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Models of Strong Metal–Support Interaction (SMSI) in Pt on TiO_2 Catalysts

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Recent studies of strong metal–support interaction (SMSI) in Pt/TiO_2 catalysts attribute the inhibition of chemisorption and catalysis to the presence of a reduced titanium oxide, TiO_x, on the surface of Pt crystallites. Equilibrium calculations show that Ti dissolved in Pt *in vacuo* is unlikely to segregate to the crystallite surface. However, the traces of water present under normal reduction conditions are sufficient to give adsorbed oxygen on surface Ti atoms, so greatly enhancing surface segregation. Also under these conditions any reduced TiO_x must be strongly bonded to Pt to avoid oxidation to TiO_2. Although adsorbed TiO_x is stable in both high- and low-temperature reduction conditions, the calculated rates of diffusion either of Ti in Pt metal or of adsorbed species on the Pt surface are too slow at low temperatures for significant SMSI. The inhibiting effect of added potassium compounds is more likely to be due to a "fluxing" effect, aiding the spread of titanium oxides, than to electron donation. © 1985 Academic Press, Inc.

INTRODUCTION

The characteristics of supported metal catalysts had been known for many years to be influenced by the nature of the support, but Tauster *et al.* (*1*) found a surprisingly strong inhibition of CO and H_2 chemisorption by Pt/TiO_2 catalysts after reduction at 500°C. The phenomenon, described by Tauster *et al.* as strong metal–support interaction (SMSI), has been widely studied and discussed (*2*), but without agreement about its origin. It has been widely ascribed to electron transfer from a partially reduced support to Group VIII metal crystallites (*2*), but recently several workers (*3–8*) have proposed that the inhibition of chemisorption and catalysis is due to the local geometric and electronic effects of a partially reduced titanium oxide, TiO_x, on the surface of the Pt crystallite. In principle this surface layer can be formed in two ways. Reduction conditions may allow the formation of Pt/Ti solid solutions or intermetallic compounds (*1*) and the partial oxidation of Ti atoms in the Pt surface (*8*) could give a surface species of Ti bonded both to Pt atoms and adsorbed oxygen, i.e., an adsorbed TiO_x. Alternatively, there is much evidence of partial reduction of bulk TiO_2 close to the Pt crystallites, probably by hydrogen spillover (*2*), and the subsequent diffusion of TiO_x across the Pt surface could give the same final state (*3–7*).

In this paper macroscopic properties of the relevant components are used first to calculate some of the equilibrium properties of the system and then to assess rates of diffusion under high- and low-temperature reduction conditions. The equilibrium properties of the final state are, of course, independent of the mechanism by which it is formed: for convenience of calculation it is assumed to be formed via Pt/Ti solid solution.

EQUILIBRIUM STATES OF PLATINUM CRYSTALLITES

Bulk Composition

In their original paper on SMSI, Tauster *et al.* (*1*) used thermodynamic data for the Pt–Ti system from Meschter and Worrell (*9*) to show that under their experimental conditions reduction of TiO_2 could give dis-

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solved Ti in the Pt crystallites. It can be shown from standard data (*10, 11*) that TiO_2 could not be reduced to a lower-valent stoichiometric titanium oxide, much less elemental titanium. Nevertheless, the Pt–Ti interaction, as predicted (*12*), is so strong (*9*) that the solution of Ti in Pt could extend to the formation of the intermetallic compounds $TiPt_8$ and $TiPt_3$.

In the subsequent treatment it will be assumed that bulk Ti levels could reach a few atom% in the Pt crystallites. This appears possible under a wide range of reduction conditions, except UHV conditions.

Surface Segregation of Ti

Three criteria frequently used to assess surface segregation in bimetallic systems all indicate that surface segregation of Ti should occur with Pt/Ti crystallites *in vacuo*. Ti has a lower melting point (Ti, 1948 K; Pt, 2042 K) and larger metallic radius (Ti, 0.147 nm; Pt, 0.139 nm). Surface free energies at 773 K can be calculated (*13*) to be Ti, 1.93 J m^{-2}; Pt, 2.42 J m^{-2}. However, the Pt–Ti system is too far from ideal for these simple criteria to be a valid guide to surface segregation.

