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Gold dispersed on TiO_2 and SiO_2: adsorption properties and catalytic behavior in hydrogenation reactions

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Titania-supported Au catalysts were given both low temperature reduction and high temperature reduction at 473 and 773 K, respectively, and their adsorption and catalytic properties were compared to identically pretreated Pt/TiO_2 catalysts and pure TiO_2 samples as well as Au/SiO_2 catalysts. This was done to determine whether a reaction model proposed for methanol synthesis over metals dispersed on Zn, Sr and Th oxides could also explain the high activities observed in hydrogenation reactions over MSI (Metal-Support Interaction) catalysts such as Pt/TiO_2. This model invokes O vacancies on the oxide support surface, formed by electron transfer from the oxide to the metal across Schottky junctions established at the metal-support interface, as the active sites in this reaction. The similar work functions of Pt and Au should establish similar vacancy concentrations, and O_2 chemisorption indicated their presence. However, these Au catalysts were completely inactive for CO and acetone hydrogenation, and ethylene hydrogenation rates were lower on the supported Au catalysts than on the supports alone. Consequently, this model cannot explain the high rate of the two former reactions over TiO_2-supported Pt although it does not contradict models invoking special *interfacial* sites.

Keywords: Au/TiO_2 catalysts; Au/SiO_2 catalysts; O_2 adsorption on Au; metal-support interactions; active sites on oxide supports; ethylene hydrogenation on supported Au

1. Introduction

The concept of metal-support interactions (MSI) was vigorously renewed in 1978 by Tauster et al. when they reported that H_2 and CO chemisorption on TiO_2-supported noble metals could be reduced to near zero after reduction at 773 K but chemisorption capacity was restored by oxygen exposure [1]. This was a reversible phenomenon that was found to also occur with other reducible transition metal oxides [2], and it has acquired the initialism of SMSI (from Strong Metal-Support Interactions). Shortly thereafter the first reports were published of enhanced catalytic activity and altered selectivity in CO hydrogenation over TiO_2-supported metals [3–6]. Numerous investigations followed which verified these enhanced activities, established that rates in other hydrogenation reactions were not increased, and found that activities in structure-sensitive reactions were, in fact, markedly decreased [7–10 and ref. therein]. Site blockage by the migration of TiO_x species onto the metal surface has been clearly established as the predominant reason for decreased chemisorption capacity [8–10], and this same explanation can account for the lower rates in typical structure-sensitive and structure-insensitive reactions [10]. However, the promoting effect on the hydrogenation of CO and carbonyl bonds [6,11,12] has not been unequivocally explained although the two most prevalent hypotheses invoke either the formation of unique active sites in the metal-support interfacial region [13,14] or a localized promotor effect by the oxide support on the surface metal atoms [9,15].

Although a number of possibilities have been proposed to explain the catalytic behavior of these MSI systems [8–10 and references therein], one different model was recently invoked by Frost which pertained to methanol synthesis [16], but it could also be considered as a possible explanation of the higher activity of TiO_2-supported metals for the hydrogenation of C=O bonds. It proposes that a Schottky junction is established at the metal-oxide interface which results in an increase in the concentration of ionized oxygen vacancies on the oxide surface and that these defect sites are responsible for the catalytic activity [16]. This picture has many similarities to a concept formulated earlier by Schwab and coworkers [17]. The applicability of this model to these MSI systems can be tested by comparing TiO_2-supported Au and Pt because Pt/TiO_2 catalysts have exhibited enhanced specific activity for CO and acetone hydrogenation whereas Au is known to be very inactive [18,19]; however, these two metals have similar work functions and should therefore establish similar defect concentrations after identical reduction pretreatments. Consequently, any enhanced activity in the Au/TiO_x system would have to be attributed to these active sites on the titania surface. This paper describes chemisorption and kinetic results with Au/SiO_2 and Au/TiO_2 which show very clearly that this model does not explain the catalytic behavior of TiO_2-supported metals.

2. Experimental

The supported gold catalysts were prepared by an incipient wetness method using $AuCl_3$ (Johnson-Matthey, $99.99^{+}\%$), SiO_2 (Davison, grade 57, 60–100 mesh powder), and TiO_2 (Degussa, P25) after both support materials were calcined in dry air at 773 K for two hours before impregnation [20]. Afterward they were dried at 393 K overnight and stored in a desiccator. Actual gold loadings were measured by DC Plasma Emission Spectroscopy after digesting the catalysts in aqua regia. Before either chemisorption measurements or kinetic runs the Au/SiO_2 sample was reduced under flowing H_2 (1 atm) for 1 h at 723 K while the low temperature reduced (LTR) Au/TiO_2 samples were reduced 2 h at 473 K and the high temperature reduced (HTR) Au/TiO_2 samples were reduced 1 h at 773 K under flowing H_2 (1 atm). Details are given elsewhere [21]. X-ray diffraction measurements were conducted using a Rigaku 4011B diffractometer.

