CO Poisoning of Pt/TiO₂: Methylcyclopropane Hydrogenolysis on a Highly Dispersed Catalyst

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The differences in poisoning of methylcyclopropane hydrogenolysis by carbon monoxide are investigated here for Pt/TiO₂ in both the "normal" and "strong metal–support interaction" (SMSI) states. High-dispersion Pt/TiO₂ ("normal") appears slightly more susceptible to carbon monoxide poisoning than comparable Pt/SiO₂ or Pt/Al₂O₃ catalysts (Önal, I., and Butt, J. B., *J. Chem. Soc. Faraday Trans. 1* **78,** 1887, 1982; and Damiani, D. E., and Butt, J. B., *J. Catal.* **94,** 203, 1985). The SMSI Pt/TiO₂ catalyst is less active than normal material for the hydrogenolysis, but apparently more resistant to poisoning. Tolerance to CO for the SMSI material would appear to be the result of capacity of the support for CO uptake under these conditions, but the interpretation of all results depends upon how one defines the turnover frequency of the SMSI catalyst. © 1985 Academic Press, Inc.

INTRODUCTION

It is well known by now that reduction at high temperatures of group VIII metals supported on titania produces a strong metal–support interaction (SMSI state), recognized by the suppression of hydrogen and carbon monoxide chemisorption on the catalyst (*1*). Depression of the chemisorption seems to be a reliable indication of the onset of the SMSI state, but so far this chemisorption phenomenon is about the only fact agreed upon by the majority of workers in the field.

In this study, the effects of carbon monoxide poisoning on methylcyclopropane hydrogenolysis have been investigated for a high-percentage exposed Pt/TiO₂ catalyst in both the normal and SMSI states. The methodology employed is similar to that used in prior studies of Pt/SiO₂ and Pt/Al₂O₃ (*2, 3*).

EXPERIMENTAL

Details of the experimental apparatus, reagents, and experimental procedures are

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similar to those described for Pt/Al₂O₃ (*3*). As before, carbon monoxide prepoisoning was carried out by pulse chemisorption from a 1.5% mixture of CO in Ar at room temperature with the catalyst in a contained fluidized bed. Separate experiments were conducted to obtained the CO/Pt (surface) stoichiometry so that the CO surface coverage could be determined from the pulse adsorption treatment. Methylcyclopropane hydrogenolysis was carried out at 0°C under differential conversion conditions with a 19/1 H₂/HC feed mixture.

The Pt/TiO₂ catalyst was a very fine powder that tended to agglomerate and form a pellet-like bed if compressed between glass-wool plugs. As a consequence, the catalyst was mixed with a similar amount of 60–80 mesh silica and fluidized to prevent both agglomeration and local heat effects. It was verified in separate experiments that the silica did not adsorb carbon monoxide from the pulses injected.

Catalyst. The titania used as a support was prepared by the procedure developed at the Center for Catalytic Science and Technology at the University of Delaware and was supplied by the Engineering Tech-

nology Laboratory of E. I. du Pont de Nemours & Co.[2] Titania prepared in this manner is in the anatase phase and is characterized by its high purity, especially with respect to concentrations of lead and silicon. The catalyst was prepared by ion exchange of $[(NH_3)_4Pt]^{2+}$ with acid sites on the support surface. The support is first uniformly permeated with the Pt complex via immersion in aqueous solution at pH 5.5 for 48 h. The exchange is then accomplished by pH adjustment to 10.0 with equilibration for 24 h. The catalyst material is recovered by filtering the solution, washed, and dried at 120°C for 24 h. Finally, the material is calcined, O_2,350°,2, and then reduced in H_2 as desired. This catalyst is typically characterized by high dispersion of the metal in small crystallites.

The relevant details of the sample examined in the present study are:

—The support, calcined at 400°C, had a BET area of 128 m^2/g.

—The Pt loading for the sample, calcined at 350°C, is 1.08%, measured by atomic absorption.

—After H_2 reduction at 200°C the BET area was 114 m^2/g and the metal area obtained by hydrogen/oxygen titration was 244 m^2/g of Pt, assuming 1 wt% Pt.