Various methods of estimating surface segregation have been critically assessed by Abraham *et al.* (*14*). They demonstrated the deficiencies of previous theories and developed a model for very dilute binary solid alloys in which the two main factors contributing to the driving force for segregation (bond strength ratio and atom size ratio) are accounted for simultaneously. Unfortunately, this model applies to ideal solutions only, so older models have to be used for the nonideal Pt–Ti system. Indeed, the model used by Abraham *et al.* (*14*) correctly predicts segregation or nonsegregation in 28 out of 31 examples and the three failures, all solutions in platinum, are attributed to possible, nonideal electronic effects. The main correction used here is that data for the Pt–Ti bonds are taken from experimental results (*9*) and not interpolated from data for Pt–Pt and Ti–Ti bonds. As in the work of Abraham *et al.* (*14*) the basic equation for surface concentrations of metals 1 and 2 is given by

$$(x_2^s/x_1^s) = (x_2^b/x_1^b)\exp(-\Delta G_s/RT), \qquad (1)$$

derived from Guggenheim (*15*), where x_i^s is the surface concentration of the *i*th component, x_i^b is the bulk concentration of the *i*th component, and ΔG_s is the free energy of segregation defined by

$$\Delta G_s = (G_s - G_s^\circ) - (G_b - G_b^\circ). \qquad (2)$$

The quantities G_b and G_s denote the free energy for a system with solute in the bulk and in the surface, respectively, and G_b° and G_s° denote the respective free energies for a pure solvent.

The free energy of segregation can be regarded as the sum of two components, a strain energy arising from a mismatch of atom sizes and a difference in surface free energy due to the differences in atom–atom bond energies. Strain energy in a dilute solution of Ti in Pt is assessed first. The atom radius of Ti in elemental Ti is larger than the equivalent value for Pt (see above), but the relevant value for the calculation of ΔG_s is that of Ti in Pt. In work on the crystal structure of Pt_8Ti, Pietrokowsky (*16*) found that the addition of titanium to platinum decreases the lattice parameter of the parent terminal phase, i.e., the effective radius of Ti in Pt is less than that of Pt itself, no doubt due to the strong Pt–Ti interaction. Conventional elasticity theory implies that surface segregation of a mismatching solute should always occur, but a better fit with experimental results is obtained (*17*) by distinguishing between small and large solutes. If the solute atom is smaller than the solvent atom, the elastic energy driving force is too small to give rise to surface segregation in a dilute alloy. However, if the solute atom is larger than the solvent atom, the elastic energy driving force is now large enough to give rise to surface segregation. Thus, in this treatment of Ti dissolved in Pt, the strain energy component of ΔG_s can be neglected, especially as the bond energy differences are large and give large values for the bond-breaking component of ΔG_s.

It is assumed that the solution of Ti in Pt is sufficiently dilute for the number of Ti–Ti bonds in the bulk to be negligible. This may not be valid for Pt/TiO$_2$ catalysts under severely reducing conditions, but as SMSI effects seem to be dependent more on the temperature of reduction than on other reduction conditions, surface segregation of Ti in dilute Pt/Ti crystallites is most relevant to SMSI. With this assumption the free energy of segregation is given by

$$\Delta G_s = \Delta Z(E_{12} - E_{11}), \tag{3}$$

where ΔZ is the difference in effective coordination number of a bulk site and a surface site, E_{12} is the nearest neighbour bond strength between solvent (1) and solute (2) atoms, and E_{11} is the nearest neighbour bond strength between solvent (1) atoms. Although enthalpies, or derived properties such as heats of sublimation, are often used for bond strengths (e.g., (*14*)), a better measure of bond strength for nonideal systems is the free energy of the bond, as Wynblatt and Ku (*18*) have pointed out. They used the difference of surface free energies of the pure components to calculate ΔG_s, but this also seems inapplicable to the Pt–Ti system.

