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Structure-sensitive Interactions of Pt/SiO_2 with Small Molecules

Activation by Oxygen and Deactivation by Carbon Monoxide for Methylcyclopropane Hydrogenolysis

By Isik Önal† and John B. Butt*

Ipatieff Laboratory and Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60201, U.S.A.

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The hydrogenolysis of methycyclopropane (MCP) has been used as a probe reaction to investigate the structure sensitivity of the interactions of a series of well-characterized platinum on silica catalysts with oxygen and carbon monoxide. A differential flow reactor combined with a pulse doser has been used to obtain turnover frequencies for the product n- and iso-butane at 273 K and feed composition *ca.* 0.05 mol fraction MCP.

Turnover frequencies for the series of Pt/SiO_2, ranging in percentage of exposed metal from 7.1 to 81, are substantially increased as a result of a standardized oxygen pulse pre-treatment as a final step before MCP reaction, and the effect is structure sensitive. Activity is most enhanced on those catalysts of highest percentage of exposed metal and is also a function of oxygen adsorption temperature, being most pronounced above 473 K. However, selectivity, defined as ($i\text{-}C_4/n\text{-}C_4$), is decreased by oxygen pretreatment.

The same series of Pt/SiO_2, though, is poisoned by carbon monoxide for the MCP hydrogenolysis under the same conditions. Again the effect is structure sensitive, with intermediate range percentage exposures preferentially retaining activity for carbon monoxide coverages $> 40\%$. Selectivity is not affected. Carbon monoxide pulse chemisorption experiments indicated a 1 : 1 adsorption stoichiometry for CO : Pt in this series at 296 K.

The fact that certain types of reactions on supported metal catalysts are structure-sensitive, that is their rates per surface metal atom vary with the percentage of metal exposed on the catalyst, is now well-known.[1] Much of the experimental work in this area has been conducted for the platinum group metals, and some examples of structure-sensitive reactions over supported Pt catalysts would include hydrogenolysis reactions such as those of n-pentane and cyclopentane.[2,3] On the other hand, hydrogenation reactions such as those of ethylene and benzene are structure-insensitive on supported Pt.[4-7] Results are most often reported in terms of turnover frequencies based on specific metal surface areas, normally measured by volumetric[8] or pulse[9,10] hydrogen chemisorption, hydrogen–oxygen titration[11] or X-ray diffraction.[12]

Various interpretations of structure sensitivity have been offered, but most have been geometric. Hence a favourite correlating parameter has been an 'average' crystallite dimension or percentage of metal exposed. However, recent results from this laboratory[13,14] suggest that structure sensitivity is far more complicated than is evident in the older literature. In studies of methylcyclopropane (MCP) hydrogenolysis, propene hydrogenation and deuterium exchange with cyclopentane on well-characterized series of both Pt/SiO_2 and Pt/Al_2O_3, it was found that the precise conditions of pretreatment had at least as large an effect on structure sensitivity (or,

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† Present address: U.O.P. Inc., Des Plaines, Illinois 60016, U.S.A.

more precisely, apparent structure sensitivity) as any geometric factor. In that work the temperature of pretreatment in hydrogen before reaction was shown to be critical and the nature of the apparent structure sensitivity could be arbitrarily varied by choice of the appropriate pretreatment conditions.

Several investigators have observed that chemical impurities such as oxygen, carbon, sulphur or chlorine present on the catalyst surface can also change the apparent structure sensitivity of a reaction. In a number of cases it has been noted that inherently structure-insensitive reactions appear to be structure-sensitive in the presence of impurities.[4, 5, 15] However, apart from occasional observation, systematic studies on the effect of impurities on structure sensitivity appear to be scarce, particularly in comparison to the abundant volume of work on structure sensitivity itself. Maurel *et al.*[3] studied the effects of sulphur poisoning on a number of Pt/Al_2O_3 catalysts in structure sensitivity for hydrogenolysis of cyclopentane and deuterium exchange with benzene. Fuentes and Figueras[16, 17] investigated sulphate contamination for cyclopentane hydrogenolysis on supported palladium. In both these cases structure sensitivity becomes more pronounced in the presence of sulphur. Recently, in what has been perhaps the most systematic study, Barbier *et al.*[18] reported the effect of a number of different compounds on the structure sensitivity of several reactions, including benzene hydrogenation and exchange, and cyclopentane hydrogenolysis and exchange. The catalysts used were Pt/Al_2O_3 with percentage of exposed metal ranging from 5 to 80. A particularly striking example was offered for the conversion of a structure-insensitive reaction, benzene hydrogenation, into a structure-sensitive one upon progressive poisoning of the series of catalysts by ammonia, which is preferentially adsorbed on catalysts of higher percentage exposed.