—After H_2 reduction at 400°C the BET area was 118 m^2/g and there was no detectable H_2 chemisorption.

—Transmission electron microscopy analysis of the catalyst reduced at 200 and 400°C revealed no difference.

The percentage metal exposed can be estimated on the basis of an assumption of Pt atom density. Using a value of 1.24×10^{15} atom/cm^2 (assuming that the low Miller index planes are the ones exposed and that all appear in the same proportion), one calculates a percentage of metal exposed of 98%. This result was experimentally verified by hydrogen-pulse chemisorption at room

temperature (4), reported subsequently as D_h. Two consecutive determinations on a sample of 0.4028 g resulted in measured exposures of 92.6 and 97.8%. Pretreatment before these chemisorption experiments started with catalyst stored in air, H_2,200°, 1;Ar,350°,1; cool in Ar. This differs from prior work with Pt/SiO$_2$ and Pt/Al$_2$O$_3$ in that an initial step, O_2,300°,0.5, was not employed (see below for the code describing pretreatment sequences).

Pretreatment. Before poisoning the catalyst was pretreated in one of the following ways:

Pretreatment a: reduction in flowing H_2 at 200°C for 1 h followed by purge in Ar at 350°C for 1 h (H_2,200°,1;Ar,350°,1).

Pretreatment b: H_2,350°,1;Ar,350°,1.

Pretreatment c: O_2,350°,1;H_2,200°,1;Ar, 350°,1.

Pretreatment a rendered a clean highly dispersed "normal" (free of SMSI) catalyst. Pretreatment b introduced a SMSI state and pretreatment c restored "normality."

RESULTS AND DISCUSSION

Modification of chemisorption. The hydrogen chemisorption measurements described above were carried out after the pretreatment H_2,200°,1;Ar,350°,1 and the good agreement with the theoretical exposure value also implies that (i) H_2,200°,1 is sufficient to reduce the catalyst and (ii) Ar, 350°,1 is sufficient to remove residual hydrogen and produce a completely reduced Pt metal surface.

The modification of the hydrogen chemisorption capacity for this catalyst was investigated as a function of temperature of reduction. In these experiments the pretreatment consisted of H_2,T,1;Ar,350°,1 where T varied from 200 to 360°C. The results of several cycles are shown in Fig. 1. It is seen that substantial reduction in chemisorption, D_h, occurs as pretreatment temperature, T, is increased (for example, Expts 1–7 in the figure). Chemisorption capacity of the normal catalyst is restored,
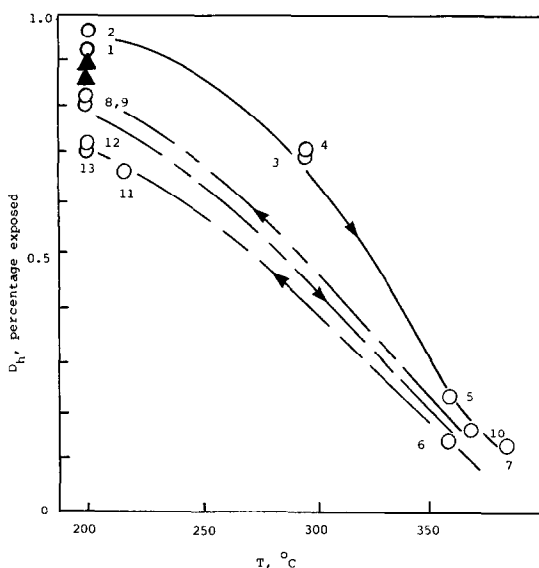
FIG. 1. Percentage exposed as a function of reduction temperature. Numbers beside Circular Symbols denote the sequence of experiments. Experiments 8 and 11 were performed after Expts 7 and 10 following: $O_2,350°,15$; $H_2,200°,1$; $Ar,350°,1$. (▲) Comparison of percentage exposed measured by CO chemisorption for Expts 1 and 8.

although not to the initial level, by means of $O_2,350°,1;H_2,200°,1;Ar,350°,1$ (i.e., Expts 8 and 11 after Expts 7 and 10). It is seen that there is a progressive decrease in chemisorption capacity of the normal catalyst as the reduction–oxidation cycle is repeated. Similar modification of carbon monoxide chemisorption was also observed and is also presented in Fig. 1; however, oxidation–reduction cycling was not carried out in this case.