The free energy of the Pt–Pt bond, E_{11}, can be calculated from standard data (*19*) for the reaction

$$\mathrm{Pt_{(c)}} \rightleftharpoons \mathrm{Pt_{(g)}} \tag{4}$$

and the coordination number of Pt, 12, and is 17.70 kcal/g atom at 800 K and 19.49 kcal/g atom at 500 K. The temperatures are chosen to be representative of high-temperature reduction (HTR) and low-temperature reduction (LTR) conditions, respectively. Later data on Pt (*20, 21*) do not lead to any significant change for the segregation calculation. Similarly, values of the Ti–Ti bond free energy can be obtained from standard data (*10*): 14.09 kcal/g atom at 800 K and 15.86 kcal/g atom at 500 K. The values of E_{12}, the free energy of the Pt–Ti bond, can now be estimated. Meschter and Worrell (*9*) derived the equation

$$\Delta G_f^\circ(\mathrm{TiPt_8}) = -90.44 + 12.83 \times 10^{-3}\, T \text{ kcal/mole} \tag{5}$$

from their experimental results between 1150 and 1300 K. Extrapolation to lower temperatures gives $\Delta G_f^\circ(\mathrm{TiPt_8}) = -80.18$ kcal/mole at 800 K and -84.13 kcal/mole at 500 K. With the assumption as above that there are no Ti–Ti bonds in TiPt$_8$, the reaction

$$\mathrm{Ti} + 8\,\mathrm{Pt} \rightleftharpoons \mathrm{TiPt_8} \tag{6}$$

involves the loss of 6 Pt–Pt bonds and 6 Ti–Ti bonds with the formation of 12 Pt–Ti bonds for each atom of Ti forming TiPt$_8$. Therefore:

$$E_{12} = \frac{(E_{11} + E_{22})}{2} + \frac{\Delta G_f^\circ(\mathrm{TiPt_8})}{12}. \tag{7}$$

Equation (7) gives the values of E_{12}, of 22.58 kcal/g atom at 800 K and 24.68 kcal/atom at 500 K.

Let the surface segregation ratio, ϕ, be defined by

$$\phi = \left[\frac{x_2^s/x_1^s}{x_2^b/x_1^b}\right] \tag{8}$$

and then from Eqs. (1), (3), and (8):

$$\phi = \exp\left[-\frac{\Delta Z}{RT}(E_{12} - E_{11})\right]. \tag{9}$$

Values of ΔZ, and therefore those of ϕ, depend on the crystal face at which segregation occurs. Wandelt and Brundle (*22*) have shown surface enrichment of a Cu–Ni alloy to vary with crystal face as predicted by theory. The values of ΔZ are 4 for (100), 5 for (110), and 3 for (111) faces of the fcc structure of Pt metal. Table 1 gives the values of ϕ for different crystal faces calculated from Eq. (9). These values are so small, for all crystal faces at both temperatures, that it is most improbable that any significant concentration of Ti atoms will be found in the surface of dilute Ti in Pt alloys.

TABLE 1

Surface Segregation Ratio (ϕ) of Ti *in Vacuo*

Temperature (K)	Crystal face of Pt		
	(100)	(110)	(111)
500	8.4×10^{-10}	4.5×10^{-12}	1.6×10^{-7}
800	4.6×10^{-6}	2.2×10^{-7}	1.0×10^{-4}

Errors in the values of ϕ due to approximations in the calculations are unlikely to affect this conclusion.

The virtual absence of Ti atoms in the Pt surface can be understood qualitatively in this way. The strength of the Pt–Ti bond is much greater than that of either Pt–Pt or Ti–Ti bonds, so the most stable system maximizes the number of Pt–Ti bonds. Thus, in a dilute Ti in Pt alloy the most Ti–Pt bonds are obtained when all the Ti atoms are in the bulk surrounded by Pt atoms. Calculations of segregation in the Pt–Ti system have been extended elsewhere (*23*) to cover wider ranges of composition and comparison with other segregation models. Finally, it is worth emphasizing that the simple criteria given at the start of this section predict the opposite conclusion to that calculated by segregation theory.

Surface Segregation of TiO_x

As few experiments on SMSI have been carried out under UHV conditions, some extent of oxidation of metal surfaces could occur, to limits set by the H_2/H_2O ratio. The effect of surface oxidation on the segregation of Ti can be calculated by a modification of the analysis of the previous section. As Ti–O bond strengths are greater than Pt–O bond strengths, it is assumed that any adsorbed oxygen is bonded primarily to a Ti atom in the Pt surface. Equation (3) for the free energy of segregation can be modified to allow for this reaction

$$\Delta G_s = \Delta Z(E_{12} - E_{11}) - E_{20}, \qquad (10)$$

where E_{20} is the free energy of the Ti–O bond.

