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Metal–Support Effects on Acetone Hydrogenation over Platinum Catalysts

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Acetone hydrogenation was studied over Pt/TiO_2, Pt/η-Al_2O_3, Pt/SiO_2, Pt powder, and Pt/Au catalysts to test the hypothesis that the metal-support effect responsible for higher CO hydrogenation rates over certain metal/TiO_2 catalysts represents a phenomenon capable of activating carbonyl bonds in general. Compared with the other catalysts, the high-temperature reduced (HTR) Pt/TiO_2 samples had turnover frequencies more than 500 times higher than those of unsupported Pt and Pt/SiO_2 catalysts, and the specific activity (per g Pt) of the Pt/TiO_2 catalyst was 10 times that of a Pt/SiO_2 catalyst with comparable dispersion. Complete hydrogenation to C_3H_8 and H_2O occurred only on large, unsupported Pt crystallites; however, partial hydrogenation to isopropyl alcohol appeared to be structure insensitive and activation energies were similar over all catalysts, as were pressure dependencies, which associates the higher activity with a larger preexponential factor. Only one Langmuir–Hinshelwood model provided a rate expression consistent with experimental results—that which assumed competitive adsorption of H_2 and acetone on the same sites and addition of the second H atom as the rate-determining step. This model is consistent with previous TPD, IR, and EELS studies and is also substantiated by theoretical calculations based on the bond-order conservation method. The much higher activities over Pt/TiO_2 catalysts are attributed to an increase in the active site concentration in the Pt–titania interface region. These special sites are presumed to be defects on the titania surface near the Pt that can activate the carbonyl bond in the presence of atomic hydrogen provided by the Pt. This model is very similar to that proposed to explain higher CO hydrogenation activities over TiO_2-supported Pt. © 1988 Academic Press, Inc.

INTRODUCTION

Modification of the catalytic properties of a dispersed metal by the substrate was first discussed by Schwab and Schultes (*1*), and most of the earlier work related to support effects in heterogeneously catalyzed reactions has been reviewed by Schwab (*2*) and Solymosi (*3*). Some of these studies dealt with the decomposition of formic acid over metal/metal oxide systems, and the bulk semiconducting properties of the oxide were correlated with the apparent activation energy for this reaction. More recently, the finding by Tauster and coworkers of a support effect on the chemisorption properties of a metal underscored the importance of metal-support effects as a surface phenomenon and spurred renewed interest in this area of research (*4*). The results of these last studies are well established—after a reduction at high temperature, group VIII metals supported on reducible oxides such as TiO_2 undergo a drastic reduction in their ability to chemisorb H_2 and CO that is not attributable to sintering.

The benefits of titania-supported group VIII metals as catalysts for CO hydrogenation were first reported in a paper by Vannice and Garten in which they obtained not only an increase in specific activity, but also a shift in selectivity toward higher hydrocarbons with the Ni/TiO_2 system (*5*). Since then the CO hydrogenation reaction has been extensively used as a probe to investigate metal-support effects, and rate enhancements have been observed over many, but not all, group VIII metals supported on titania (*6–15*). Ethylene hydroge-

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nation (*16*), hydrogenolysis of ethane and butane (*17–19*), and hydrogenation of benzene (*20–23*) and styrene (*20*) have also been studied over titania-supported catalysts. A few clear facts emerge from these studies: (i) the reaction of CO with H_2 has been the only reaction to date for which large enhancements in turnover frequency (10- to 100-fold) have been clearly established for the titania-supported group VIII metals; (ii) the hydrogenation activity for unsaturated olefinic and aromatic carbon bonds is typically suppressed by a factor of 5–10 (on a gram of metal basis); and (iii) there is a drastic suppression in hydrogenolysis (C–C bond breaking) activity.

The present study stemmed primarily from these observations and was predicated on the following question: *Is the rate enhancement in the hydrogenation of the CO molecule by titania-supported metals due to a phenomenon that can be extended to increase hydrogenation rates of carbonyl groups in general?* To help answer this intriguing question, a study of the vapor-phase hydrogenation of acetone was initiated over a family of well-characterized platinum catalysts supported on SiO_2, η-Al_2O_3, and TiO_2. In addition, the activity of ultrahigh-purity platinum powder was examined to establish a standard for comparison, and the influence of Au on this Pt powder was also studied. This paper describes the catalytic behavior of these catalysts in acetone hydrogenation and discusses a reaction model capable of explaining the observed kinetics of isopropanol formation.

EXPERIMENTAL

Catalyst Preparation

Support materials used in this study were SiO_2 (Davison Grade 57, 220 m^2/g), η-Al_2O_3 (Exxon Research and Eng. Co., 245 m^2/g), and TiO_2 (Degussa P 25, 80% anatase and 20% rutile, 50 m^2/g). The SiO_2 and TiO_2 were calcined in air for 4 h at 773 K prior to catalyst preparation. Most of the supported catalysts used in this study were prepared by impregnating the support with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (Sigma Chemical Co.), and details of the catalyst preparation procedure are given elsewhere (*24*). One of the silica-supported catalysts was prepared by an ion-exchange method (*25, 26*) using $Pt(NH_3)_4Cl_2$ (Strem Co.) as the precursor. All the catalysts were dried in air at 393 K for 2 h prior to storage in a desiccator. The platinum weight loadings were determined by neutron activation analysis using a known amount of $Pt(NH_3)_4Cl_2$ physically mixed with the appropriate support as the standard. The unsupported Pt used was Puratronic grade powder (99.999%) from Johnson Matthey.

Three samples of gold dispersed on the Pt powder surface were prepared by dissolving the appropriate weight of $AuCl_3$ (Johnson Matthey) in 20 ml of water, then adding 2 g Pt powder to the solution, stirring slowly, and heating at 360 K until all the water had evaporated. The powder was then transferred to the adsorption system for hydrogen adsorption and Ar BET surface area measurements. The samples contained 0.3, 1, and 10 monolayers of Au, if uniform distribution on the Pt surface is assumed, and are designated 0.3 Au/Pt, 1 Au/Pt, and 10 Au/Pt, respectively.

Chemisorption Measurements

The adsorption studies were conducted in two high-vacuum stainless-steel systems each of which provided an ultimate vacuum of 10^{-8} to 10^{-9} Torr (1 Torr = 133 Pa). Further details on the two systems are given elsewhere (*27, 28*). Approximately 1 g of each catalyst was placed in a Pyrex adsorption cell and prior to an adsorption run each sample was given pretreatment A ($T_{reduction}$ = 723 K), B (T_{red} = 473 K), or C (T_{red} = 773 K) as detailed in Ref. (*27*). The samples of Pt supported on η-Al_2O_3 and SiO_2 were subjected to pretreatment A, while either pretreatment B or C was used for Pt/TiO_2. The 0.7% Pt/SiO_2 sample was calcined in 20% O_2 at 673 K for 1 h to decompose the precursor prior to pretreatment A. The low-temperature reduction at 473 K is designated LTR, whereas the high-temperature reduction at 773 K is designated HTR. The high-purity Pt powder was calcined in 20% O_2 and 80% He at 673 K for 1 h and then subjected to pretreatment C. The Pt powder used in the physical mixture was similarly treated; however, since a second adsorption measurement was performed, to ensure a clean surface it was again reduced in 20% H_2–80% He for 1 h at 773 K and evacuated at 723 K for 1 h. For the Au/Pt catalysts a pretreatment method similar to that adopted by Foger and Anderson (*29*) was followed. The catalyst was calcined in 20% O_2 at 623 K for 1 h, reduced in pure H_2 at 773 K for 1 h, and evacuated at 723 K for 1 h prior to H_2 adsorption measurements. The Ar BET surface area measurements were done after H_2 chemisorption and after evacuation for 1 h at 723 K.

