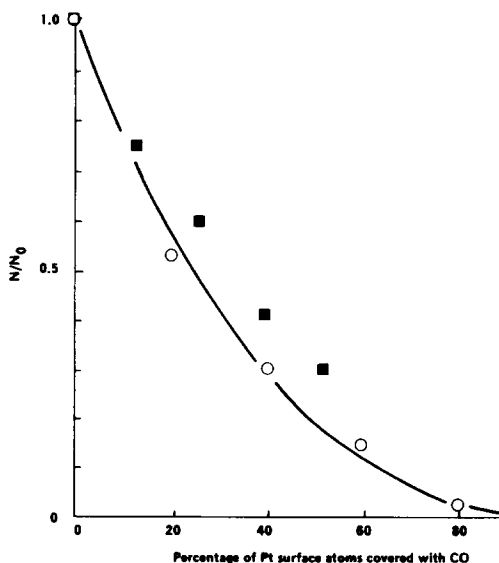


FIG. 8. Relative activity vs level of poisoning for 96.7- Al_2O_3 -PtNN. Reaction at 0°C . Symbols as in Fig. 7.

39.4-Al₂O₃-PtNN so that the hydrogen competes on a more favorable basis for adsorption sites on the high-percentage exposed material. The result is a slight decrease in apparent coverage compared to that expected from the CO pulse size, as reflected in Fig. 8.

In practice this implies that if the poison is fed to the reactor together with the reactant mixture and competes for adsorption sites, the relative strength of the adsorption can play a part in determining which particle size is more resistant to poisoning. In this event, the apparent structure sensitivity of deactivation may be different from that observed in prepoisoning experiments.

The effect of poisoning on the activity of regenerated catalysts. Each poisoning experiment was carried out on fresh catalyst except for the 26.1-Al₂O₃-PtNN catalyst. The activities measured for this catalyst were not as reproducible as those determined for the rest of the series and it was felt that more self-consistent results could be obtained with progressive poisoning experiments on this material with a single catalyst charge. This provided the opportunity to investigate the effect of successive cycles of carbon monoxide poisoning and reactivation of the catalyst. This was done using the pulse mode of poisoning. Table 4 gives a summary of the history of the sample employed in the experiments at 0°C. The results suggest that there is no significant memory effect in the catalyst after the poisoning-reativation sequence.

CONCLUSIONS

The progressive poisoning by carbon monoxide of Pt/alumina catalysts used in the methylcyclopropane hydrogenolysis did not alter the sensitivity of the reaction to the structure of the surface. These results contrast with those obtained previously for Pt/SiO₂ catalysts. In that case a maximum of activity was observed for a 63.5% exposed catalyst for poisoning levels higher than 40%. In the present case, the

TABLE 4

The Effect of Poisoning on the Activity of Regenerated Catalysts^a

Catalyst: 26.1-Al ₂ O ₃ -PtNN			
Percentage of area poisoned	<i>N</i> (isobutane) (sec ⁻¹)	Selectivity ^b (i-C ₄ / <i>n</i> -C ₄)	
0	0.28	14.2	
		13.7	
		14.8	
20	0.19	15.5	
		40	18.8
		60	19.8
80	0.010	12.3	
		0	17.1

^a Same catalyst sample pretreated: O₂,300°,0.5;H₂,300°,1;Ar,480°,1 before each experiment.

^b Selectivity obtained as the average of the selectivities found at each sampling of the reaction products.

activity vs *D_h* curve for increasing levels of poisoning falls parallel to that for unpoisoned catalysts and no maximum is developed.

The apparent activation energy for isobutane (and *n*-butane) formation increases slightly with increasing poisoning. The change is small and within experimental error, but consistently observed for all catalysts at all levels of poisoning and suggestive of the selective poisoning of the sites most favorable for reaction. The independence of reaction selectivity from level of poisoning, however, suggests that site blocking is also an important contribution to deactivation. Thus we conclude that a certain amount of heterogeneity exists in the energetics associated with surface sites active for hydrogenolysis, but that CO chemisorption occurs on these sites in a manner that does not modify their nature and deactivation occurs by blockage.

Overall, the reaction is mildly structure sensitive to deactivation by CO poisoning in the sense that absolute values of the trend in relative activity with surface coverage with poison differ somewhat for different percentages of metal exposed. How-

ever, the variations in absolute turnover frequency with surface coverage are similar for all catalysts in the Pt/Al₂O₃ series investigated.

CO and H₂ coadsorption studies revealed that when the poison and one of the reactants compete for adsorption sites the relative strength of their adsorption on different surfaces is important in determination of the deactivation rate. This is obviously dependent on the poison-reactant pair.

Poisoning Pt/Al₂O₃ catalysts by partial desorption of a preadsorbed monolayer of CO gives similar results to those obtained using the pulse mode of poisoning when poisoning was extensive. For low poisoning levels, a somewhat higher relative activity was detected compared to that of similar poison coverage in the pulse mode. The differences at low coverage may be explained in terms of changes in the CO adsorbate layer induced by thermal reconstruction.