The stainless steel adsorption system (base pressure 5×10^{-7} Torr) has been described previously [22]. Adsorption isotherms for hydrogen (MG Industries, UHP grade, 99.999%) and oxygen (MG Industries, scientific grade, 99.999%) were recorded between 1 and 30 Torr at either 300 or 473 K while isotherms for CO (Matheson 99.99%) were obtained between 20 and 120 Torr at 300 K. Each uptake datum point was taken after no change in the pressure reading was observable during a 5 min period with 1 g catalyst, i.e., the adsorption rate was less than 0.0002 μmole/min/g cat; consequently, the exposure time at each pressure was typically about 1 hour. Two consecutive isotherms were recorded for every sample with a 30 min evacuation in between. Adsorption isobars were also obtained for oxygen at 9 ± 1 Torr.

The reactor system used for acetone (Fisher, 99.5^+%) hydrogenation has been described previously [11], but it has been upgraded by the installation of a new H–P gas chromatograph. The stainless steel reactor used for CO (Matheson, 99.99%) and ethylene (Linde, CP grade, 99.5^+%) hydrogenation has also been described elsewhere [22]. The CO was passed first through a heated trap to decompose any metal carbonyls then through an Oxytrap (Alltech Asso.) while the C_2H_4 was passed through a water trap (Supelco) followed by an Oxytrap. The acetone was stored under N_2 in a glovebag and purified of dissolved gases as described before [11].

3. Results

H_2 ADSORPTION

As observed previously, the titania darkened after the HTR step. No measurable H_2 adsorption was observed on either pure support or on supported Au, except for the Au/TiO_2 (LTR) sample at 473 K as shown in fig. 1. The amount of adsorbed hydrogen on Au/TiO_2 (LTR) was low but significant, and it was greater than any possible artifact due to impurities. The isotherms show that hydrogen adsorption is completely reversible on Au/TiO_2 (LTR) and is activated because the uptake is greater at 473 K than at 300 K.

CO ADSORPTION

CO adsorbs at 300 K on all three supported Au systems, as demonstrated in fig. 2, but the titania support appears to be involved because Au/SiO_2, which

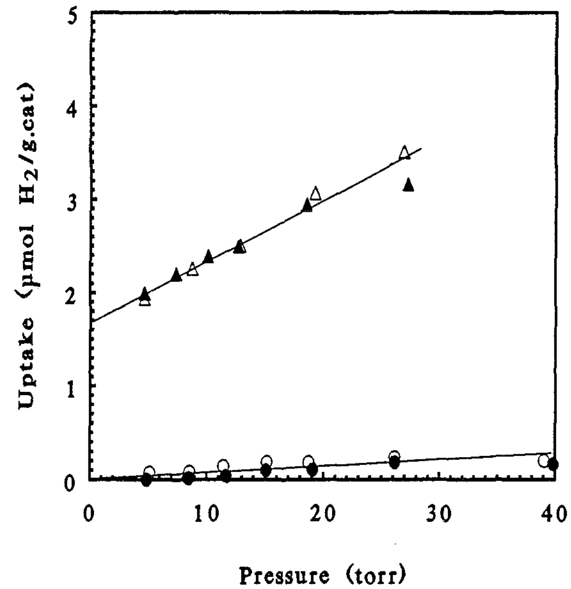


Fig. 1. Hydrogen adsorption on 2.3% Au/TiO_2 (LTR): $T = 25°C$: total uptake (●), reversible uptake (○); $T = 200°C$: total uptake (▲), reversible uptake (△).

exhibited Henry's Law behavior, had a much lower uptake than the Au/TiO_2 samples. The CO uptakes on Au/TiO_2 (HTR) were slightly lower than on pure TiO_2 after an HTR treatment whereas the uptakes on Au/TiO_2 (LTR) were