The chemisorption of H_2 on pure SiO_2, η-Al_2O_3, and TiO_2 has already been shown to be zero at room temperature (*24, 30, 31*). Isotherms for H_2 at 300 K were obtained between 40 and 200 Torr and were essentially linear in this range, so the saturation hydrogen coverages on Pt were obtained by extrapolating the isotherm to zero pressure (*32, 33*). After the initial isotherm the sample was evacuated for 1 h and a second isotherm was determined to measure the amount of weakly (reversibly) adsorbed hydrogen associated with the metal surface (*34*).

Acetone (A) Hydrogenation

The kinetic experiments were performed in a microreactor system described in detail elsewhere (*35*). Approximately 50 mg of the catalyst was loaded into a glass reactor which was immersed in a fluidized sandbath (Tecam SBS-4) equipped with a temperature controller (West 400). Ultrahigh-purity hydrogen (99.999%) and He (99.999%) were further purified by passage through an Oxytrap (Alltech Assoc.). The gas flow rates were measured by calibrated mass flowmeters (Teledyne, Hastings Raydist). Acetone (99.5%, A.C.S. Spectraanalyzed, 0.02% methanol, 0.01% isopropanol) was purified of any dissolved O_2 by subjecting it to three freeze–thaw cycles under an atmosphere of flowing nitrogen and then was stored under N_2. Acetone was introduced into the reactor system by a calibrated 5-cm^3 syringe pump (Sage Instruments Model 341A) and was vaporized in the preheated reactor inlet line. Acetone and the products from hydrogenation—isopropanol (IPA) and propane—were analyzed by a gas chromatograph (H-P 700-00) equipped with a TC detector using 1,2,3-tris(2-cyanoethoxy)propane (Supelco) as the column packing (mesh size 80/100). Conversions were typically kept below 10% to avoid heat and mass transfer effects and to keep the reaction in the differential regime to ensure interpretable analysis of the data. The absence of any diffusional limitations was also established by the application of the Weisz criterion (*36*), which gave a value of 0.004 at 303 K for the most active catalyst, thereby establishing the absence of any significant diffusion limitations.

The catalyst was reduced *in situ* in 50 cm^3 (STP) H_2 min^{-1} for 1 h prior to the kinetic run. Activity measurements were done in a sequence: temperature was increased (303–333 K) and then decreased back to the initial temperature, and the sequence of increasing temperature measurements was then repeated. A bracketing technique, which consisted of a 30-min reaction period (P_A = 181 Torr and P_{H_2} = 554 Torr) followed by regeneration of the catalyst under H_2 for 20 min, was utilized prior to activity measurement at each temperature. This was found to yield reproducible and consistent values for the activation energies. An activity maintenance study was done with the (HTR) Pt/TiO_2 sample during which the reactants were allowed to flow over the catalyst continuously for a period of 8 h and the product composition was monitored.

TABLE 1

Characterization of Pt and Au/Pt Catalysts by Hydrogen Chemisorption

Catalyst	Precursor	Preparation method	H_2 uptake (μmol/g cat)			H/Pt[c]	d[d] (nm)
			Total	Rev.	Irr.		
5% Pt/SiO_2	$H_2PtCl_6 \cdot 6H_2O$	IW[a]	39.4	15.6	23.8	0.31	3.7
0.7% Pt/SiO_2	$Pt(NH_3)_4Cl_2$	IE[b]	10.1	4.3	5.8	0.56	2.0
2.1% $Pt/\eta\text{-}Al_2O_3$	$H_2PtCl_6 \cdot 6H_2O$	IW[a]	15.7	7.5	8.2	0.29	3.9
1.9% Pt/TiO_2 (LTR)	$H_2PtCl_6 \cdot 6H_2O$	IW[a]	36.7	15.5	21.2	0.75	1.5
1.9% Pt/TiO_2 (HTR)			0.4	—	—	0.008	(141)
Pt powder			2.8	—	—	0.0011	1000
66 wt% Pt powder + 34 wt% TiO_2 (physical mixture)			1.8	0.7	1.1	0.0007	1600
Au/Pt ($\frac{1}{3}$ monolayer)			2.1[e]	1.0	1.1		
Au/Pt (1 monolayer)			0.4[f]	0.3	0.1		
Au/Pt (10 monolayers)			0[g]	0	0		

[a] Incipient wetness.
[b] Ion exchange.
[c] Based on total H_2 uptake.
[d] d (nm) = 1.13 (H/Pt).
[e] BET surface area = 0.6 m^2/g.
[f] BET surface area = 0.4 m^2/g.
[g] BET surface area = 0.5 m^2/g.

To determine partial pressure dependencies for isopropyl alcohol (IPA) formation, the partial pressure of acetone was varied from 25 to 180 Torr (1 Torr = 133 Pa) and that of hydrogen was varied from 140 to 555 Torr. All measurements were at 0.1 MPa (1 atm) using He as a diluent, and the bracketing technique was again used prior to each measurement. The most active (HTR) 1.9%/TiO_2 catalyst as well as the typical 5% Pt/SiO_2 catalyst was characterized and their kinetic parameters were determined.

RESULTS

The hydrogen uptakes on the fresh catalysts after the standard pretreatments, but prior to kinetic experiments, are listed in Table 1. The dispersions (fractions exposed) were calculated based on the total hydrogen uptake assuming an H_{ad}/Pt_{surf} stoichiometry of 1. The Pt crystallite size was calculated using d(nm) = 1.13/(H/Pt).

The kinetic behavior of the Pt catalysts is summarized in Table 2. The kinetic data followed simple Arrhenius law behavior and the apparent activation energies are listed in Table 2. The catalytic activities listed in Table 2 have been calculated both on a Pt weight basis and on the basis of surface sites, as counted by the total hydrogen uptake, to obtain turnover frequencies (TOFs). Pure SiO_2 and TiO_2 did not show any activity in acetone hydrogenation under these conditions. On the 5% Pt/SiO_2 sample three consecutive activity measurements were made after reducing the catalyst between each run. The partial pressure dependencies were obtained from the plots in Fig. 1, in which acetone conversion ranged from 0.2 to 10%. The 1.9% Pt/TiO_2 sample was given another HTR step after the acetone partial pressure run and prior to the H_2 pressure run. The rate equations and kinetic parameters defined for IPA formation over (HTR) Pt/TiO_2 and Pt/SiO_2 are listed in Table 3.

The behavior of the Pt powder and the physical mixture of Pt powder and TiO_2 was significantly different from that of the supported Pt catalysts. All the supported Pt catalysts showed 100% selectivity to IPA; however, the Pt powder and the physical mixture of Pt powder and TiO_2 produced propane as well under these conditions, as indicated in Table 2. The selectivity, defined as the ratio of IPA and C_3H_8 turnover

TABLE 2

Hydrogenation of Acetone (A) to Isopropanol (IPA) and Propane over Pt at 303 K, $P_{\text{total}} = 0.1$ MPa, and $H_2/A = 3.06$

Catalyst (sample)	Activity (μmol IPA/ s · g Pt)	Turnover frequency ($s^{-1} \times 10^2$)[a]		E_{IPA} (kcal/mol)	Conversion range (%)
		N_{IPA}	$N_{C_3H_8}$		
5% Pt/SiO_2	20.8 ± 0.4	1.31 ± 0.02	ND[b]	16.6	2–8
	28.2 ± 0.8	1.78 ± 0.12	ND	15.6	2–7
	10.0 ± 1.8	0.64 ± 0.12	ND	16.6	0.9–4
0.7% Pt/SiO_2	15.7 ± 1.4	0.52 ± 0.05	ND	15.3	0.8–3.0
2.1% $Pt/\eta\text{-}Al_2O_3$	35.7 ± 1.0	2.39 ± 0.05	ND	18.6	1.6–7.0
1.9% Pt/TiO_2 (LTR)					
I	153.2 ± 1.1	3.96 ± 0.03	ND	14.8	0.8–6.1
II	58.9 ± 2.6	1.53 ± 0.07	ND	13.4	0.9–4.3
1.9% Pt/TiO_2 (HTR)					
II	261.1 ± 38.9	620 ± 93	ND	18.2	7.9–15.0
	96.3 ± 16.3	229 ± 39	ND	14.6	4.0–9.0
III	291.6 ± 20.0	692 ± 47	ND	18.4	12–18
	303.2 ± 55.8	720 ± 133	ND	14.0	10–32
Pt powder	0.041 ± 0.01	0.74 ± 0.20	0.37 ± 0.09	16.6 (18.0)[c]	1–12
66% Pt powder + TiO_2 (physical mixture)	0.036 ± 0.003	0.66 ± 0.10	0.53 ± 0.14	17.8 (11.8)[c]	2–12
Au/Pt ($\frac{1}{3}$ monolayer)	0.013	0.3	0.1	—	0.9–1.2
Au/Pt (1 monolayer)		Not active			
Au/Pt (10 monolayers)		Not active			

[a] Based on hydrogen chemisorption (total H_2, Table 1).