A first explanation for these results is that metal is progressively lost due to occlusion caused by a possible collapse of the support. However, the temperature used here was never higher than the temperature at which the support was calcined (400°,12) and the exposure time at the highest temperature was never greater than 1.5 h. Further, one would not expect occlusion to be so readily reversible. Therefore we feel that occlusion is not a reasonable explanation for the observed results.

Chien et al. (5) detected a charge transfer

from support to metal on a Rh/titania catalyst reduced at high temperature by XPS. They initially observed a charge transfer of 0.6 e/Rh atom, but after several cycles of reduction at high temperature, then oxidation plus reduction at low temperature, the amount of electronic charge transferred stabilized at 0.2 e/Rh atom. The authors concluded that a constant value was achieved when the effect of the relaxation energy (a function of the metal particle size) was constant, indicating that the catalyst had reached a stable particle size. Very similar results were published by Sexton et al. (6).

Chung et al. (7) and Haller et al. (8) have recently proposed that the SMSI state is due to a suboxide of TiO_2 that migrates to the surface of the catalyst. An oxidation step reverses this to metal oxide/TiO_2, which can be reduced again at low temperature to give "normal" metal/TiO_2 or at high temperature to again produce SMSI. It is possible that this mechanism is not fully reversible and the initial chemisorption ability is never fully restored. At the present moment, both explanations can account for what is observed in Fig. 1.

Poisoning of Pt/TiO₂. The fraction of the surface covered with carbon monoxide was determined by knowing the amount injected in the pulse and the carbon monoxide to Pt atom ratio at each temperature as obtained from the ratio of (H/Pt total) to (CO/Pt total) from the data given in Fig. 1.

The results of the reaction experiments are shown in Fig. 2 where the relative turnover frequencies, N/N_0, for isobutane formation on Pt/TiO_2 reduced at low temperature (pretreatment a) are plotted vs the level of poisoning. For comparison,the same information concerning similar highly dispersed Pt/SiO_2 and Pt/Al_2O_3 catalysts is also shown. In principle, all three catalysts were in a normal state. From Fig. 2 it would appear that Pt/TiO_2 is slightly more sensitive to comparable levels of carbon monoxide surface coverage than Pt on the other supports.

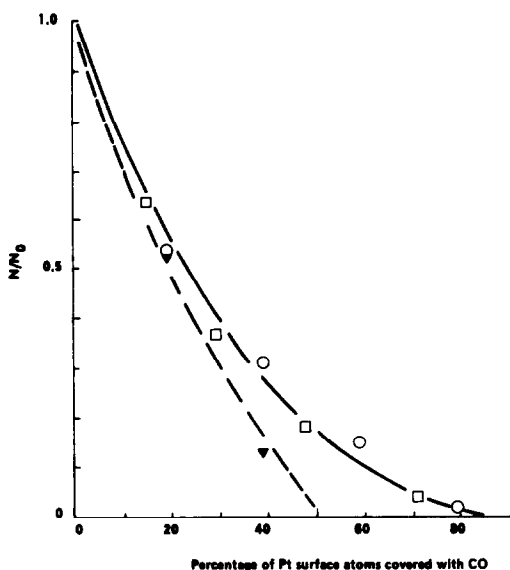*Poisoning in the SMSI state and after re-*

FIG. 2. Relative activity for isobutane formation vs surface coverage of CO$_x$ for Pt/TiO$_2$ reduced at low temperature. (O) 96.7-Al$_2$O$_3$-PtNN (Ref. (23)), (□) 81-SiO$_2$-Ion X (Ref. (22)), (▼) 95.2-PtTiO$_2$.