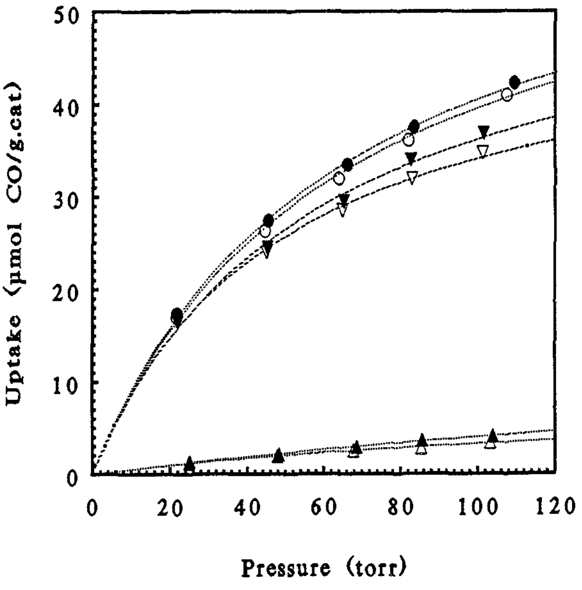


Fig. 2. CO adsorption on supported gold at 25°C: 2.0% Au/TiO_2 (LTR) – total (●), reversible (○); 2.0% Au/TiO_2 (HTR) – total (▼), reversible (▽); 1.8% Au/SiO_2 – total (▲), reversible (△). Lines indicate the fit obtained with a Langmuir isotherm.

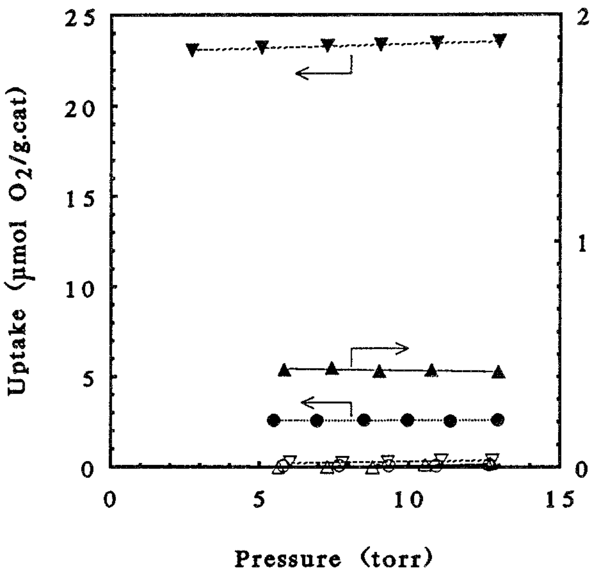


Fig. 3. O_2 adsorption on supported gold at 200°C: 2.0% Au/TiO_2 (HTR) – total (▼), reversible (▽); 2.0% Au/TiO_2 (LTR) – total (●), reversible (○); 1.8% Au/SiO_2 – total (▲), reversible (△).

the same as on TiO_2 [20], and all these uptakes fit the Langmuir adsorption isotherm very well. A small amount of irreversible adsorption is indicated after the highest pressure exposure, and from the saturation coverages obtained with the fitted parameters it corresponds to 2 μmole CO/g cat on the LTR sample and 6 μmole CO/g cat on the HTR sample [23].

O_2 ADSORPTION

The results for oxygen were more interesting because they represent a probe for O vacancies as well as Au surface atoms. From isotherms at 473 K such as those in fig. 3, irreversible adsorption was found to occur on supported Au catalysts. These values are given in table 1. On the pure TiO_2 support after an HTR pretreatment, the oxygen uptake was significant and very similar to that on the Au/TiO_2 (HTR) catalyst whereas it was much lower on TiO_2 alone after the LTR step but still higher than the O_2 uptake on the Au/TiO_2 (LTR) sample. After each of the O_2 isotherms, a hydrogen titration isotherm was obtained at 473 K because oxygen chemisorbed on Au is removable by reaction with H_2 [24]. The ratios of titrated H atoms to chemisorbed O atoms are also given in table 1. Isobars for oxygen adsorption at 9 Torr were determined between 423 and 673 K for Au/SiO_2 and Au/TiO_2 (LTR) as well as for the corresponding pure support, and they are shown in figs. 4 and 5. The uptakes in each isobar were first measured at the lowest temperature, then determined at

Table 1
Oxygen and hydrogen uptakes (μmole/g cat) at 473 K on supported gold catalysts and the supports alone