[b] Not detected.

[c] Activation energy for propane formation.

frequencies, was 2 for the powder and 1.2 for the physical mixture.

Three samples of gold on platinum powder were studied. Addition of 0.3 monolayer of Au on the Pt powder surface reduced the total hydrogen uptake by one-third, and 1 monolayer Au (nominally) reduced the hydrogen uptake from 2.9 to 0.4 μmol/g Pt. The TOF for IPA formation on the 0.3 Au/Pt catalyst was 0.3×10^{-2} s^{-1}, but the 1 Au/Pt sample gave no detectable activity for acetone hydrogenation be-

TABLE 3

Kinetic Parameters for Isopropanol (IPA) Formation from Acetone (A) over Supported Pt at 303 K and 0.1 MPa

Catalysts	N_{IPA} ($s^{-1} \times 10^2$)	E (kcal/mol)	X[a]	Y[a]	Preexponential factor, A [$10^9/s \cdot (\text{atm})^{X+Y}$]
5% Pt/SiO_2	1.2[b]	16.0[b]	−0.2 ± 0.1	1.2 ± 0.4	0.6[b]
1.9% Pt/TiO_2 (HTR)	560[b]	16.3[b]	−0.6 ± 0.3	1.3 ± 0.5	1900[b]

[a] $N_{\text{IPA}} = Ae^{-E/RT} P_A^X P_{H_2}^Y$, $E = E_{\text{IPA}}$.

[b] Average values from Table 2.

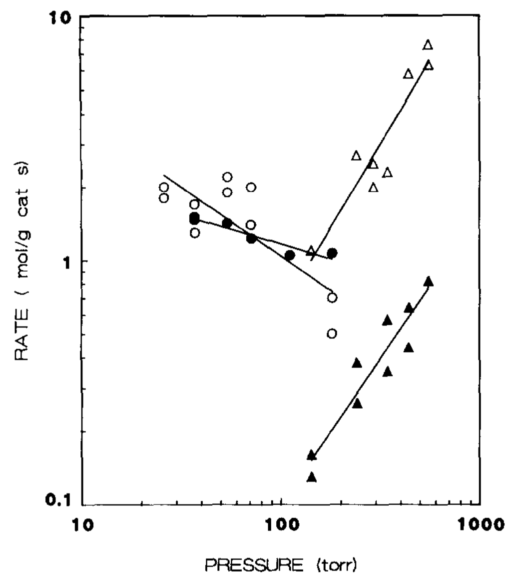


FIG. 1. Partial pressure dependencies at 303 K on acetone (circles) and H_2 (triangles) over 5% Pt/SiO_2 (filled symbols) and (HTR) 1.9% Pt/TiO_2 (open symbols).

tween 303 and 368 K. The addition of 10 monolayers of gold completely suppressed both hydrogen chemisorption and catalytic activity for acetone hydrogenation. The TOFs for the formation of IPA and propane are listed in Table 2, and the selectivity of this Au/Pt catalyst was 3. Because of the low activity and deactivation of this catalyst, activation energies are not reported.

The activity of the (HTR) Pt/TiO_2 sample was monitored for approximately 8 h during which period the activity declined by one-third, with most of the decrease occurring during the first 4 h before stability could be achieved, as shown in Fig. 2.

The most important results from this study can be summarized as follows:

(i) The Pt/TiO_2 system is by far the most efficient catalyst reported to date for the hydrogenation of acetone to IPA, particularly after an HTR step. Under identical reaction conditions, the average turnover frequency over the (HTR) Pt/TiO_2 samples is over 500 times greater than the average TOF measured on Pt/SiO_2 catalysts, as shown in Fig. 3, and it is close to 1000 times more active than the Pt powder. Of course the reduced chemisorption capacity is partially responsible for the high TOF values; however, even on a gram of Pt basis the specific activity is 10 times higher, as shown in Fig. 4, thereby producing catalysts that are intrinsically more active at comparable dispersion. This large activity enhancement due to TiO_2 is very similar to that found for CO hydrogenation over Pt (*9*, *10*).

(ii) The apparent activation energies for the (HTR) Pt/TiO_2 samples fall within the range of values obtained for the typical Pt catalysts and the average value is essentially the same as that for Pt/SiO_2 catalysts; consequently, the higher TOFs cannot be explained by a decrease in this kinetic parameter, a situation again similar to methanation (*9*, *10*).

(iii) The H_2 partial pressure dependencies for IPA formation over Pt on SiO_2 or TiO_2 are similar and near first order while the dependency on acetone is more negative over the Pt/TiO_2 catalyst, but under these reaction conditions the surfaces of both catalysts appear to be highly covered with adsorbed acetone. The slightly greater than

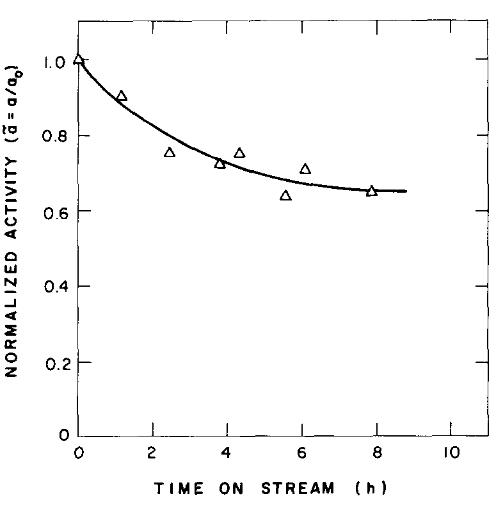


FIG. 2. Activity maintenance profile for (HTR) 1.9% Pt/TiO_2 in the hydrogenation of acetone to IPA at 311 K, P_{H_2} = 554 Torr, P_A = 181 Torr.

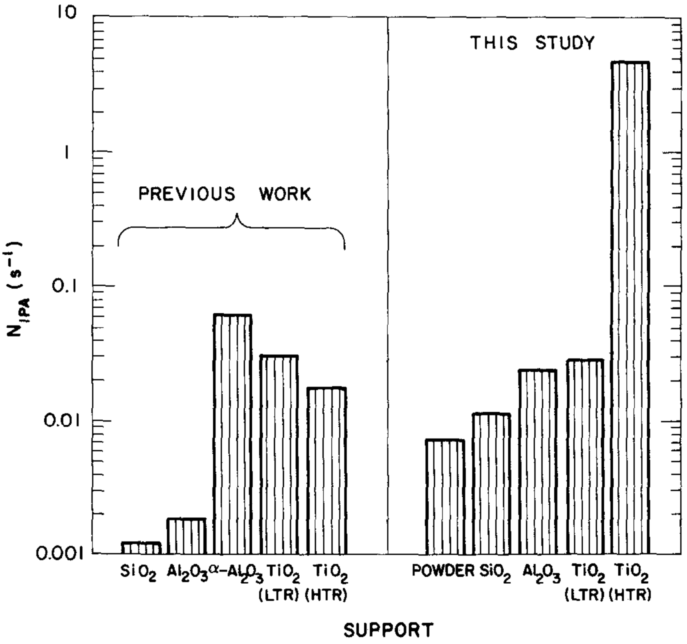


FIG. 3. Comparison of turnover frequencies at 303 K for the formation of IPA from acetone over supported Pt (P = 0.1 MPa, P_{H_2}/P_A = 3.06). Previous work includes Refs. (*39, 44, 54*); results from this study are average values obtained from Table 2.

first-order dependency on H_2 is attributed to removal of surface carbonaceous species by hydrogen in a manner proposed previously for benzene hydrogenation (*23*).