The work on impurity effects on structure sensitivity cited above has centred upon the view that such impurities act as poisons for the catalysts investigated. In the present study we have chosen to extend this to a system in which there is activity enhancement as well as deactivation. Methylcyclopropane hydrogenolysis is a convenient probe reaction, since it may be run under mild conditions and a selectivity factor between iso-and n-butane products is measurable in addition to activity. For supported platinum catalysts carbon monoxide is an effective poison for this reaction, since it is strongly chemisorbed even at low temperatures (273 K), is not displaced from the surface by hydrogen and does not react appreciably with hydrogen below *ca.* 470 K.[19] On the other hand, there is evidence available[13, 14, 20-22] that oxygen may act to enhance the activity of platinum for this reaction under certain conditions, and that this effect may be structure-sensitive.[22] Oxygen has also been identified as a promoter for ethylene hydrogenation on a number of metals.[23-26]

EXPERIMENTAL

CATALYSTS

The preparation and characterization of the series of Pt/SiO_2 catalysts used in this work has been described by Uchijima *et al.*[10] We use five catalysts from that series, ranging in percentage exposed, D_h (as determined by hydrogen pulse chemisorption),[10] from 7.1 to 81. Included in this set are catalysts prepared both by ion exchange with $Pt(NH_3)_4^{2+}$ and by impregnation with H_2PtCl_6. We have shown previously[13] that the presence of chloride does not affect the activity of these Pt/SiO_2 catalysts for MCP hydrogenolysis. The catalysts ranged in weight loading from 1.91% ($D_h = 7.1$) to 0.49% ($D_h = 63.5$) and 0.825% ($D_h = 81$); the support in all cases was Davison grade 62 silica gel. Properties are given in table 1.

TABLE 1.—PROPERTIES OF PLATINUM-ON-SILICA CATALYSTS[10]

catalyst[a]	preparation	Pt (%)	D_h av.	surface area /m^2 g-metal^{-1}
7.1-SiO_2-PtCl-S	impregnated/calcined H_2PtCl_6	1.91	7.1	18.2
21.5-SiO_2-IonX-L	ion-exchanged/calcined $Pt(NH_3)_4^{2+}$	1.48	21.5	55.8
40-SiO_2-PtCl-S	impregnated/H_2PtCl_6	1.17	40	103.7
40-SiO_2-PtCl-L	impregnated/H_2PtCl_6	1.10	40	103.7
63.5-SiO_2-IonX-L	ion-exchanged/$Pt(NH_3)_4^{2+}$	0.49	63.5	164.7
81-SiO_2-IonX-S	ion-exchanged/$Pt(NH_3)_4^{2+}$	0.825	81	204

[a] S, supported on 120-140 mesh SiO_2; L, supported on 60-80 mesh SiO_2.

APPARATUS

The reaction apparatus employed, a differential flow reactor, was the same as that described by Otero-Schipper *et al.*,[13] modified so that calibrated pulse chemisorption of oxygen or carbon monoxide could be conducted before the reaction experiments. Details are given by Önal.[27]

REAGENTS AND PURIFICATION PROCEDURE

Ultrahigh-purity hydrogen and helium, 99.999% with 3 ppm maximum moisture content, were employed. In reaction experiments the hydrogen was further purified by sequential passage through a Deoxo unit (Englehard 10-2500), a 3A molecular sieve trap at liquid-nitrogen temperature to remove water, and finally a 15% MnO/SiO_2 trap that is capable of removing oxygen to the ppb range. Ultrahigh-purity oxygen (Linde, 99.99%, 3 ppm maximum moisture) was used for catalyst pretreatment without further purification. Methylcyclopropane (98%, K & K Co.) was purified by passage through a $Cu(NH_3)_4^{2+}/SiO_2$ trap to remove olefins. Since it was found that the major impurities in MCP from this source were butenes, the absence of olefins was further ensured during the reaction experiments by passing the hydrogen + hydrocarbon feed mixture through a Pt/Filtros silica bed upstream of the reactor. This bed, maintained at 296 K, is highly selective for hydrogenation to n-butane for the feed compositions employed (H_2:MCP = 16:1). The resulting feed mixture was then analysed for n-butane before introduction into the reactor, and conversions from the main hydrogenolysis reaction determined by difference in inlet and outlet concentrations of n-butane. Analysis of reactants and products was as described previously.[13]