As oxygen adsorption will tend to cause electron transfer from Ti to O, the effective diameter of Ti will be further decreased. The effective diameter of Ti in the bulk remains unchanged and, as before, the contribution of strain energy to ΔG_s can be neglected. It follows that the surface segregation ratio is now given by equation

$$\phi = \exp\left[-\frac{\Delta Z(E_{12} - E_{11}) - E_{20}}{RT}\right]. \qquad (11)$$

An approximation in the previous section is the assumption that the atom–atom bond strengths in the surface layer are the same as those in the bulk. For Eqs. (10) and (11) it is further assumed that the Ti–Pt bond strength is unaffected by the oxygen adsorption. Thus, the errors in the calculation of surface segregation of Ti as TiO_x must be greater than those for the unoxidised metals.

The strength of any O_a–Ti(Pt) bond is not known experimentally but some limits can be deduced. If, as assumed above, any changes in Pt–Ti bonds on O adsorption are negligible, then the free energy change for the reaction

$$H_2O_{(g)} + Ti(Pt) \rightleftharpoons H_{2(g)} + O_a - Ti(Pt) \qquad (12)$$

is given by

$$\Delta G^\circ_{12} = -E_{20} - \Delta G^\circ_f(H_2O). \qquad (13)$$

Equation (13) can be rearranged to

$$E_{20} = RT \ln([H_2]/[H_2O]) - \Delta G^\circ_f(H_2O). \qquad (14)$$

The reduction conditions quoted by Tauster *et al.* (*1*) are typical for HTR, i.e., $[H_2O]/[H_2] = 8$ ppm after 1 h. This value, with standard data (*10*), then gives a minimum value for E_{20} of 67 kcal/g atom at 800 K. Comparable conditions at 500 K give minimum $E_{20} = 64$ kcal/g atom. Thus, any TiO which had, for instance, diffused across the Pt surface, and was held by Pt–Ti bonding, would be reduced to Ti(Pt) unless E_{20} was greater than or about equal to

TABLE 2

Values of Free Energy of Ti–O Bond

Compound	ΔG_f°(Ti–O) (kcal g atom^{-1})	
	at 800 K	at 500 K
$TiO_{(g)}$	138.26	146.52
$TiO_{2(g)}$	128.81	137.96
$TiO_{(c,x)}$	48.75	53.12
$Ti_2O_{3(c)}$	51.88	56.38
$TiO_{2(c,rutile)}$	61.89	67.31

70 kcal/g atom. This limit on the value of E_{20} may be compared with the free energy of Ti–O bonds in various titanium oxides (Table 2), calculated from the known structures and standard data (*10*, *11*). The revised JANAF estimates for TiO (*11*) have been confirmed by a later work (*24*). As the oxygen in the model considered here is bonded to one Ti atom only, the minimum values of E_{20} are plausible. Neither enthalpy nor free energy of adsorption of oxygen on titanium metal, which could be related to E_{20}, appear to have been measured.

Equation (11) can be rearranged to give the value of E_{20} required to reach a given value of the surface segregation ratio:

$$E_{20} = \Delta Z(E_{12} - E_{11}) + RT \ln \phi. \quad (15)$$

Values of E_{20} calculated from Eq. (15) are given in Table 3. Comparison with the minimum values deduced above shows clearly that if surface oxidation occurs under HTR then very extensive surface segregation of Ti can be expected. The intrinsic errors in the calculations are unlikely to be large enough to affect this qualitative conclusion.

At high levels of surface segregation of Ti, some Ti–Ti bonding can be expected in the surface. Equation (14) can be modified appropriately for various O_x–Ti_y(Pt) ensembles to give values of E_{20} which are higher than those for O–Ti(Pt) but still about or greater than 70 kcal/g atom. However, the validity of the models of the O_x–Ti_y(Pt) ensembles is rather doubtful and the calculations show perhaps little more than that coverage of TiO_x produced by HTR may stop at individual O–Ti(Pt) ensembles.

Oxidation of a surface TiO_x, by breaking Ti–Pt bonds, leads to the formation of TiO_2 on the Pt surface, as shown by Cairns *et al.* (*8*). The Pt crystallites lose all dissolved Ti, so allowing an oxidation/LTR cycle to reform an active catalyst.