(iv) The activity enhancement for acetone hydrogenation on the (HTR) Pt/TiO_2 catalyst appears to be due primarily to an increase in the preexponential factor, as observed for methanation (*9, 10*).

(v) A marked difference in the selectivity behavior was observed between the supported Pt catalysts and Pt powder. All the former catalysts produced IPA with 100% selectivity, whereas the Pt powder gave only 67% selectivity to IPA, the remainder being propane.

(vi) The TOF for IPA formation on the 0.3 Au/Pt catalyst was only a factor of 2 lower than that obtained on Pt powder, which was near that of the Pt/SiO_2 catalysts, while the TOF for propane formation was reduced by a factor of 4 or more on 0.3 Au/Pt. Hydrogen uptake measurements in-

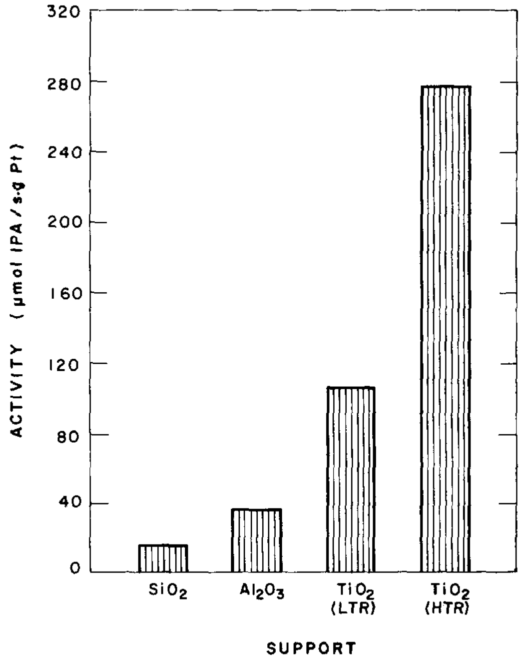


FIG. 4. Comparison of specific activity (per g Pt basis) at 303 K and 1 atm for the formation of IPA from acetone as a function of the support (P_{H_2}/P_A = 3.06).

dicated that a third of the Pt surface was covered by Au.

DISCUSSION

A. Rates of Acetone Hydrogenation

Hydrogenation of acetone over transition metals has been studied by various workers (*37–57*), and most of the work prior to 1962 has been reviewed by Bond (*58*). IPA and propane are the two primary products of this reaction and, depending on the temperature and particularly on the nature of the catalyst, either product may be formed exclusively or both may be formed together. It is generally agreed that these two products are formed simultaneously by different paths and that IPA is not an intermediate in the formation of propane (*37, 58*). Based on the studies of Stoddart and Kemball, the order of relative activities for the formation of IPA is Pt > Ni > Fe ≅ W > Pd > Au (*49*). Assuming the surface areas of the metal films were the same as those determined earlier by Kemball (*48*), turnover frequencies were estimated and are given in Table 4. Subsequent studies have provided TOF values that are generally consistent with this ranking, as can be seen in Table 4. The order of relative activi-

TABLE 4

Kinetic Parameters for IPA Formation from Acetone (A) over Group VIII Metals: Activities Adjusted to 303 K, P_{H_2} = 554 Torr, PA = 181 Torr Using the Rate Expression in Each Reference When Given

Catalyst	Experimental temperature range (K)	Average crystallite diameter (nm)	Turnover frequency ($s^{-1} \times 10^2$)	Apparent E_{act} (kcal/mol)	Ref.
2% Pt/γ-Al_2O_3	337–365	6.0	6	~2–8	(*39*)
0.5% Pt/Al_2O_3	303–363	3.3	0.067	10.2	(*44*)
		18.4	0.18	10.2	(*44*)
		26.4	0.14	10.5	(*44*)
		39.0	0.15	11.0	(*44*)
6.4% Pt/SiO_2	330	1.9	0.12[a]	—	(*54*)
0.5% Pt/TiO_2 (LTR)	330	2 (est.)	3.1[a]	—	(*54*)
0.1% Pt/TiO_2 (HTR)	330	2	5.2[a]	—	(*54*)
1.0% Pt/TiO_2 (HTR)	330	2	1.2[a]	—	(*54*)
0.5% Pt/Al_2O_3	303–363	3.3	0.067	10.2	(*44*)
Raney Ni	333–363	13.9	2.6	—	(*45*)
Raney Ni	308	—		13[b]	(*47*)
Ni black	337–365	520.2	3.0	6.0	(*42*)
Ni/γ-Al_2O_3	333–363	2.4	1.3	6.0	(*42*)
Raney Ni	273–287	—	4.2[b]	8.6	(*53*)
Co black	337–365	28.4	0.049	15.0	(*42*)
Co/γ-Al_2O_3	333–363	7.5	0.23	9.7	(*42*)
5% Pd/SiO_2	423–498	23.8	0.13	8.1	(*46*)
Rh (II) and Rh (III)[c]	303	—	0.56–8.6	—	(*92*)
Pt film	227–251	—	14[d]	5.0	(*49*)
Pd film	298–389	—	0.009[d]	5.8	(*49*)
Ni film	228–297	—	3.2[d]	8.8	(*49*)
W film	273–361	—	0.012[d]	9.1	(*49*)
Fe film	273–371	—	0.012[d]	12.5	(*49*)
Au film	403–476	—	0.0008[d]	5.7	(*49*)

[a] Adjusted to reaction conditions above using rate equations in Table 3.

[b] Liquid phase, $P_{H_2} \approx$ 1 atm.

[c] Homogeneous system, liquid phase, $P_{H_2} \approx$ 1 atm.

[d] Estimated from metal surface areas reported in Ref. (*48*).

ties for propane formation is Pt > W > Ni > Fe > Pd = Au between 333 and 373K, with no propane formation reported over Pd and Au (*58*).

Before the question of selectivity is addressed, the thermodynamics associated with the two distinct pathways that have been identified for acetone hydrogenation over transition metal catalysts can be considered (*37*, *38*, *58*): mild hydrogenation, in which the addition of hydrogen takes place across the carbon–oxygen double bond resulting in the formation of IPA, and extensive hydrogenation, which results in the hydrogenolysis of the C=O bond and the formation of propane and water. The standard free energy change for the former reaction is −4.8 kcal/mol and that for the latter, more exothermic reaction is −23.6 kcal/mol; therefore, the formation of propane is thermodynamically favored over that of alcohol. In spite of the less favorable thermodynamics, all the supported Pt catalysts we studied produced IPA with 100% selectivity thereby providing an example of the role catalysts can play by inducing kinetic, rather than thermodynamic, control of product formation. Unsupported Pt powder produced propane as well as IPA with a selectivity ratio ($N_{IPA}/N_{C_3N_8}$) between 1 and 2 (Table 2); however, the addition of 0.3 monolayer of Au on Pt increased this ratio to 3. The behavior of our ultrahigh-purity Pt powder is very consistent with previous results as supported Pt catalysts and unsupported Pt promoted with $FeCl_3$ or $SnCl_2$ have shown 100% selectivity to IPA (*39*, *44*, *54–57*) whereas propane has been formed in detectable amounts only on large Pt crystallites, i.e., platinized Pt foils and evaporated Pt films (*37*, *38*, *49*).