PRETREATMENT PROCEDURE

Since consistent pretreatment procedures have been found to be of critical importance for obtaining meaningful results,[13] a standard procedure was strictly adhered to, as follows. (1) The catalyst was first heated in oxygen at 573 K for half an hour to remove any possible carbonaceous deposits. (2) It was then cooled in oxygen to room temperature and subsequently flushed with helium for 0.5 h. (3) The catalyst was then heated to 573 K in hydrogen and maintained at that temperature for 1 h. (4) Finally the sample was purged with helium at 723 K for 1 h and then cooled either to the reaction temperature (273 K) or the preadsorption temperature of carbon monoxide (always 296 K) or of oxygen (variable). (5) The sequence described above will be described subsequently by the code O_2, 573 K, 0.5; He, 296 K, 0.5; H_2, 573 K, 1; He, 723 K, 1, or 'standard pretreatment'.

PULSE DOSING PROCEDURE

After the standard catalyst pretreatment was completed, the carrier gas helium for the pulse system was introduced into the reactor. A pulse containing a predetermined amount of oxygen or carbon monoxide was then introduced *via* a six-port sampling valve, and effluent gas analysed with a thermal conductivity detector. Carbon monoxide dosing was carried out at 296 K while oxygen treatment was at variable temperature from 373 to 753 K. After pulse treatment, the catalyst was cooled to reaction temperature of 273 K under the carrier-gas flow. In all pulse treatments, the catalyst in the reactor was maintained in a fluidized condition to eliminate concentration gradients of adsorbate during the subsequent fixed-bed reaction experiments.

REACTION PROCEDURE

Following pretreatment and dosing, the feed+reactant mixture which had been passed through the reactor by-pass line at desired flow rate and composition was then introduced into the reactor line. Reactor product gas was sampled for analysis approximately every 15 min and a typical run duration was 60-90 min. Conditions were maintained such that in general differential conversion levels (*ca.* 5%) were obtained, although in some experiments after oxygen dosing this was not possible. Under differential conditions, rates can be obtained from conversion data *via*

$$R_i = F_t X_i / W \qquad (1)$$

where R_i is rate of product formation in gmol (g-catalyst s)$^{-1}$, X_i is the mole fraction of product i, F_t is total molar flow in gmol s^{-1} and W is weight of catalyst sample in g. Turnover frequency is evaluated from the rate by

$$N_i = R_i (M)_{Pt} / D_h W_{Pt} \qquad (2)$$

where N_i is the number of molecules of product formed per second per surface metal atom, $(M)_{Pt}$ is the molecular weight of platinum, D_h is the percentage of metal exposed determined by hydrogen chemisorption[10] and W_{Pt} is the weight fraction of platinum on the catalyst. Selectivity, S, is defined as the ratio of the isobutane turnover frequency to that of n-butane. The values of N_i and S reported subsequently are the averages of 4-6 determinations in a single run.

RESULTS

Prior to experimentation with oxygen or carbon monoxide treatment, a number of reproducibility experiments were carried out with fresh catalysts. These were conducted after standard pretreatment and the results agree within ±10% with the values reported by Otero-Schipper *et al.*[13] In the present study, turnover frequencies have been adjusted as $N = N_i/(X_{MCP})^{\frac{1}{2}}$, since a slight dependence on MCP feed mole fraction has been observed both here and previously.[13] As an example of reproducibility, four replicate runs on 21.5-SiO_2-IonX-L gave an average N value of 0.69 s^{-1} with standard deviation of ±0.13.

EFFECT OF OXYGEN ON STRUCTURE SENSITIVITY OF MCP HYDROGENOLYSIS

It was reported by Uchijima *et al.*[10] that the degree of reduction of these Pt/SiO_2 catalysts by hydrogen is structure-sensitive; however, subsequent work on structure–reactivity effects centred more on hydrogen than oxygen treatments. In the present work, a series of standardized oxygen pulses (nominal conditions, 3 pulses of 0.2 cm^3, 296 K, with 250 Torr oxygen partial pressure) was injected onto the catalyst sample (nominal weight, 0.05 g) that had been previously subjected to standard pretreatment. The size of the pulses was normally adjusted in proportion to the total metal surface