generation. A similar series of poisoning experiments was carried out for material in the SMSI state and after regeneration, i.e.,

after pretreatments b and c. However, as so well stated by Resasco and Haller (9), those working with noble metals supported on TiO$_2$ have been struggling since the beginning with the problem of how to report rates on catalysts following high-temperature reduction. The problem is compounded here with how to report CO uptakes on the SMSI catalyst, since both the apparent percentage exposed, D_h, and the CO/H ratio vary with pretreatment as shown in Table 1. One approach is simply to account for the variation by ratio compared to the normal catalyst. Thus, for the catalyst after pretreatment a in these experiments it was necessary to chemisorb a pulse of 0.15 μmole of CO to attain 20% coverage and 0.30 μmole to attain 40% coverage. The same pulse sizes were used for the samples after pretreatments b and c. Correcting for changes in D_h via blockage and CO/H (4), one estimates that 0.15 μmole of CO covers 56% of the Pt surface atoms produced by pretreatment b (Sample B) and 23% of those produced by pretreat-

TABLE 1

Activity of Pt/TiO$_2$ for Isobutane Formation as a Function of Surface Coverage of CO after Different Pretreatments

Sample	D_h (%)	Coverage	Pretreatment	CO/H	N (sec^{-1})		Relative activity, N/N_o	Selectivity (i-C$_4$/n-C$_4$)
A	95.2	0	a	0.87	0.31		1	9.3
	95.2	20	a	0.87	0.16		0.52	8.6
	95.2	40	a	0.87	0.04		0.13	5.2
B	16.3	0	b	1.84^c	1.33	0.23^e	1	8.2
	16.3	56	b	1.84	0.89	0.15^e	0.67	8.5
	16.3	112	b	1.84	0.51	0.09^e	0.38	8.6
C	80.5^a	0	c	0.91^c	0.43		1	8.6
	80.5^d	23	a	0.91	0.29		0.67	8.9
	80.5^d	46	a	0.91	0.13		0.30	8.7

Note. Pretreatments: a—H$_2$,200°,1;Ar,350°,1 (non-SMSI). b—H$_2$,350°,1;Ar,350°,1 (SMSI). c—O$_2$,350°,1;H$_2$, 200°,1,Ar,350°,1 (restore non-SMSI). Comparison: N (isobutane) for a Pt/SiO$_2$ catalyst of D_h similar to sample B (21.5%) under the same conditions of reaction is about 0.14 per sec following O$_2$,300°,0.5;H$_2$,370°,1;He,450°,1. Corresponding selectivity value is 15 (13).

^{a} Unpoisoned sample B after pretreatment c.
^{b} Isobutane turnover frequency at 0°C based on D_h.
^{c} Average value of about five measurements.
^{d} Samples after pretreatment a.
^{e} Isobutane turnover frequency at 0°C based on D_h measured for A.

ment c (Sample C). Similarly, the 0.30 μmole correspond to 112 and 46% for samples B and C, respectively. A summary is provided in Table 1.

The turnover frequency data for the SMSI catalyst, based on apparent D_h in the SMSI state, indicate that this material is much more active than its "normal" counterpart (Sample A), and is more resistant to poisoning. However, most workers have chosen to report the turnover frequency data on TiO_2 catalysts reduced at high temperature based on the percentage exposed measured for the low-temperature reduction material. These values (footnote e in Table 1) indicate lower activity after high-temperature reduction and are in accord with prior observations reporting depression of hydrogenolysis activity for SMSI catalysts (10). The suppression of hydrogenolysis activity, however, seems to be somewhat less for the cyclic bond here than for the paraffinic bonds of ethane and n-butane reported by Resasco and Haller (9).