Golodets *et al.* studied vapor-phase acetone hydrogenation between 337 and 365 K over a Pt/γ-Al_2O_3 catalyst and found that 6.0-nm Pt crystallites produced IPA with 100% selectivity (*39*). Cunningham and Al-Sayyed produced IPA with 100% selectivity at 330 K over well-dispersed Pt/SiO_2 and Pt/TiO_2 catalysts (*54*). Rositani *et al.* studied this reaction between 303 and 363 K over Pt/Al_2O_3 catalysts and found that only IPA was produced over a reported range of 3.3- to 39-nm particles (*44*), and over a 10% Pt/charcoal catalyst promoted with Fe, Friedman and Turkevich also formed only IPA (*55*). Maxted and Akhtar studied liquid-phase acetone hydrogenation over an Adam's catalyst promoted with salts of Fe and Zn, and they obtained IPA with 100% selectivity at 293 K (*57*).

Propane formation has been observed only over unsupported Pt catalysts. Stoddart and Kemball studied vapor-phase acetone hydrogenation over evaporated Pt films between 220 and 250 K at low pressures (ca. 1 Torr), and under these conditions the selectivity to propane was about 8% (*49*). However, the production of propane increased with temperature and at a temperature of 336 K the initial TOF for the formation of propane was estimated to be 3×10^{-3} s^{-1}. Farkas and Farkas (*37*) and Kauder and Taylor (*38*) also observed propane production, and at a temperature of 260 K propane was formed with 82% selectivity over a platinized Pt film (*37*).

The reason for this difference in selectivity is not clear but at least two possibilities can be considered: the effect of crystallite size and the effect of promoters.

(*i*) *Effect of crystallite size*. It is tempting to ascribe the change in selectivity to a variation in the statistical density of surface sites (*59*), but it is difficult to reconcile the 100% selectivity to IPA over 39-nm crystallites observed by Rositani *et al.* (*44*) since the distribution of edge, corner, and face atoms on a 39-nm particle can be expected to be essentially the same as that for bulk unsupported Pt (*59*). However, a critical evaluation of the pretreatment procedure adopted by Rositani *et al.* (*44*) to obtain varying degrees of dispersion may provide an explanation. Their 0.5% Pt/Al_2O_3 catalyst initially had 3.3-nm Pt crystallites, as estimated from H_2–O_2 titration measurements, and it was subsequently treated in oxygen at 1073 K for progressively longer times to obtain larger particles. This calcination step could affect the reducibility of the Pt if the high-temperature treatment led to an extremely stable solid solution between metal oxide and support, as reported for Ni/alumina and Co/alumina catalysts (*60*), it could induce a bimodal Pt size distribution (*61*), or it could result in Pt poisoning by the migration of Na_2O and Fe_2O_3, which are typically present in high-surface-area alumina supports (*62*). However, the most likely explanation is that little sintering occurred at this low loading, but the Pt became partially covered by Al_2O_3 as found by Cairns *et al.* after heating the Pt/Al_2O_3 system in O_2 at 1273 K for 18 h (*63*). Consequently, it is extremely likely that Pt crystallite sizes did not change significantly and were grossly overestimated by Rositani *et al.* due to the Al_2O_3 overlayer.

Despite this likelihood, because of the uncertainty associated with the high-temperature treatment in oxygen, only supported Pt catalysts not treated in O_2 at high temperature will be considered, and this encompasses a range of particle size varying from 1.9 to 6.0 nm (see Table 4) over which IPA was produced with 100% selectivity. The unsupported Pt catalysts that have produced propane, i.e., films, foils, and powders, have consisted of particles larger than 1 μm; consequently, the selectivity behavior is tentatively attributed to the structure- sensitivity of the propane-forming reaction. This postulate is consistent with the fact that hydrogenolysis reactions (C–C bond breaking) are typically structure sensitive and are affected by different surface sites (*64*). However, rates of C–C bond breaking have been reported to increase as crystallite size decreases (*65*); therefore, this analogy between C–O bond and C–C bond breaking has its limitations. Regardless, the influence of gold on acetone conversion on platinum lends further credence to this argument for structure sensitivity because the selectivity for IPA formation did show a small increase from 1–2 on pure Pt powder to 3 when 0.3 monolayer of Au was dispersed on Pt. Gold forms epitaxial layers on Pt, and on heating an alloy is formed in the near-surface region (*66*). This Au–Pt system has markedly different activity and selectivity for the conversion of *n*-hexane to other hydrocarbons, and Wedler and co-workers found that the isomerization rates goes up as compared with that on Pt while hydrogenolysis and dehydrocyclization rates are reduced exponentially with increasing gold concentration (*67*). This alteration in selectivity and activity has been explained by the more rapid removal of threefold Pt sites than the twofold or on-top sites on Pt (111) surfaces as Au is added. Hence, structure sensitivity is again indicated.

The variation in selectivity behavior in propionaldehyde hydrogenation over Ni/SiO_2 that has been reported by Ueno *et al.* (*68*) is consistent with this picture. The selectivity to propyl alcohol increased smoothly as the Ni crystallite size decreased, with particles smaller than 5 nm giving only the alcohol. They proposed that hydrogenation of the C=C bond proceeds on edge and corner atoms, whereas the face atoms of the crystallite induce hydrogenolysis. Since the supported Pt particles in this study were less than 4 nm, mild hydrogenation proceeded exclusively on these catalysts, whereas the higher coordination sites on Pt powder appear to have initiated C=O bond scission.

(*ii*) Effect of promoters. Unsupported Pt promoted with Fe and Zn salts produces IPA exclusively (*57*), but the chemistry underlying this promotional effect is not understood. A comparison can be made of the TOFs for the formation of IPA in Tables 2 and 4. The TOF values obtained in this study on the typical supported Pt catalysts fall between 0.5×10^{-2} and 2.4×10^{-2} s^{-1}, which is well within the reported range of $0.07–6 \times 10^{-2}$ s^{-1} calculated for supported Pt from previous studies, although the value of 0.06 s^{-1} determined from the kinetic data reported by Golodets *et al.* (*39*) seems unusually high. On an evaporated Pt film Kemball and Stoddart obtained a rate per milligram of Pt deposited which was extrapolated to 303 K using their E_a value of 5 kcal/mol. By use of the film area reported previously by Kemball (*48*), an estimated TOF of 0.14 was obtained; however, this high value is only approximate and may well be a consequence of variations in specific surface area from one film to another. In our results the TOFs for IPA formation on Pt powder and Pt on silica were quite similar.

The apparent activation energies reported by Rositani *et al.* lie between 10 and 11 kcal/mol (*44*), while values on the Pt catalysts in our study fall between 13 and 18 kcal/mol. However, comparison of the apparent activation energies should be treated with caution as these values are extremely sensitive to the deactivation behavior of the catalyst, which may have resulted in the low value of 5.0 kcal/mol reported by Stoddart and Kemball, although this difference could also be due to the low temperatures they used (*49*).

In comparing the TOF values for the 1-μm Pt powder particles with those for 2.0- and 3.7-nm Pt crystallites on a noninteracting SiO_2 support, a range of 0.005 to 0.018 is observed. This relatively small variation that exhibits no trend with crystallite size leads to the conclusion that IPA formation from acetone is structure insensitive. This conclusion is substantiated by the work of Rositani *et al.* (*44*), as indicated in Table 4. The most active catalyst for acetone hydrogenation was the (HTR) Pt/TiO_2 sample, which had an average TOF over 500 times higher than the average TOF obtained on the Pt/SiO_2 catalysts, and 800 times higher than that on the Pt powder. The specific activity is still 10 times higher than that for Pt/SiO_2 catalysts if the comparison is made on a gram of Pt basis at comparable loading and dispersion. This clearly implies the existence of a support effect in acetone hydrogenation.