Catalyst	Irreversible O_2 adsorption [a]	$[O_{ad}/Au]$	H_2 titration [a]	$[H_a/O_a]$
1.8% Au/SiO_2 (I)	0.37 ± 0.03	0.008	0.42 ± 0.03	1.1
1.8% Au/SiO_2 (II)	0.44 ± 0.1	0.010	0.46 ± 04	1.0
	0.51 ± 0.02	0.012	0.45 ± 0.01	0.8
2.0% Au/TiO_2 (LTR)	2.57 ± 0.03	0.050	4.84 ± 0.7	1.9
2.3% Au/TiO_2 (LTR)	1.51 ± 0.08	0.026	1.4 [b]	0.9
2.0% Au/TiO_2 (HTR)	23.0 ± 0.02	0.075	7.65 ± 0.27	0.33
2.3% Au/TiO_2 (HTR)	82 [c]	0.25	29.0 [d]	0.35
SiO_2	0 ± 0.03		0	–
TiO_2 (LTR)	4.57 ± 0.07		0	–
TiO_2 (HTR)	23.1 ± 0.06		0	–

[a] With 95% confidence limits.

[b] One data point titration, not two isotherms as others.

[c] Uptake after 12 h.

[d] Uptakes obtained after 30 min of no observable change of pressure.

successively higher temperatures, and finally measured as the temperature decreased to the initial value. At the completion of each isobar sequence, a H_2 titration was conducted.

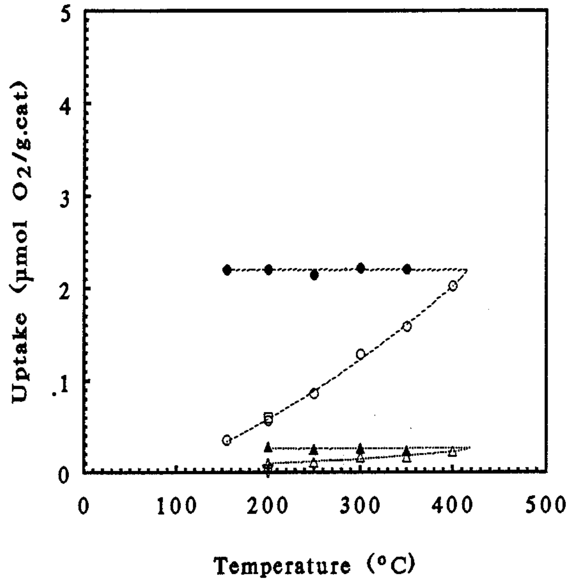
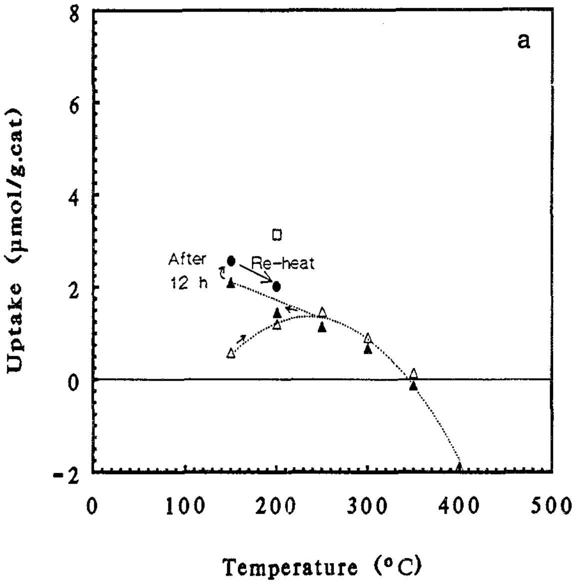


Fig. 4. Oxygen adsorption isobars for 1.8% Au/SiO_2 and pure SiO_2 at 9 ± 1 Torr: 1.8% Au/SiO_2 – ascending temp. (○), descending temp. (●), H_2 titration value (□); SiO_2 – ascending temp. (△), descending temp. (▲), H_2 titration value (▽).