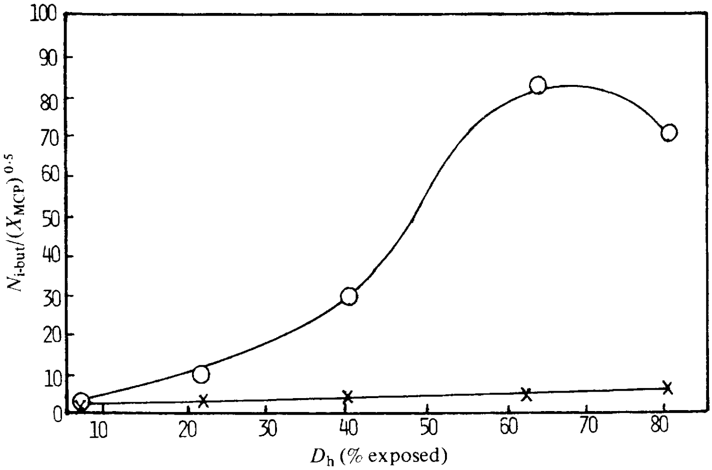

FIG. 1.—Isobutane turnover frequency plotted against percentage of exposed metal with oxygen pulse pretreatment at 573 K after standard pretreatment (○), or after standard pretreatment only (×).

area such that the first pulse was always substantially more than required for $Pt_sO = 1$.*

In fig. 1 are shown typical experimental results for isobutane for the series of experiments conducted with pulse adsorption at 573 K. The enhancement in turnover frequency is large and structure-sensitive, at least in the lower range of D_h. There is some uncertainty in calculation of the turnover frequencies for higher D_h catalysts since under attainable experimental conditions the conversions approached 100%. In fig. 1, for example, 100% conversion was obtained for D_h of 40 and 63.5; thus the points indicated represent *lower limits* of the activity for these samples. Conversions for $D_h = 81$ was 60%, so there is an apparent maximum in the effect of oxygen adsorption at this temperature. Lower conversions were not practically attainable since these required very high flow rates and associated large pressure drops in the apparatus.

The effect of oxygen adsorption temperature was investigated in detail for 7.1–SiO_2–PtCl–S and 81–SiO_2–IonX–L. These results are shown in fig. 2 for rates after oxygen treatment, N_O, compared with standard treatment, N_F. For both there is a substantial increase in the ratio N_O/N_F for temperatures of 473 K and above, although the effect is much larger at high D_h. A summary of all turnover-frequency data is given in table 2.

The turnover frequencies given in these figures were determined from steady-state conversion levels (in the case of 100% conversions after 90 min) after equilibrium of initial thermal transients in the MCP hydrogenolysis. In preliminary experimentation it was observed that temperature excursions as high as 9-10 K occurred in the initial stages of a run, subsequently relaxing to 0-2 K. This was presumably the result of hydrogen reaction with the preadsorbed oxygen, and was most prominent for the low-D_h catalysts where the oxygen is most reactive.[10] A representative run for catalyst

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* We must note here that oxygen surface coverage cannot be a controlled variable in these experiments, since the oxygen uptake depends upon the percentage of exposed metal and the temperature of adsorption,[10] and can be greater than $Pt_sO = 1$. Under MCP reaction conditions with hydrogen in large excess, it is likely that most of the adsorbed oxygen will react with hydrogen over the course of an experiment conducted with catalyst of low percentage of exposed metal, but not with high-D_h catalysts.[10]

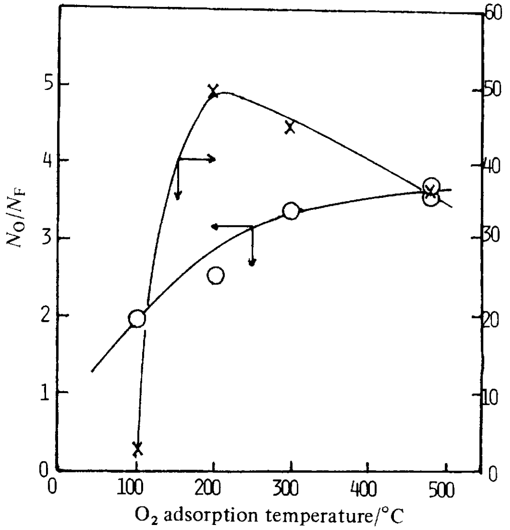

FIG. 2.—Enhancement in turnover frequency plotted against oxygen adsorption temperature: N_O after oxygen pretreatment, N_F after standard pretreatment; $D_h = 7.1$ (○); $D_h = 81$ (×).