During this study, Cunningham and Al-Sayyed reported higher acetone hydrogenation activity over a 0.5% Pt/TiO_2 catalyst compared with a Pt/SiO_2 catalyst. Pt surface areas were not measured and conversions, which were typically high (up to 75%), were used to compare activity. Calculating actual rates and adjusting them to our standard conditions using the rate expressions in Table 3 provided the values given in Table 4. The estimated TOFs on their Pt/TiO_2 catalysts are indeed higher than those over the Pt/SiO_2 catalyst, in agreement with our results. However, there are three important points to note. First, the TOF values for the (LTR) Pt/TiO_2 catalysts from the two studies are in excellent agreement, but those for the Pt/SiO_2 catalyst in Ref. (*54*) were substantially lower, thereby leading to an indication of higher activity. The values over the (LTR) Pt/TiO_2 catalyst in either study are not unusually high compared with other supported Pt catalysts, as shown in Table 4. Second, the much higher TOFs and order-of-magnitude increase in specific activity (g Pt) after the HTR step were not observed by Cunningham and Al-Sayyed, and in fact they were usually lower than those for the (LTR) sample. Finally, the assumption in Ref. (*54*) of 2-nm Pt crystallites (fraction exposed of 0.55) in the catalysts with low loading (0.1–1% Pt) may not be accurate as fractions exposed near unity are routinely achieved—this would enhance the activity of the Pt/TiO_2 catalysts relative to the Pt/SiO_2 sample.

B. Kinetic Model for IPA Formation

To postulate a model to explain the rate enhancement, it is useful to examine the mechanistic aspects of acetone hydrogenation on Pt and other metals at temperatures between 300 and 370 K where the reverse reaction, the dehydrogenation of isopropyl alcohol, can be neglected. Previous workers have described the kinetics of mild acetone hydrogenation to IPA by the sequence of elementary steps shown in Table

TABLE 5

Elementary Steps in the Hydrogenation of Acetone to Isopropanol[a]

$H_{2(g)}$	$\overset{K_1}{\rightleftharpoons\!\!\!\!\!\!\bigcirc}$	$2H_{(ad)}$	(I)
$(CH_3)_2CO_{(g)}$	$\overset{K_2}{\rightleftharpoons\!\!\!\!\!\!\bigcirc}$	$(CH_3)_2CO_{(ad)}$	(II)
$(CH_3)_2CO_{(ad)} + H_{(ad)}$	$\overset{K_3}{\rightleftharpoons}$	$(CH_3)_2COH_{(ad)}$	(III)
$(CH_3)_2COH_{(ad)} + H_{(ad)}$	$\overset{K_4}{\rightleftharpoons}$	$(CH_3)_2CHOH_{(ad)}$	(IV)
$(CH_3)_2CHOH_{(ad)}$	$\overset{1/K_5}{\rightleftharpoons\!\!\!\!\!\!\bigcirc}$	$(CH_3)_2CHOH_{(g)}$	(V)

[a] Either step III or step IV has been chosen by investigators as the rate-determining step.

5 (*39–51*). Two Langmuir–Hinshelwood (L-H) models have been proposed that differ only in the assumed rate-determining step (rds). Step III in Table 5 has been reported to be the rds over Pt/γ-Al_2O_3 (*39*), Ni black and Ni/γ-Al_2O_3 (*42*), Raney Ni (*53*), and Co black and Co/γ-Al_2O_3 (*42*), whereas step IV has been chosen as the rds over Pt/Al_2O_3 (*44*) and films of Pt, Pd, Ni, W, Fe, and Au (*50*). Acetone pressure dependencies of -0.7 for Pt and Pd on kieselguhr and -0.5 for Rh on kieselguhr have been reported (*52*).

The rate expressions for the overall reaction can be readily obtained by using the normal assumptions associated with L-H kinetics; that is, steps I, II, and V are in quasi-equilibrium and either step III or IV is the rds. Four different possibilities can be proposed. The first two cases involve the assumption that H_2 and acetone compete for the same adsorption sites, whereas in the last two cases it is postulated that H_2 and acetone adsorb on different sites, with atomic H adsorbing on sites which for steric reasons are not available for acetone adsorption. Golodets and co-workers (*39–43*) and Rositani *et al.* (*44*) have utilized the latter postulate in their kinetic analyses, whereas Kemball and Stoddart (*50*), Lemcoff (*53*), and Simonikova *et al.* (*51, 52*) have not. An analysis of the four derived rate expressions show that only one case produces a rate expression that simultaneously allows H_2 partial pressure dependencies greater than $\frac{1}{2}$ and acetone pressure dependencies between 0 and -1 (*69*). This model assumes that step IV is the rds and that H atoms and acetone molecules (A) compete for the same sites. The rate expression is

$$r = k_4 K_1 K_2 K_3 P_A P_{H_2} / (1 + K_1^{1/2} P_{H_2}^{1/2} + K_2 P_A + K_1^{1/2} K_2 K_3 P_A P_{H_2}^{1/2})^2, \tag{1}$$

where K_1, K_2, and K_3 are the equilibrium constants for steps I, II, and III, respectively. This equation can give negative dependencies on acetone and zero to first-order dependencies on H_2; for example, as an approximation, if acetone is the most abundant species adsorbed on the surface, this expression simplifies to

$$r = \frac{k P_A P_{H_2}}{(1 + K_2 P_A)^2}, \tag{2}$$

which itself comes close to providing the partial pressure dependencies reported in Table 1. The inhibitive influence of IPA is not included for two reasons. First, under the conditions in this study acetone conversions were low, hence IPA concentrations were also. Second, if the acetone conversion versus acetone pressure obtained by Cunningham and Al-Sayyed are converted to *rates*, then the rate increases with acetone pressure even up to very high conversions, indicating IPA has no significant inhibiting effect, as noted by these authors.

There does not appear to be a general consensus on identification of the rds over group VIII metals, as indicated previously. Regardless of the uncertainty regarding the rds (if indeed there is one that is universal), it appears to be quite clear that on all the group VIII metals acetone hydrogenation can be described by the same sequence of elementary steps and that Pt is one of the two most active metals. To gain additional insight into the energetics associated with the different steps of this reaction and to see if one of the models might be preferred, the bond-order conservation approach developed by Shustorovich (*70*) was applied. Two questions were considered:

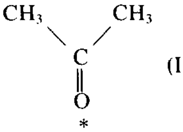
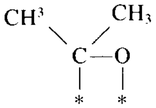
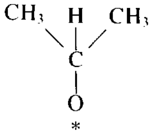
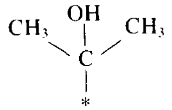
(i) Which H atom addition is favored—bonding to the C atom to form an isopropoxide species or to the O atom to form the half-hydrogenated 2-hydroxy-2-propyl species?

(ii) Which elementary surface step (III or IV) is the more likely rds within a Langmuir–Hinshelwood framework?

Spectroscopic studies by different groups (*71–81*) have indicated that various forms of adsorbed acetone can occur on transition metal surfaces, as shown in Table 6. Species I is assumed to be weakly coordinated to the metal surface through donation of the lone-pair electrons of the oxygen, while species II forms two σ bonds with two surface sites. A third species, π-bonded to the surface, has also been proposed. If the reaction is presumed to occur in a manner analogous to the Horiuti–Polanyi mechanism for ethylene hydrogenation, i.e., the stepwise addition of H atoms to a di-σ-bonded C_2H_4 species, then species II would be expected; however, species I has also

TABLE 6

Calculated Heats of Adsorption for Species on a Pt(111) Surface[a]

Species	Radical A	Radical B	D_{AB}	Q_{OA}	Q_{OB}	Q_A	Q_{AB} (Q_{ad})	Ref.
$H_{(ad)}$	H	—	—	37	—	61	—	(*70*)
$C_{(ad)}$	C	—	—	90	—	150	—	(*70*)
$O_{(ad)}$	O	—	—	51	—	85	—	(*70*)
 (I)	O	$(CH_3)_2C$	176[b]	51	—	—	12	(*72, 73*)
 (II)	$C(CH_3)_2$	O	176[b]	21	51	—	16	—
	O	$CH(CH_3)_2$	90[c]	51	—	-	18	—
	C	$(CH_3)_2OH$	281[d]	90	—	—	22	—

[a] An adsorption site is represented by an asterisk. All energies are in kcal/mol. D_{AB} = bond dissociation energy of species AB, Q_{OA} = Pt–A bond energy, Q_{OB} = Pt–B bond energy, Q_A = atomic heat of adsorption, Q_{AB} = Q_{ad} = molecular heat of adsorption.