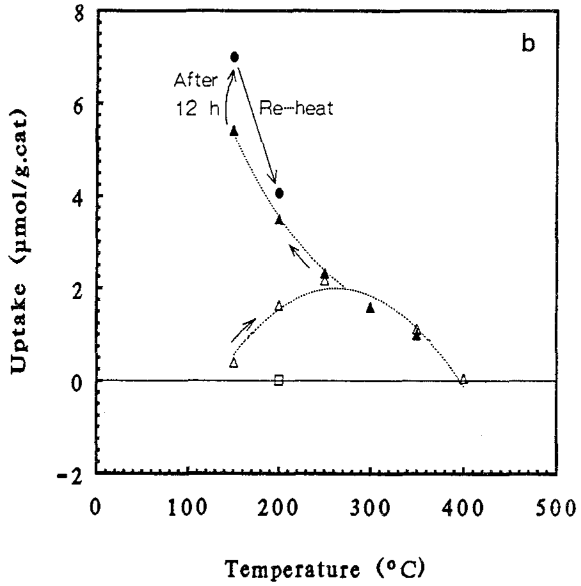


Fig. 5a. Oxygen adsorption isobars for Au/TiO_2 (LTR) at 9±1 Torr: initial heating (△), cooling (▲), reheating (●), H_2 titration value (□).

Fig. 5b. Oxygen adsorption isobars for TiO_2 (LTR) at 9±1 Torr: initial heating (△), cooling (▲), reheating (●), H_2 titration value (□).

CATALYTIC BEHAVIOR

All Au/SiO_2 and Au/TiO_2 samples were exposed to a syngas feed stream at 1 atm (H_2/CO = 3), and they were inactive at temperatures between 523 and

Table 2
Kinetic parameters for ethylene hydrogenation

Catalyst	E_a (kcal/mol)	Activity at 453 K			Ref.
		(μmol C_2H_4/g cat·s	(μmol/g Au·s)	TOF (s^{-1})	
1.8% Au/SiO_2	9.1±2.6	0.068	3.8	3.9×10^{-2} [e]	
SiO_2	8.1±4.9	0.086	–		
2.3% Au/TiO_2 (LTR)	14.3±7.3	0.962	41.8	32×10^{-2} [e]	
TiO_2 (LTR)	12.4±2.4	2.100	–		
2.3% Au/TiO_2 (HTR)	6.7±3.8	0.036	1.6	6×10^{-4} [f]	
TiO_2 (HTR)	8.4±5.6	0.041	–		
0.05% Au/SiO_2	–	0.09(ave)	180	3.5×10^{-2} [g]	[30]
5% Au/SiO_2	–	0.23	4.7	9.1×10^{-4} [g]	[30]
Au film	–	2.6×10^{-3}	–	1.3×10^{-4} [h]	[29]
ZrO_2 [a]	4.3±0.2	1.993	–		[36]
La_2O_3 [b]	8.6±0.5	18831	–		[37]
ZnO [c]	7.6±0.7	3.590	–		[38]
SiO_2 [d]	6.0–12.0	–	–		[39]
Pt(111)	6.0	–	–		[58]

[a] Based on 70 m^2/g ZrO_2.
[b] Based on 29 $m^2/_2$g La_2O_3.
[c] Based on 10 m^2/g ZnO.
[d] Activated by hydrogen-spillover at 673–703 K.
[e] Based on O_2 uptake assuming $O_{ad}/Au_s = \frac{1}{2}$.
[f] Based on H_2 titration assuming $O_{ad}/Au_s = \frac{1}{2}$.
[g] Assuming 100% dispersion.
[h] Extrapolated using $E_{act} = 8$ kcal/mole.

723 K. They were also found to be inactive for acetone hydrogenation to isopropanol at 1 atm (H_2/acetone = 3.06) over a temperature range of 303 to 673 K. Only for ethylene hydrogenation was activity observed, as listed in table 2; however, in every case the Au catalyst was *less* active than the corresponding pure support over the temperature range studied (313 to 383 K). Kinetic results from other studies are also given in this table for comparison.

4. Discussion

Among the various models proposed to explain the catalytic activity patterns of titania-supported metals, the recent proposal of Frost [16] must be considered. Although it was applied to methanol synthesis catalysts utilizing Zn, Zr, and Th oxides, the general principle involved is applicable to "SMSI" catalysts; i.e., a Schottky junction exists at the metal-support interface which allows electron transfer to occur from the conduction band of the oxide to the metal thereby increasing the concentration of oxygen vacancies at the oxide surface, and these vacancies constitute active sites for the hydrogenation of CO (or CO_2). The unique feature of this model is that the activity is associated *only* with the oxygen vacancies residing at the oxide surface, i.e., the TiO_x support, and not with the metal, because Herrmann and coworkers have proposed a similar band-bending picture for electron transfer between crystallites (Pt, Rh, Ni) and TiO_2 [25,26]. Oxygen vacancies *adjacent to Group VIII metal atoms* have been proposed as active sites at the metal-support interface [13,14], and evidence for methoxy species on the support, which are more reactive with hydrogen to form CH_4 than CO chemisorbed on Pt, has been provided recently [27,28]. Because of the need for activated hydrogen, the reactive methoxy species contributing to the *steady-state* hydrogenation rate are relegated to the interfacial region.