There is, though, still indication that a catalyst with apparent monolayer coverage of CO (Sample B, pretreatment b) possesses measurable activity for the hydrogenolysis reaction. It must be concluded that the assignment of CO uptake to available Pt surface as measured by D_h is incorrect and a significant portion of the CO ends up elsewhere on the catalyst. This can be explained in terms of the results of Anderson et al. (10), who have proposed that there is an appreciable bonding of CO with Ti^{3+} ions in the high-temperature reduced material with corresponding uptake associated with the support as well as the catalytic metal. The relative trends of activity as shown for the various catalysts in Fig. 3 are representative, but the absolute magnitudes of the SMSI catalyst in comparison to the "normal" materials are not. To make a quantitative comparison, one would have to be able to distinguish between CO uptake on the active metal and on the support. To date, this has not been done. Selectivity, as
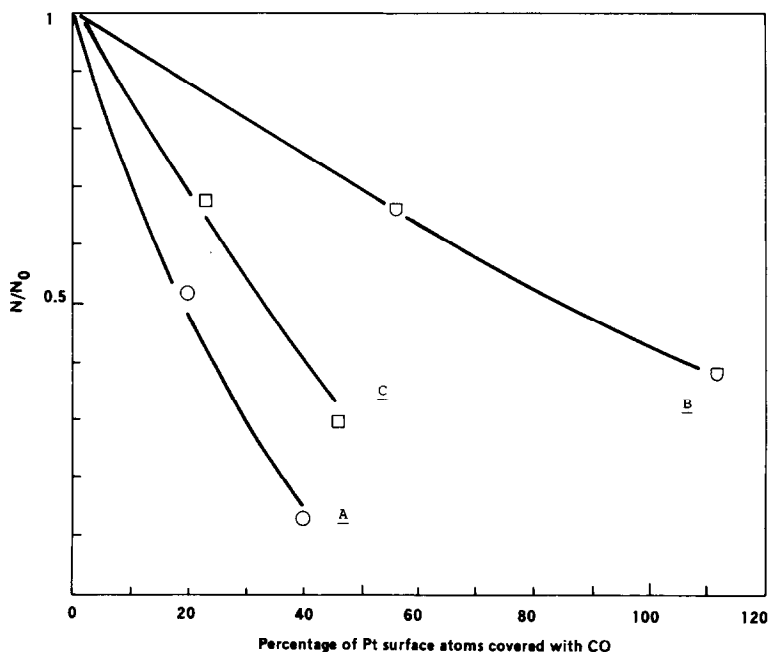

FIG. 3. Relative activity of Pt/TiO_2 as a function of pretreatment and level of poisoning. Isobutane turnover frequency at 0°C. Sample: (A) 95.2-Pt/TiO_2 after pretreatment a (non-SMSI), (B) 16.3-Pt/TiO_2 after pretreatment b (SMSI), and (C) 80.5-Pt/TiO_2 after pretreatment c (restore non-SMSI).
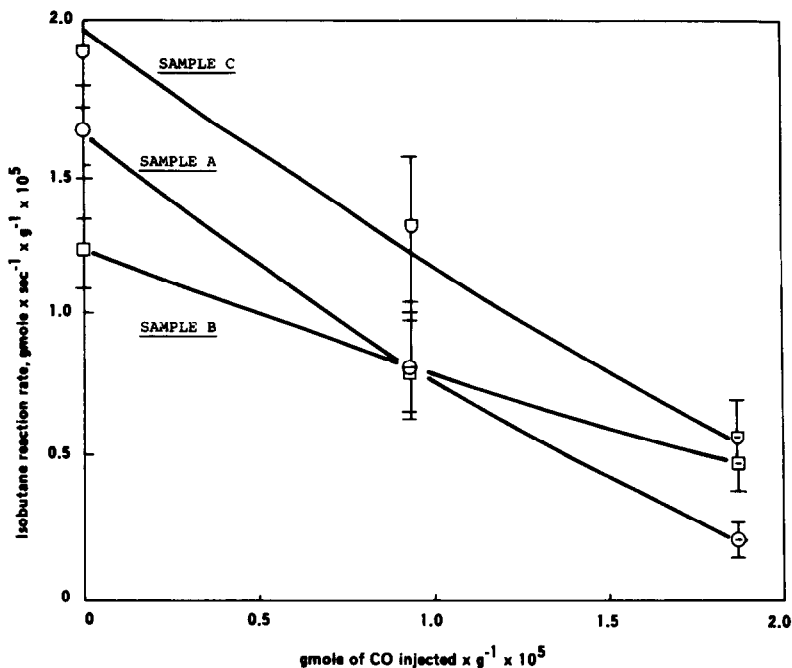
FIG. 4. Activity of Pt/TiO$_2$ on a per weight basis as a function of poisoning. Samples as listed in Table 1.

shown in Table 1 is relatively constant at a value of 8.5 and is unaffected by poisoning. This is a characteristic pattern and has been observed in poisoning studies of Pt/Al$_2$O$_3$ as well.