[b] From Ref. (*130*).

[c] Assumed to be 90 kcal/mol since C–O bond energies typically range from 81 to 106 kcal/mol in alcohols and acids (*130*).

[d] $D_{AB} = 2D(C–C) + D(C–O) = 2 \times 100 + 81 = 281$ kcal/mol. Bond energy of C–C from Ref. (*131*) and C–O from Ref. (*130*).

been proposed as a reaction intermediate (*71*). Low-temperature UHV studies of acetone adsorbed on the Pt(111) surface have found that species I predominates, but it is more weakly adsorbed than species II which remains on the surface at higher temperatures, is more reactive, and decomposes in the absence of hydrogen (*73*). Consequently, attention will be focused on species I and II (*71*).

By utilizing the bond-order conservation (BOC) method of Shustorovich (*70*), the heats of adsorption of species I and II in the zero-coverage limit were calculated to be 12 and 16 kcal/mol, respectively (*69*). Reported values for species I on the Pt(111) surface are near 11 kcal/mol (*71–73*), which agree well with the value of 12 kcal/mol obtained by the BOC approach. The estimated heats of adsorption of the various species that can form during acetone hydrogenation were calculated (*69*), based on the bond strengths utilized by Shustorovich (*70*) and the Q_{ad} value of 11 kcal/mol for IPA on Pt(111) reported by Rendulic and Sexton (*75*), and are listed in Table 6. The similarity between the surface bond strengths of these species and heats of adsorption for H_2 on Pt (*27*) provides support for the competitive adsorption model discussed previously. After these values were obtained, the activation energy barriers and the enthalpy changes for the various elementary steps were calculated subject to the assumptions of the BOC approach (*70*), and the results are shown in Figs. 5 and 6.

Conclusions drawn from these calculations must be considered as tentative, but they are informative, nonetheless. The results indicate the following: (1) The di-σ-bonded species is more strongly adsorbed than the species sharing its lone-pair electrons with the surface, in agreement with the UHV results of Avery (*73*), but a choice between the two cannot be made unequivocably. (2) The difference in the surface bond strength of the species formed by the addition of H to the C atom first and the species formed by addition of H to the O atom first is not large, but formation of the –OH group first appears to produce a more strongly bound surface intermediate by 4 kcal/mol. IR spectroscopic studies have provided evidence for isopropoxide species formed from acetone on Ni and Co, but the –OH bonds expected from the 2-hydroxy-2-propyl species have not been reported (*78–80*). (3) Although H addition to the oxygen first may be slightly favored, a preferred choice of the reaction pathway is not apparent because of the lower activation barrier associated with the isopropoxide intermediate and the relatively small energy differences. (4) Most important of all, perhaps, is that all reaction pathways show that addition of the second H atom involves a higher activation barrier than addition of the first, consistent with the proposal that step IV is the rate-determining step.

This theoretical approach is therefore in agreement with the conclusion based on the pressure dependencies associated with the reaction kinetics in this study that step IV in the L-H sequence is the rds during acetone hydrogenation to IPA. From their IR and TPD results, Miyata *et al.* have proposed that coordinated acetone (Species I) is the reactive species for IPA formation (*81*), while Avery and co-workers have shown that concentrations of species I are much higher on a Pt(111) surface but that the di-σ-bonded intermediate is more reactive, dissociating to produce adsorbed CO and hydrogenation fragments (*72, 73*). Restricting its application to unsupported Pt or Pt/SiO_2 catalysts, a pathway consistent with experimental results and theoretical calculations would be one involving hydrogenation of species II first to isopropoxide and then addition of a second H atom to give IPA, i.e., the lower path in Fig. 5. Although IR spectra have resulted in assignments for isopropoxide species on Co and Ni (*79, 80*), the possibility of a 2-hydroxy-2-propyl intermediate on Pt is suggested by its somewhat stronger surface

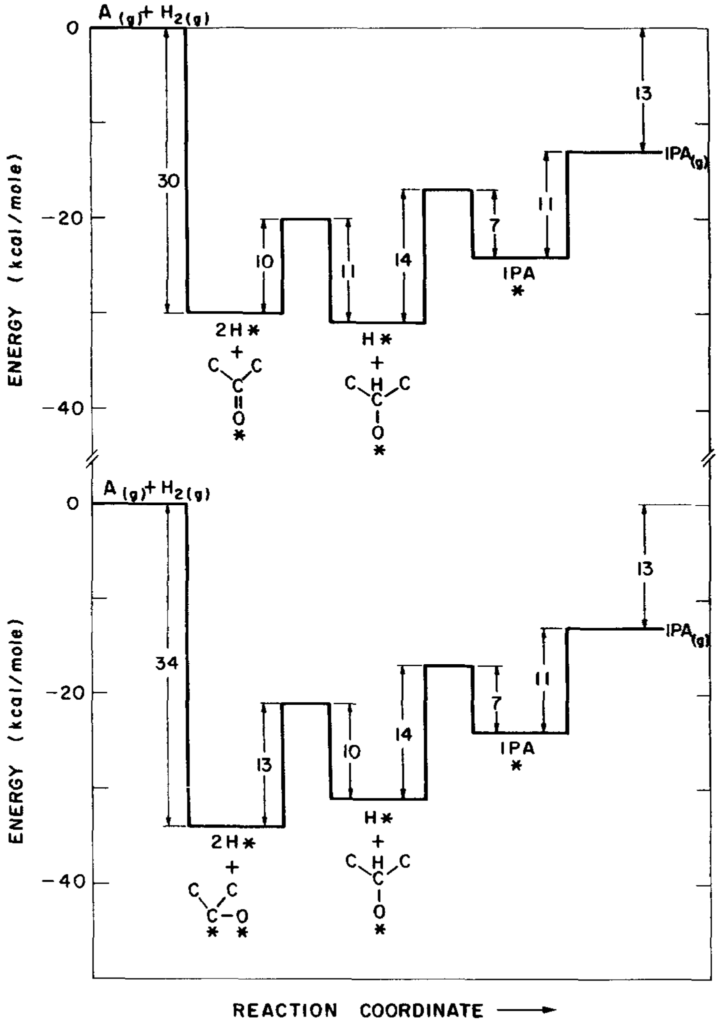


FIG. 5. Thermochemical kinetic profile of the elementary steps associated with the formation of IPA from acetone (A) via addition of a hydrogen atom to the C atom first: Upper figure assumes A is bonded through the lone pair on the oxygen (species I in Table 6); lower figure assumes A is adsorbed in a di-σ-bonded form (species II in Table 6).

bond and the excellent agreement in actual and calculated activation energies, which admittedly may be fortuitous.

It has been found in this study that (HTR) Pt/TiO_2 catalysts are at least 10 times more active on a gram of Pt basis than Pt/SiO_2 catalysts of similar dispersion and over 500 times more active on a turnover frequency basis. Similar behavior has been observed for CO hydrogenation over Pt/TiO_2 systems (*9, 10*), and the general model proposed to explain the higher activity in that reaction (*82, 83*) will be applied to acetone hydrogenation to test the hypothesis that similar surface sites are responsible for each rate enhancement.