TABLE 2.—TURNOVER FREQUENCIES, $N_{\text{i-but}}/(X_{\text{MCP}})^{\frac{1}{2}}$, FOR METHYLCYCLOPROPANE HYDROGENOLYSIS ON THE Pt/SiO_2 SERIES AFTER OXYGEN PRETREATMENT

pretreatment T/K =	373	473	573	753	standard
$D_h = 7.1$	1.17	1.49	2.03	2.20 2.08	0.60
21.5	—	—	9.51	—	0.69^a
40–L	—	—	—	—	0.91
40–S	—	—	23.3^b 34.3^b	—	0.92
63.5	—	—	82.0^b 84.5^b	—	1.15
81	1.91	75.5^c	70.0^d	55.0^e	1.53^f

[a] Average of four replicate experiments. [b] 100% conversion; lower limit for N. [c] 67% conversion. [d] 59% conversion. [e] 96% conversion. [f] Average of two replicate experiments.

7.1–SiO_2–PtCl–S, where a thermocouple was placed within the catalyst bed, is shown in fig. 3. For this run (open symbols) there was a sharp increase in reaction temperature to the vicinity of 9 K after the reaction started, then a gradual decrease. As shown also, the isobutane turnover number similarly declined very rapidly initially and came to a steady-state value later on. Another experiment with no thermocouple (cross symbols) demonstrated parallel behaviour. Preliminary experiments showed no further decline in apparent catalyst activity after steady-state was reached for as long as 2 h of reaction time. Thus, in the worse case we believe the reaction temperature to be within 2 K of the nominal reaction temperature of 273 K.

Catalysts subjected to oxygen pulse pretreatment exhibited markedly lower selectivities than those of standard pretreatment. This change was due to a large

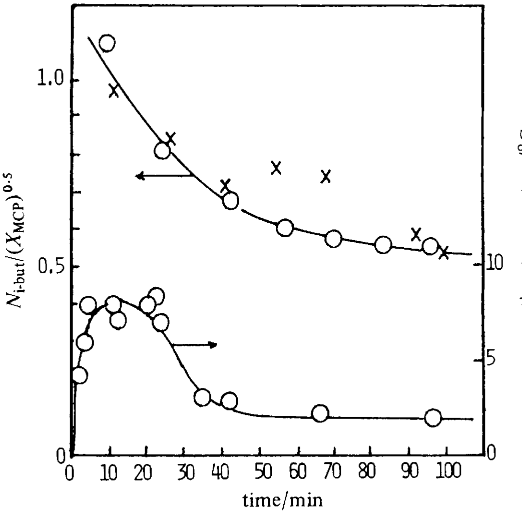

FIG. 3.—Turnover frequency and reaction temperature plotted against time for MCP hydrogenolysis on 7.1-SiO_2-PtCl-S. Upper open symbols are turnover frequency and lower catalyst temperature.

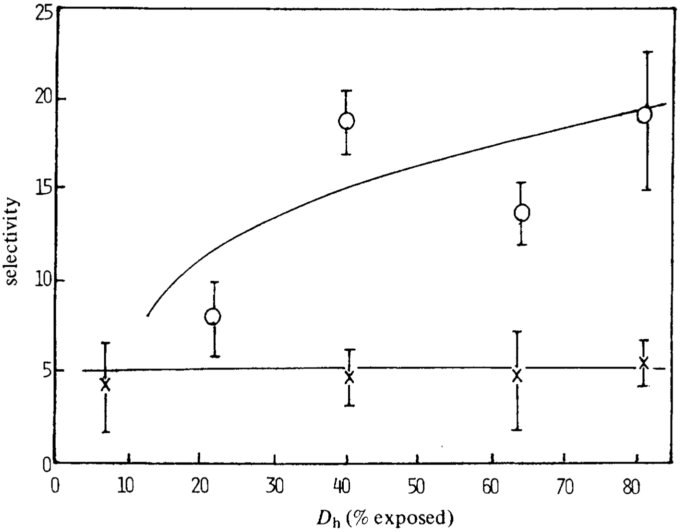

FIG. 4.—Selectivity plotted against percentage of exposed metal with oxygen pulse treatment at 573 K after standard pretreatment (×), or after standard pretreatment only (○).

enhancement in n-butane production rather than diminution of isobutane. Since there was n-butane in the feed to start with, and since the n-butane turnover frequency was still much smaller than that for isobutane, the determination of selectivities involved larger uncertainties than corresponding turnover frequencies, as seen in fig. 4. However, there is still apparent a substantial decrease, by a factor of *ca.* 3, with respect to the standard pretreatment.