The calculations for 500 K (LTR conditions) show no essential difference from the HTR results. Thus, catalysts reduced under LTR conditions should, given time, reach a similar quasi-equilibrium state to HTR catalysts, i.e., they should show SMSI effects.

Experimental work (*25*) with a 2 atom% Fe in Pt alloy showed similar results to those calculated here for Ti in Pt alloys. No segregation of Fe occurred *in vacuo* but exposure to 1.3 × 10^{-5} Pa of O_2 at 973 K brought Fe to the surface.

KINETICS OF FORMATION OF SMSI STATE

Diffusion of Ti Through Pt Crystallites

The rate of reduction of bulk TiO_2 to give dissolved Ti in the adjacent Pt crystallites can be expected to be much slower under LTR than HTR conditions. Evidence from ESR studies (*2*, *26*) shows that some reduction of TiO_2 does occur under LTR conditions. Furthermore, the rates of diffusion of Ti through Pt are likely also to be very dif-

TABLE 3

Values of O_a–Ti(Pt) Bond Free Energy for a Given Segregation Value

Crystal face	ΔZ	Value of E_{20} (kcal g atom^{-1})		
		$\phi = 1$	$\phi = 10$	$\phi = 100$
800 K				
(100)	4	19.5	23.2	26.8
(110)	5	24.4	28.1	31.7
(111)	3	14.6	18.3	22.0
500 K				
(100)	4	20.8	23.0	25.3
(110)	5	26.0	28.2	30.5
(111)	3	15.6	17.9	20.2

ferent under HTR and LTR conditions. The diffusion coefficient for Ti in Pt appears not to have been determined, but data for Pd in Pt (*27*), Co in Pt (*28*), and Pt in Pt (*29*) suggest diffusion (D) values of 10^{-33} to 10^{-35} m^2 s^{-1} at 500 K and 10^{-23} to 10^{-24} m^2 s^{-1} at 800 K for Ti in Pt. Application of the diffusion equation

$$l = \sqrt{2}Dt \qquad (16)$$

for $t = 24$ h then gives characteristic diffusion distances of about 10^{-5} nm at 500 K and about 1 nm at 800 K. Even if values of D are in error by several orders of magnitude it is clear that bulk diffusion in Pt crystallites is negligible at 500 K, but may well be significant at 800 K, especially in the thin "pill-box" crystallites from HTR (*30*). Some reservations must be made in view of the large extrapolation in temperature for values of D and indeed the applicability of bulk diffusion coefficients to microcrystallites.

The plausibility of these calculations for microscopic crystallites is supported by experimental work (*25*) with macroscopic slices of a 2 atom% Fe in Pt alloy. Equilibrium surface segregation of Fe was reached in 1 h under 1.3×10^{-5} Pa of O_2 at 973 k.

Diffusion of TiO_x across Pt Crystallites

There is no clear experimental evidence on which of the steps in the conversion of bulk TiO_2 to TiO_x/Pt is rate determining. Calculations indicate that the surface diffusion of TiO_x across the platinum surface is fast enough under HTR but not LTR. However, the limiting step under a given set of LTR conditions may instead be the reduction of Ti^{4+}, the formation of anion vacancies or the transport of TiO_x from TiO_2 to Pt.

As the Ti–Pt bonds are stronger than Pt–Pt bonds, the critical factor in the diffusion of adsorbed TiO_x across the surface of a Pt crystallite is probably the mobility of the Pt surface itself. Many years ago Hüttig (*31*) suggested that the onset of surface mobility in metals occurred at about one-third of the melting point (in K). Recently Schrammen and Holzl (*32*) studied surface self-diffusion of Ni atoms on the Ni (100) plane and found that full surface mobility was reached between 500 and 620 K, i.e., between T/T_m values of 0.29 and 0.36. The melting point of platinum is 2042 K, so surface mobility would be expected to be significant at temperatures above about 700 K. Thus, the rapid diffusion of TiO_x across a Pt surface would be expected at 800 K (HTR) but not at 500 K (LTR), in agreement with experimental observation. Resasco and Haller (*7*) found the same activation energy for the migration of a suboxide of Ti and for the migration of Ag over Rh particles. In these rhodium systems, the silver tends to cluster because the Ag–Ag bond energy is greater than the Ag–Rh bond energy (*33*), so the diffusion of Ag clusters, like that of TiO_x, depends on the mobility of the underlying Rh (Hüttig temperature, about 750 K). However, the Hüttig temperatures of TiO_2 (rutile) and TiO are also about 700 K, so that insofar as SMSI effects depend on the mobilities of these oxides the same difference between LTR and HTR should be observed.