A number of phenomena have been associated with "SMSI" behavior brought about in metal/TiO_2 systems by an HTR step, such as (i) electron transfer from the support to the metal (*84–92*); (ii) morphological changes in the metal particles (*93*);

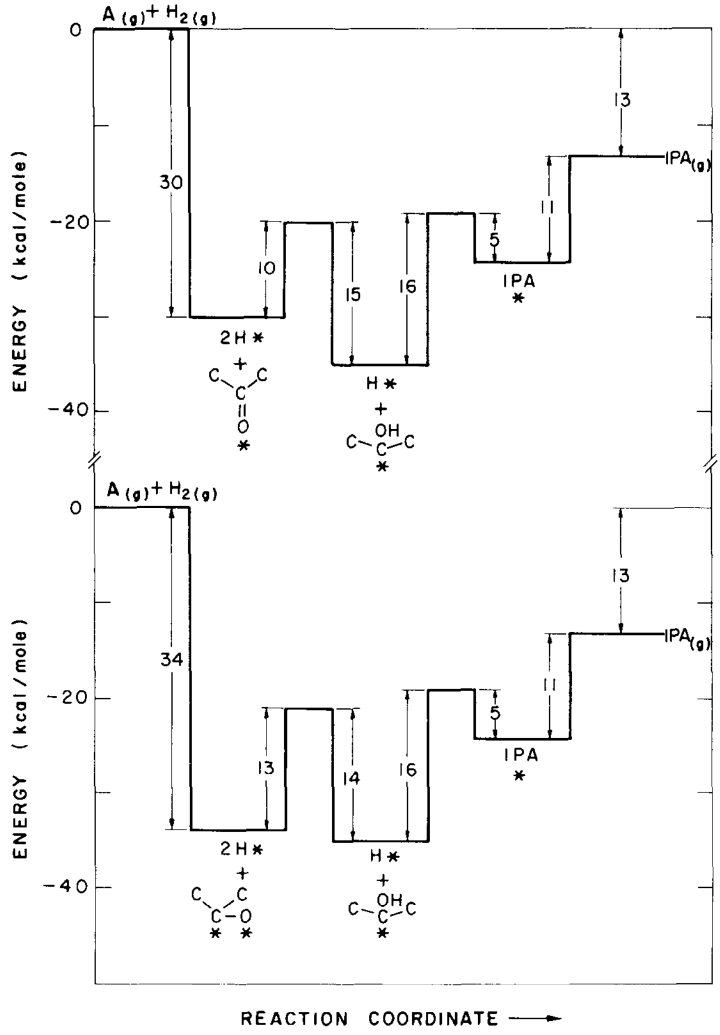


FIG. 6. Thermochemical kinetic profile of the elementary steps associated with the formation of IPA from acetone (A) via addition of a hydrogen atom to the O atom first: Upper figure assumes A is bonded through the lone pair on the oxygen (species I in Table 6); lower figure assumes A is adsorbed in a di-σ-bonded form (species II in Table 6).

(iii) decoration of the metal surface by TiO_x species (*94–112*); (iv) formation of intermetallic compounds (*113–118*); and (v) hydrogen spillover (*119–125*). These factors will be assessed for their capability in enhancing acetone hydrogenation.

It has been argued convincingly by Ponec that no charge transfer can occur from titania to significantly alter the bulk electronic properties of Pt crystallites, but localized charge transfer between surface Pt atoms and the support is possible. In a simple context this would increase the occupancy of electrons in the *d* band of Pt and make it more similar to Au; however, Au has a very low hydrogenation activity (see Table 4). Since Pt appears to be the most active transition metal catalyst for acetone hydrogenation, it is unlikely that any change in its electronic properties would increase its catalytic activity. This would also argue against any significant effect due to the formation of intermetallic compounds.

Morphological changes induced by HTR might be expected to change the distribution of Pt surface sites; however, this should not enhance the rate because hydrogenation of acetone to IPA appears to be a structure-insensitive reaction, a conclusion that is further substantiated by the small change in TOF that occurs on partial coverage of the Pt surface with gold (Table 2).

To explain the higher activity and TOF values on (HTR) Pt/TiO_2 catalysts, we propose the same general model as that previously proposed for CO hydrogenation over Pt (*10, 82, 83*). We suggest that the di-σ-bonded species is the important reaction intermediate but that its concentration on normal Pt surfaces is very low, relative to species I, a suggestion supported by the work of Avery (*73*). Consequently, the creation of active sites at the Pt–titania interface to form species II would markedly enhance the rate. Such a site could allow activation of the oxygen atom via its coordination with an interstitial Ti^{3+} cation or an oxygen vacancy in the lattice. The interaction of acetone with Lewis acid sites on alumina has already been reported by Golodets and co-workers (*41*), and poisoning experiments by Cunningham and Al-Sayyed have indicated that acid sites on the titania surface are involved (*54*). The postulate that only those sites in the interfacial region are important is supported by the result that the TOF is the same for physical mixtures of Pt + TiO_2 and for Pt powder, as shown in Table 2.

This is the underlying commonality of the two models, i.e., the interface sites that interact with the oxygen end of an adsorbed CO molecule can also promote activation of the carbonyl bond in acetone by interaction of the oxygen atom with sites on the titania. This proposal is consistent with the experimental results showing that there is a large increase in the preexponential factor, and this model does not require a drastic change in the partial pressure dependencies, or a significant change in the entropy factor, or a change in the rds for acetone hydrogenation; it requires only that a ready source of activated hydrogen be available at all sites. An increase in the surface concentration of species II, and hence the half-hydrogenated intermediate, due to these interfacial sites could produce the rate enhancement over (HTR) Pt/TiO_2, and the presence of isopropoxide species on reduced TiO_2 surfaces has already been reported (*126, 127*). Consequently, the applicability of the BOC calculations and the steps represented in Figs. 5 and 6 to these Pt/TiO_2 catalysts is quite possible. This proposal is also consistent with the observation that Pt/TiO_2 is an active catalyst for the photocatalytic dehydrogenation of IPA where the adsorption and the dissociation of IPA are believed to proceed on the titania surface, with Pt crystallites serving as a porthole for H_2 desorption (*128*). Finally, this model is consistent with both the finding of Lemcoff that rates of liquid-phase acetone hydrogenation are highest when polar solvents such as water are used (*53*) and the work of Vanselow and Mundschau which showed that migration of Ti suboxides onto metallic surfaces created islands with a high work function (*129*). Such islands could tend to provide a surface analog of the liquid-phase polar solvent and thereby enhance the rate, perhaps by favoring the formation of the isopropoxide intermediate.

SUMMARY

The most significant result of this study is that turnover frequencies for acetone hydrogenation to isopropyl alcohol on Pt can be enhanced over 500-fold, compared with Pt powder or Pt/SiO_2, by an HTR pretreatment for Pt/TiO_2 catalysts. Even on a gram Pt basis at similar Pt dispersion, activities are 10 times greater over (HTR) Pt/TiO_2 compared with Pt/SiO_2. Average activation energies are similar for all catalysts; consequently, the activity increase is associated with the preexponential factor. The least active catalysts are

unsupported Pt and Pt on SiO_2; the use of Al_2O_3 produces a small increase in the TOF, which can be further enhanced by the use of TiO_2, even after an LTR step. The TOF for IPA formation shows only a small variation and no trend with Pt crystallite size, and this reaction appears to be structure insensitive. These factors demonstrate a clear support effect and a catalytic behavior pattern remarkably similar to that for methanation over Pt (*9*, *10*).

The observed partial pressure dependencies are consistent only with one Langmuir–Hinshelwood model—that which assumes competitive adsorption of hydrogen and acetone on the same sites and addition of the second H atom to the half-hydrogenated species as the rate-determining step. This kinetic model is not only consistent with previous TPD, IR, and EELS results, but is also substantiated by theoretical calculations based on the bond-order conservation method of Shustorovich (*70*). The higher activity over the Pt/TiO_2 catalysts is associated primarily with the preexponential factor and is attributed to an increase in the number of active sites in the Pt–titania interface region. The nature of these active sites is not exactly known, but it is anticipated that they are electron-deficient sites such as oxygen vacancies or cationic Ti Lewis acids in close proximity to Pt. This would allow coordination of the lone pair of electrons on the oxygen atom in acetone and would activate the carbonyl bond in the presence of atomic hydrogen provided by the Pt surface. Consequently, the metal-support effect which enhances CO hydrogenation does indeed seem to be a more general phenomenon which has the potential to increase rates of hydrogenation of other carbonyl bonds. Future IR studies of this reaction over supported Pt are planned to test this model.

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