HYDROGEN REDUCTION AFTER OXYGEN PULSE PRETREATMENT

Experiments involving hydrogen reduction of catalyst 63.5–SiO_2–IonX–L, already subjected to an oxygen pulse treatment at 573 K, were also conducted in order to test the effect of extent of reduction by hydrogen on the enhancement of turnover numbers. These experiments were carried out at two different temperatures, 296 and 423 K, as described in table 3. One observes that hydrogen pretreatment at 423 K for 1 h as a final step before the reaction is started results in almost the same turnover frequency as those of runs after standard pretreatment. This indicates that hydrogen at 423 K completely removes the oxygen previously adsorbed on the catalyst surface by the pulse treatment. On the other hand, hydrogen pretreatment at 296 K for 2 h only partially removes the adsorbed oxygen, thus resulting in a turnover frequency enhancement factor of *ca.* 4, instead of the enhancement factors of *ca.* 70 observed in table 2.

TABLE 3.—EFFECT OF HYDROGEN PRETREATMENT AFTER OXYGEN PULSE FOR 63.5–SiO_2–IonX–L

pretreatment	$N_{\text{i-but}}/(X_{\text{MCP}})^{\frac{1}{2}}$
standard	1.15
std + oxygen pulse, 573 K	81.9
std + oxygen pulse, 573 K	84.5
std + oxygen pulse, 573 K, + H_2, 423 K, 1	1.10
std + oxygen pulse, 573 K, + H_2, 396 K, 2	4.46

EFFECT OF CARBON MONOXIDE POISONING ON STRUCTURE SENSITIVITY OF MCP HYDROGENOLYSIS

Since carbon monoxide is unreactive with hydrogen at the temperature of the MCP reaction, it was possible to control the surface coverage in this series of experiments. A set of pulse chemisorption measurements[9] was carried out on the catalysts of $D_h = 7.1$, 21.5, 63.5 and 81 that yielded, within experimental error, a CO:Pt_s ratio of unity.[27] These data are in agreement with earlier determinations of the stoichiometry of carbon monoxide chemisorption on this series of catalysts determined *via* infrared spectroscopy.[28]

Carbon monoxide treatment prior to the reaction experiments involved passing calibrated pulses over the catalyst at 396 K, following the standard pretreatment. The amount of carbon monoxide pulsed was established by the desired surface coverage, assuming a 1:1 stoichiometry for CO:Pt_s, and carbon monoxide injected in this way was always completely adsorbed and not detected in the reactor effluent. Variation in pulse size was accomplished by varying sampling loop pressure.

Fig. 5 gives the experimental results in terms of the isobutane turnover frequency term $[N_{\text{i-but}}/(X_{\text{MCP}})^{\frac{1}{2}}]$ as a function of the number of molecules of carbon monoxide adsorbed per surface platinum atom for four different types of catalyst. It is seen that these catalysts, with a wide variation in D_h, do not have the same poisoning curve as a function of carbon monoxide surface coverage. Although the poisoning curve exhibits an approximately linear nature for the catalyst with the largest platinum particle size, 7.1–SiO_2–PtCl–S, there is considerable tailing for the catalysts with smallest particle sizes, particularly 63.5–SiO_2–IonX–L and 81–SiO_2–IonX–S. The poisoning curves shown in this figure were obtained using different batches of catalyst

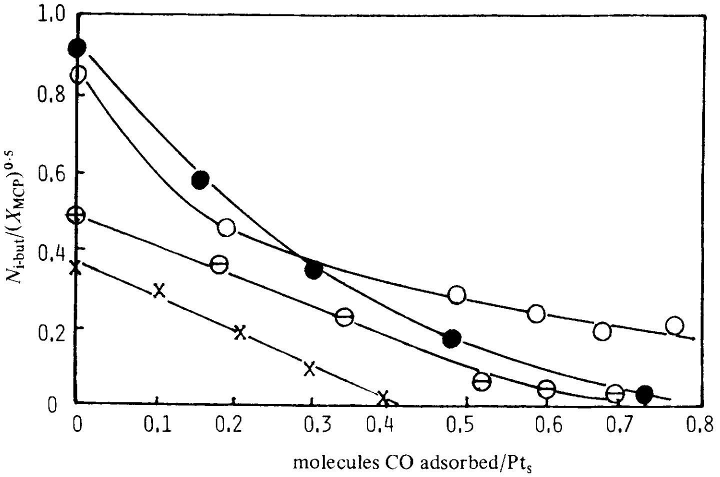

FIG. 5.—Isobutane turnover frequency plotted against carbon monoxide surface coverage at different percentages of exposed metal: D_h = ×, 7.1; ⊖, 21.5, ○, 63.5, ●, 81.