In spite of the above uncertainties, the present results have significance from a practical point of view. The designer is interested ultimately in a net activity per weight or volume vs net CO uptake. If catalyst activity and CO uptake are evaluated on a per gram basis, as shown in Fig. 4, a useful picture appears for design purposes. On this basis, the activity of the SMSI catalyst (Sample B, pretreatment b), not poisoned, is about 75% of the normal (Sample A, pretreatment a) catalyst. Increasing CO loading on the SMSI material, however, still seems to yield results indicative of preferential resistance to deactivation as indicated by the crossover in activity curves for Samples A and B at a loading of about 10^{-5} g mole CO/g catalyst. These data also indicate that the net activity on a per gram basis is somewhat higher for the "regener-

ated" catalyst (sample C) than for the original preparation. This is outside the range of experimental uncertainty, but in view of either of the mechanisms discussed above (5, 7) one would not expect it to be a persistent effect (i.e., completely reversible) and further experimentation would be required to determine where repeated cycling would end up in this type of activity correlation.[3]

CONCLUSIONS

High-dispersion Pt/TiO$_2$ catalysts in the normal state appear to be slightly more susceptible to CO poisoning for methylcyclopropane hydrogenolysis than comparable Pt/SiO$_2$ or Pt/Al$_2$O$_3$ catalysts. The Pt/TiO$_2$ catalyst under SMSI is less active than

[3] This result may also be a result of incomplete reduction after pretreatment c. We have shown that these conditions are sufficient for reduction of Pt/SiO$_2$ and Pt/Al$_2$O$_3$ (11, 12), but have not investigated the matter specifically for Pt/TiO$_2$. It is known that small amounts of residual O$_2$ have a promotional effect on this reaction on Pt/SiO$_2$ (2).

"normal" Pt/TiO_2 for the hydrogenolysis but more resistant to poisoning.

Care must be exercised in comparing activities of catalysts under SMSI and catalysts free of it, since the way data are reported is most important. If the activity of the catalysts reduced at different temperatures is reported as turnover number and the number of sites is counted by hydrogen adsorption, it could be concluded that the catalyst reduced at high temperature is quite active and has an unusual resistance to poisoning. This is, however, subject to interpretation of both D_h and CO chemisorption measurements. From a more practical point of view, if activity is reported on a per gram of catalyst basis, which assigns only total CO uptake, it would appear that the SMSI catalyst is more tolerant to this posion and in terms of catalytic bed performance a per gram basis seems more meaningful for comparison.

REFERENCES

1. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211**, 1121 (1981).
2. Önal, I., and Butt, J. B., *J. Chem. Soc. Faraday Trans. 1* **78**, 1887 (1982).
3. Damiani, D. E., and Butt, J. B., *J. Catal.* **94**, 203 (1985).
4. Damiani, D. E., Ph.D. dissertation. Northwestern University, 1984 (available from University Microfilms, Inc.).
5. Chien, S. H., Shelimov, B. N., Resasco, D. E., Lee, E. H., and Haller, G. L., *J. Catal.* **77**, 301 (1982).
6. Sexton, B. A., Hughes, A. E., and Foger, K., *J. Catal.* **77**, 85 (1982).
7. Chung, Y. W., Xiong, G., and Kao, C. C., *J. Catal.* **85**, 237 (1984).
8. Haller, G. L., Henrich, U. E., McMillan, M., Resasco, D. E., Sadeghi, H. R., and Salellsom, S., "Proceedings, 8th International Congress on Catalysis, Berlin." V-135. DECHEMA, July, 1984.
9. Resasco, D. E., and Haller, G. L., *J. Catal.* **82**, 279 (1983).
10. Anderson, J. B. F., Bracey, J. D., Burch, R., and Flambald, A. R., "Proceedings, 8th International Congress on Catalysis, Berlin," V-111. DECHEMA, July, 1984.
11. Uchijima, T., Herrmann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50**, 464 (1977).
12. Kobayashi, M., Inoue, Y., Takahashi, N., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **64**, 74 (1980).
13. Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **53**, 414 (1978).