ACKNOWLEDGMENTS

We are indebted to the National Science Foundation, Grant CPE-7915234, The Stauffer Chemical Company, and the Mobil Foundation for partial support of this research. DED also gratefully acknowledges the fellowship support of the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina.

REFERENCES

- Mitrofanova, A. N., Boronin, V. S., and Polotorak, O. M., *Russian J. Phys. Chem.* **46**, 32 (1972).
- Ostermaier, J. J., Katzer, J. R., and Manogue, W. H., *J. Catal.* **33**, 457 (1974).
- Rabo, J. A., Schomaker, V., and Pickert, P. E., in "Proceedings, 3rd International Congress of Catalysis" (Sachtler, Schuit, and Zuitering, Eds.), p. 1264. North-Holland, Amsterdam, 1961.
- Davis, S. M., and Somorjai, G. A., *J. Catal.* **65**, 78 (1980).
- Ponec, V., in "Metal-Support and Metal Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.). Elsevier, Amsterdam, 1982.
- Hertz, R. K., Gillespie, W. C., Petersen, E. E., and Somorjai, G. A., *J. Catal.* **67**, 372 (1981).
- Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37**, 324 (1978).
- Barbier, J., Morales, A., Marecot, P., and Maurel, R., *Bull. Soc. Chim. Belg.* **88**, 569 (1979).
- Hegedus, L. L., and McCabe, R. W., "Advances in Catalysis," Vol. 23, p. 377. Academic Press, New York, 1981.
- Önal, I., and Butt, J. B., *J. Chem. Soc. Faraday Trans. 1* **78**, 1887 (1982).
- Önal, I., Ph.D. dissertation. Northwestern University, 1981.
- Komers, R., Amenomiya, Y., and Cetanovic, R. J., *J. Catal.* **15**, 293 (1969).
- Norton, R. R., Goodale, J. W., and Selkirk, E. B., *Surf. Sci.* **83**, 189 (1979).
- Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **53**, 414 (1978).
- Uchijima, T., Hermann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50**, 464 (1977).
- Kobayashi, M., Inoue, Y., Takahashi, N., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **64**, 74 (1980).
- Damiani, D. E., Ph.D. dissertation. Northwestern University, 1984.
- McCabe, R. W., and Schmidt, L. D., *Surf. Sci.* **66**, 101 (1977).
- Fujimoto, K., Kokeyama, M., and Kunugi, T., *J. Catal.* **61**, 7 (1980).
- Foger, K., and Anderson, J. R., *Appl. Surf. Sci.* **2**, 335 (1979).
- Maxted, E. B., *Trans. Faraday Soc.* **41**, 406 (1945).
- Herington, E. F. G., and Rideal, E. K., *Trans. Faraday Soc.* **40**, 505 (1944).
- Verma, A., and Ruthven, D. M., *J. Catal.* **19**, 401 (1970).
- Verma, A., and Ruthven, D. M., *J. Catal.* **46**, 160 (1977).
- Clay, R. D., and Petersen, E. E., *J. Catal.* **16**, 32 (1970).
- Wheeler, A., in "Catalysis" (P. H. Emmett, Ed.), Vol. II. Reinhold, New York, 1955.
- Anderson, J. R., and Avery, N. R., *J. Catal.* **8**, 48 (1967).
- Chevreau, T., and Gault, F. G., *J. Catal.* **50**, 124 (1977).
- Wong, S. S., Otero-Schipper, P. H., Wachter, W. A., Inoue, Y., Kobayashi, M., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **64**, 84 (1980).
- Dautzenberg, F. M., and Wokers, H. B. M., *J. Catal.* **51**, 26 (1978).
- den Otter, G. C., and Dautzenberg, F. M., *J. Catal.* **53**, 116 (1978).
- Crossley, A., and King, D. A., *Surf. Sci.* **95**, 131 (1980).
- Bartok, M., Sarkany, J., and Sitkei, A., *J. Catal.* **72**, 236 (1981).

34. Peebles, D. E., Creighton, J. R., Belton, D. N., and White, J. M., *J. Catal.* **80**, 482 (1983).
35. Basset, J. M., Dalmai-Imelik, A., Primet, M., and Martin, R., *J. Catal.* **22** (1975).
36. Vannice, M. A., Twn, C. C., and Moon, S. H., *J. Catal.* **79**, 70 (1983).
37. McKee, D. W., *J. Catal.* **8**, 240 (1967).
38. Nishiyama, Y., and Wise, H., *J. Catal.* **32**, 50 (1974).
39. Morgan, H. E., and Somorjai, G. H., *Surf. Sci.* **12**, 405 (1968).
40. Anderson, J. R., Foger, K., and Breakspere, R. J., *J. Catal.* **57**, 458 (1979).