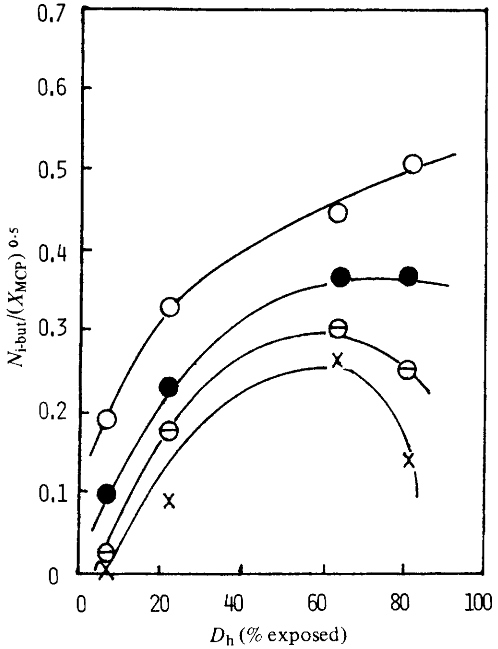

FIG. 6.—Structure sensitivity of MCP hydrogenolysis as a function of carbon monoxide surface coverage: ○, 20; ●, 30; ⊖, 40; ×, 50%.

samples every two experiments in most cases. For those runs where the catalyst sample from the previous experiment was used, the first step in the standard pretreatment experiment, namely flowing oxygen over the catalyst sample at 573 K for 0.5 h, was considered sufficient to remove the residual carbon monoxide and the reactant hydrocarbon adsorbed on the catalyst surface.

An interesting feature of the alteration of structure sensitivity here is given in fig. 6, where the isobutane turnover frequency term $N_{\text{i-but}}/(X_{\text{MCP}})^{\frac{1}{2}}$ is plotted against dispersion, D_h, at several carbon monoxide surface coverages. One can see that the structure-sensitive behaviour of the MCP hydrogenolysis goes through a continuous change as carbon monoxide surface coverage is increased from 20 to 50%. A maximum in the structure-sensitive behaviour of turnover frequency is exhibited in the vicinity of $D_h = 63.5$, which becomes very pronounced at carbon monoxide surface coverages > 40%.

Selectivity values as a function of percentage of exposed metal for the carbon monoxide poisoning experiments are in the same range of those for the fresh catalyst shown in fig. 4. There is a slight maximum at $D_h = 63.5$ owing to the low selectivity observed for 81–SiO_2–IonX–S, but for all catalysts the selectivity was insensitive to the surface coverage of carbon monoxide.

DISCUSSION

EFFECT OF OXYGEN ON STRUCTURE SENSITIVITY

The experimental results with regard to oxygen pulse pretreatment lead to four important conclusions. (1) Isobutane and n-butane turnover frequencies are substantially increased for all catalysts in the series by the oxygen pulse pretreatment before reaction. (2) The enhancement in turnover frequencies is structure-sensitive, with activity being most enhanced on materials having a high percentage of exposed metal. (3) This enhancement is also a function of oxygen pulse adsorption temperature, as shown in fig. 2. The functional trend, moreover, can be considered only slightly different for high- and low-D_h catalysts, since conversions in the case of 81–SiO_2–IonX–S approach 100%. We attribute no particular significance to the apparent maximum for that catalyst in fig. 2 because of this. (4) Selectivities for all catalysts are substantially decreased by oxygen treatment.

The role that oxygen plays in altering the activity and selectivity of platinum catalysts is complex and is not yet well-understood. In the present case, the structure-sensitive hydrogen–oxygen reaction on supported platinum must, however, play an important part. It would seem from the results of Uchijima *et al.*[10] and the experiment of fig. 3 that the low D_h catalysts, and in particular 7.1–SiO_2–PtCl–S, are reduced under the MCP reaction conditions, while high-D_h catalysts, in particular 81–SiO_2–IonX–S, are not. Yet there is an enhancement in activity in both cases.

While the reduction by hydrogen can be interpreted in terms of the structure-sensitive oxidation–reduction results reported by Uchijima *et al.*,[10] the results given in table 2 are also not inconsistent with the concept of 'non-reactive' oxygen. Smith *et al.*[22] report oxygen adsorbed on platinum single crystals above 773 K to be non-reactive; considering the much lower pressures involved in those experiments (10^{-5}-10^{-6} Torr) it seems possible that non-reactive oxygen could form at lower temperatures under atmospheric pressure on very small metal crystallites, as in this investigation.