This role for oxygen vacancies, which would be associated with the entire support surface, can be tested by comparing the adsorption and catalytic behavior of Au/TiO_2 to that of Pt/TiO_2 as gold has extremely low activity for hydrogenation reactions compared to Pt [18,19,29,30]. Thus, if oxygen vacancies alone are responsible for the enhanced activities for CO and acetone hydrogenation over Pt/TiO_2 catalysts [11,12], similar increases in O vacancies should occur for the Au/TiO_2 systems because the work function of Au (5.1–5.5 eV) is similar to that of Pt (5.7 eV) [31,32]. A study of $Pt-TiO_2$ and $Au-TiO_2$ diodes has shown that Schottky junctions are indeed established in both systems and the two systems are sensitive to H_2 in air [33]. Also, Ocal and Ferrer have observed diffusion of both Pt and Au atoms through thin films of TiO_x [34]. Finally, a reduction temperature of 773 K is sufficient to partially reduce TiO_2 by the removal of lattice oxygen [35]. Consequently, we would expect comparable metal-TiO_x interfaces and overlayers to be established with these two metals. The experiments discussed in this paper were designed to test the hypothesis that O vacancies alone are responsible for the enhanced rates of carbonyl bond hydrogenation. The complete absence of activity for either CO or acetone hydrogenation is overwhelming evidence against the proposal that defect sites, i.e., O vacancies, at the TiO_x surface by themselves are responsible for the rate enhancements obtained with Pt/TiO_2 compared to typical Pt catalysts. These activity increases can be very large; for example, increases of over 100-fold in the turnover frequencies for both CO and acetone hydrogenation occur, and activities per g Pt can increase 10-fold [6,11,14]. However, the present results with Au are not in conflict with the model relegating active centers to the *metal-support interface region* where the appropriate metal (i.e., Pt) may facilitate adsorption of the reactants and provide activated hydrogen.

When these Au catalysts were used for a typical structive insensitive reaction such as ethylene hydrogenation, both the Au/SiO_2 and the Au/TiO_2 (LTR) samples had *lower* activities than the comparable SiO_2 or TiO_2 (LTR) support alone whereas the Au/TiO_2 (HTR) and TiO_2 (HTR) samples had comparable activity, as listed in table 2. Both Au/TiO_2 (LTR) and TiO_2 (LTR) had significantly higher activities and activation energies than the other four catalysts, which had values closer to those reported for this reaction on pure oxides [36–39], as given in table 2. These results clearly demonstrate that no active sites for C_2H_4 hydrogenation are created upon the addition of gold and, in fact, the gold (or residual chloride) decreases the rate compared to the support alone. Both SiO_2 and the 1.8% Au/SiO_2 catalyst have activities similar to those reported previously for SiO_2-supported Au [30]; however, the intrinsic activities of these oxides, including SiO_2 [39], make it difficult to ascertain the contribution from Au. In fact, our results imply either that Au may be deactivating these sites on the oxide support giving lower rates per gram due to the inertness of Au or that residual chloride may be blocking sites on the support. However, chloride can be stripped from silica by hydrogen relatively easily and the reduction at 723 K should have removed essentially all of the chloride [40]. It is more strongly bound on titania surfaces but it begins to be removed by hydrogen near 473 K [41], thus the 1-h reduction at 773 K would have removed most of the chloride from the TiO_2 support. It should also be mentioned that these Au catalysts do exhibit catalytic activity in other reactions and a very high activity for CO oxidation at room temperature occurs with the Au/TiO_2 (HTR) sample or an Ag/TiO_2 (LTR) catalyst prepared from a calcined Au/TiO_2 (HTR) sample [42].

In this study no H_2 adsorption at either 298 or 473 K was observed on any catalyst except the 2.3% Au/TiO_2 (LTR) sample at 473 K, as shown in fig. 1, but the amount was small and completely reversible. It has been reported that adsorption of molecular H_2 does not occur on Au at temperatures up to 300 K although adsorption of H atoms from the gas phase is possible [43–45]; however, dissociative H_2 adsorption on a nonannealed Au film deposited at 78 K has recently been reported [46]. The increase in adsorption at 473 K compared to 298 K shows that an activated adsorption process, which is very likely associated with H_2 dissociation, exists for this catalyst, but from these results alone it cannot be unequivocally stated that adsorption occurs only on the Au surface. This may be possible because of the ability of hydrogen to titrate oxygen adsorbed on gold, but slow H_2 uptakes at 300 K on TiO_2-supported metals have been reported and associated with the titania surface [47].