Recently Chen and White (*34*) found that the addition of very small amounts of potassium to Pt/TiO_2 catalysts strongly suppressed H_2 chemisorption after LTR, i.e., induced characteristic SMSI effects, and this was attributed to electron charge transfer from K to Pt. It can be shown (*35*) that the potassium was present in an oxidized form and its role in promoting SMSI was more likely to be that of a "flux" promoting the diffusion of TiO_2 or TiO_x on the catalyst surface, thus simulating under LTR conditions the mobility of HTR conditions. Only low concentrations of potassium would be needed for this mechanism and once a steady state of reduced titanium oxide layer had been formed on all Pt crystallites, no further change in chemisorption properties would be seen on further potassium addition. This is also in agreement with the results of Chen and White.

COMPARISON WITH OTHER SYSTEMS

The broad characteristics of other systems which show comparable SMSI phenomena to Pt/TiO_2 catalysts are the combination of a Group VIII metal with an oxide support capable of some limited, possibly nonstoichiometric reduction (*1, 36*). Fewer thermodynamic data are available for most of these systems than for the Pt/TiO_2 system, so it is difficult to repeat the calculations above. Nevertheless, analogues of the strong Pt–Ti bonds, which greatly aid the stability of the surface TiO_x, are found in other Group IV/Group VIII systems (*12*). The same pattern of SMSI effects following HTR, but not LTR, is seen with these systems: the actual temperature dependence seems to be a function of both metal and oxide. Thus after reduction at 773 K the most refractory of the platinum metals, Os (Hüttig temperature about 1100 K), supported on titania still has about 50% of the chemisorption capacity generated by LTR (*1*), in broad agreement with the model proposed here. Both relative reducibility and relative surface mobility could be significant in the dependence on oxide support (*36*).

At higher temperatures than those of conventional HTR, normally irreducible oxides can give Pt alloys, with comparable SMSI effects due to suboxide monolayers. Reduction of Pt/Al_2O_3 at 1273 K (*8*), above 773 (*37, 38*), and in the range 723 K to 873 K (*39*) gives SMSI effects.

VALIDITY OF THE USE OF BULK PROPERTIES

As thermodynamic and diffusion data are not available for the microscopic particles of real Pt/TiO_2 catalysts, the corresponding bulk properties have been used in these calculations. Errors could arise both from the presence of surfaces and from the very small particle size. Modifications to bulk thermodynamic properties required (*40, 41*) for surface segregation calculations for several platinum alloys, if applied to Pt/Ti alloys, do not alter any of the conclusions reached here. The effects of small particle size are more difficult to assess, especially on the properties of the small platinum crystallites made by HTR (*30*), as noted above. Some properties, e.g., surface diffusion, are probably little affected. However, even if there are order of magnitude errors in segregation ratios or bulk diffusion coefficients, the models of the processes which could occur in SMSI in Pt/TiO_2 catalysts would still be valid.

CONCLUSIONS

1. The equilibrium and surface segregation calculations support the proposition that the SMSI effects in Pt/TiO_2 catalysts are due to a monolayer (or less) of strongly adsorbed titanium suboxide on the platinum surface.

2. The failure of Pt/TiO_2 catalysts to show SMSI after low-temperature reduction is due to kinetic rather than equilibrium limitations.

3. Two mechanisms of formation of the TiO_x layer are possible:
(i) Reduction of TiO_2 to give a Pt/Ti alloy, followed by surface segregation and oxidation;
(ii) Formation of TiO_x at the Pt/TiO_2 interface, followed by transport across the Pt surface. Diffusion calculations indicate that both routes are sufficiently fast in high-temperature reduction but both are too slow in low-temperature reduction. Experimental evidence so far suggests that (ii) is more important than (i).

4. Similar considerations probably apply to other systems showing comparable SMSI effects.

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