McCabe and Schmidt[20, 21] have postulated three possible interactions of strongly adsorbed oxygen: (i) the formation of a surface layer of oxide results in a change in the electronic structure of the surface platinum atoms, (ii) strongly adsorbed oxygen is active in compound formation with other adsorbates and (iii) oxidation of the platinum surface results in a reconstruction of the surface atoms. The results obtained here are best explained by the first and third of these three postulates. Ratnasamy *et al.*[7, 29] report that the chemisorption of oxygen on supported platinum, even at room temperature, creates a surface with many vacancies in the outer layer. We have shown, for the low-D_h catalysts of this series, that these vacancies persist in subsequent low-temperature (300-425 K) hydrogen treatment, but are apparently annealed out on treatment at *ca.* 475 K.[13] Hence the enhancement of activity for low-D_h catalysts would seem to be explained reasonably by the formation of a disordered surface. This effect has also been cited by Pareja and co-workers[23-26] as the reason for the promotion of ethylene hydrogenation by a number of unsupported metals. On the other hand, oxygen treatment of high-D_h catalysts results in the disappearance of metallic platinum and formation of a material of stoichiometry close to PtO.[10] In this case, hydrogen may remove surface oxygen but there is most certainly subsurface oxygen present under MCP reaction conditions. The subsurface oxygen would tend to remove platinum valence electrons and induce a positive charge on the surface, thereby influencing the activity and selectivity.

The experimental result that the enhancement in isobutane turnover frequency is structure-sensitive accords with the platinum single-crystal results of Smith *et al.*[22] if we make an analogy between supported-metal crystallites that have a high number of corner and edge atoms and single-crystal surfaces that have a high number of kinks and steps. It is also known that the presence of large concentrations of step and kink defect sites has a large effect on the electronic structure of clean platinum surfaces.[30] The formation of a surface oxide might change the electronic structure of each surface site differently, giving rise to the structure sensitivity observed by Smith *et al.* on platinum single-crystal surfaces, with particularly favourable surface electronic changes promoted by kink sites. An interesting observation made by those workers, which casts doubt upon the idea of compound formation, is that upon low-temperature adsorption of oxygen on platinum the work function increases by *ca.* 1 eV, while with high-temperature oxidation the work function has been shown to decrease by *ca.* 1 eV.[22] The decrease was interpreted as evidence that oxidation leads to adsorbed oxygen atoms beneath the surface platinum atoms; the positively charged metal atoms would thus be readily available for bonding with hydrogen and hydrocarbons.

The present selectivity results can also be explained by similar lines of reasoning. It is well-known that for methylcyclopropane hydrogenolysis n-butane production increases as a function of support acidity in dual-function, supported platinum catalysts.[31] If we consider the positively charged platinum atoms mentioned above to have some acidic character, then the n-butane reaction rate will be preferentially enhanced, as observed, on these sites and consequently the selectivity will be lower.

EFFECT OF CARBON MONOXIDE ON STRUCTURE SENSITIVITY

The important conclusions with regard to carbon monoxide poisoning can be summarized as follows. (1) The chemisorption stoichiometry, CO : Pt_s, is in the vicinity of unity ($\pm 10\%$) and is independent of platinum particle size. The absence of bridge-bonded carbon monoxide is further substantiated by the existence of only one CO infrared band at 2082 cm^{-1} for all catalysts of the series.[29] (2) Structure sensitivity of the MCP hydrogenolysis changes as a function of carbon monoxide surface coverage and the isobutane turnover frequency exhibits a maximum in the vicinity of $D_h = 60$ for coverages > *ca.* 40%. It is also seen in fig. 6 that low-D_h catalysts are *more* severely poisoned than higher-D_h materials. (3) Selectivity is similar to that for unpoisoned catalysts, although exact comparison is probably not warranted because of the scatter in experimental data. Selectivity is not a function of surface coverage.

Since the adsorption stoichiometry is structure-insensitive, yet the results of poisoning quite the opposite, the interaction of carbon monoxide with surface platinum atoms under reaction conditions cannot be a simple site-blocking type of interaction. We can understand the lack of any significant effect on reaction selectivity as the result of equivalent blocking of the parallel reaction paths for isobutane and n-butane products; however, the peculiar alteration of structure sensitivity shown in fig. 6, dependent upon both crystallite size and surface coverage, can be considered neither simply geometric nor electronic. In the latter case one might expect larger interactions for high-D_h catalysts, yet 7.1–SiO_2–PtCl is completely deactivated at a surface coverage of 50% while 63.5–SiO_2–IonX still retains considerable activity at this coverage. The preferential resistance to poisoning by this latter catalyst is an unexpected result, although the possibility of tailoring optimum particle size for poison resistance is certainly attractive in technological applications.

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