The CO adsorption isotherms for Au/SiO_2 are very consistent with the results of Yates [48] as they show that uptakes are low and essentially no irreversible adsorption exists at 300 K However, our Au/TiO_2 catalysts exhibit much stronger pressure dependencies and higher uptakes than those of Shastri et al. after the same reduction temperature [49], but as mentioned previously, the CO uptakes on either Au/TiO_2 catalyst are very similar to that reported for pure Degussa P25 titania. For example, at 100 Torr the uptakes on Au/TiO_2 (HTR) and Au/TiO_2 (LTR) were 35 and 42 μmol/g, respectively, compared to 42 μmol/g for a TiO_2 (HTR) sample [20]. These coverages on titania (5×10^{13} molecule $\cdot$ cm^{-2}) are near that reported on a TiO_2 (110) single crystal (3×10^{13}

molecules · cm^{-2}) although the CO pressure in the latter case was much lower [50]. CO adsorbs weakly on Au and desorbs at 110 K [45]; therefore, no irreversible adsorption on Au at 300 K is expected and any such small amounts indicated in fig. 2 are most likely associated with the titania surface. Consequently, we are hesitant to associate any of the adsorbed CO with Au, as was done previously [49], and we attribute the difference in adsorption behavior to the different titania (Glidden, ca. 110 m^2/g, 100% anatase) and pretreatment procedure used by Shastri et al. [49]. Regardless, fig. 2 establishes that adsorption on TiO_2-supported Au is very similar to TiO_2 alone and that an HTR step decreases CO adsorption somewhat on this Au/TiO_2 catalyst.

In an effort to measure the Au surface area, O_2 uptake measurements were made on all samples because oxygen adsorption at 473 K along with the assumption of an adsorption stoichiometry of $O_{ad}/Au_s = \frac{1}{2}$ has been proposed as an adequate method [51]. The validity of this technique has been questioned by Sault et al. because they found no oxygen adsorption on a clean Au (110)-(1x2) single crystal up to pressures of 1400 Torr [24], but Shastri et al. reported consistent chemisorption, WAXS and TEM results for dispersed Au [49]. Atomic oxygen readily adsorbs on Au and is reactive to gas-phase H_2 and CO [24,52]; therefore, using the H_2 titration reaction to selectively react with the oxygen on the Au surface appeared to be a reasonable approach to distinguish between oxygen on the Au and that on the titania surface because there was no reactive oxygen on the pure oxide at 473 K, as shown in table 1. The use of O_2 adsorption with these Au/TiO_2 systems is difficult because a straightforward correction for irreversible oxygen adsorption on the titania itself cannot be guaranteed because it is sometimes greater than that on the Au/TiO_2 catalyst.

The data in table 1 for 1.8% Au/SiO_2 clearly verify that O_2 adsorption can occur on dispersed Au crystallites and, furthermore, it is reactive to hydrogen at 473 K. This adsorption capability is not attributed to impurities because of the high purity gold used and the knowledge that Cl on Au surfaces reacts readily with H_2 at temperatures near 800 K [53]; therefore, reduction at either 723 or 773 K should completely reduce the gold and remove the chlorine from the silica [40]. The titration ratio near unity could imply either that not all the adsorbed oxygen was titrated by the hydrogen or that the water formed did not adsorb completely on the silica at 473 K, thus decreasing the apparent H_2 uptake by increasing the residual pressure. The latter is more likely because the heat of adsorption of H_2O on silica is only about 11 kcal/mole [54,55], thus limited adsorption would occur at 473 K. In addition, analyses of the residual gas phase by mass spectroscopy showed that substantial amounts of water vapor were present [23]. Verification of this explanation will require either a different method or a water trap if a volumetric technique is used again, but this difficulty prevents the quantitative use of the titration reaction with these Au/SiO_2 catalysts.

The data for TiO_2 and the Au/TiO_2 samples show the enhancement in O_2 uptakes on titania that occurs as the reduction temperature is increased, they illustrate the difficulty in correcting for oxygen adsorption on the titania support by subtracting uptakes on the pure TiO_2, and they demonstrate the inability of gas-phase H_2 to react with the oxygen adsorbed on pure titania in the absence of a metal. The darkening of the titania and the increase in oxygen chemisorption capacity on the TiO_2 sample after an HTR step are indicative of the formation of surface defects, i.e., oxygen vacancies [50], by the removal of lattice oxygen [33]. A similar effect occurs with the Au/TiO_2 samples as the HTR pretreatment again increases O_2 uptakes, and verification that most of the increase is associated with the titania is provided by the inertness of about two-thirds of the adsorbed oxygen towards H_2 during the titration reaction. Furthermore, O_2 uptakes on the (HTR) Au/TiO_2 sample continue over longer periods of time, increasing from 23 to 82 μmole O_2/g cat, and this increase is very likely due to oxygen diffusion into the bulk to remove additional lattice oxygen vacancies [50]. An activated process in which molecular oxygen interacts with the titania after even a LTR step is indicated by the isobars in fig. 5, in which higher final uptakes are obtained at 423 K after exposing either pure TiO_2 or (LTR) Au/TiO_2 to oxygen at 673 K, thus, a small amount of O vacancies appears to be formed during the LTR treatment in H_2, most likely in the Au-TiO_2 interface region. Consequently, the O_2 chemisorption results provide direct evidence that the concentration of O vacancies has been markedly increased during the HTR pretreatment.

The assumption that the H_2 titration uptakes on the Au/TiO_2 samples represent reaction only with oxygen on the Au surface does not give good agreement with the XRD results for Au, as indicated in table 3, even if all the water formed is presumed to adsorb on the titania. For three of the four Au/TiO_2 samples, Au particle sizes are significantly smaller than those from

Table 3
Comparison of calculated average Au particle size (nm) of gold on supported catalysts

Catalyst	XRD	O_2 adsorption at 200 °C	
		Au/O = 2/1	Au/O = 1/1
1.8% Au/SiO_2-I	31	72	144
1.8% Au/SiO_2-II	30	53	106 (27) [a]
2.0% Au/TiO_2 (LTR)	25	12	24
2.3% Au/TiO_2 (LTR)	25	22	44
2.0% Au/TiO_2 (HTR)	25	1.3 (8) [b]	2.6 (16) [b]
2.3% Au/TiO_2 (HTR)	35	0.5 (2.4) [b]	0.9 (4.7) [b]

[a] From uptake at 673 K (fig. 4).

[b] Based on the oxygen uptakes in table 2; numbers in parentheses use the titration uptake in table 2 and assume $H_{ad}/O_{ad} = 2$.

XRD line broadening which implies either that some of the hydrogen is reacting with oxygen from the titania, presumably the TiO_x in direct contact with the gold, or that some of the Au crystallites are too small to be detected by this XRD technique. Even the O_2 uptakes do not provide crystallite sizes consistent with those obtained by the XRD results. Part of the difficulty may be the uncertainty of the adsorption stoichiometry because the isobar for O_2 adsorption on the Au/SiO_2 catalyst (fig. 4) clearly shows that it is an activated process, with uptakes increasing up to 673 K. This behavior is consistent with the results of Endow et al. [56], who reported a weak maximum between 700 and 800 K on an Au foil, while a maximum near 630 K was reported for MgO-supported Au [51]. Taking the uptake at 673 K in fig. 4 and correcting it for the uptake on the pure SiO_2 gives a value of 1.9 μmole O_2/g cat, and if an O_{ad}/Au_s adsorption stoichiometry of unity is assumed, a crystallite size of 27 nm is obtained, which is in far better agreement with that from the XRD pattern than the value calculated from the results obtained at 473 K. Despite these uncertainties, our O_2 uptakes indicate that Au surfaces are available for chemisorption, and therefore for catalysis; however, a quantitative measure of Au surface areas using O_2 chemisorption is difficult and we believe that this technique remains ambiguous at this time.

5. Summary

Titania-supported Au catalysts were prepared and given both LTR and HTR pretreatments at 473 and 773 K respectively, and their adsorption and catalytic properties were compared to identically pretreated Pt/TiO_2 catalysts. The similar work functions of the two metals should result in similar increases in O vacancies on the titania surface thus allowing a test of a model specifying that these defect sites are responsible for the enhanced hydrogenation activities reported in the literature. Chemisorption measurements, particularly those related to oxygen uptakes, established that Au surface areas were detectable and that oxygen vacancies had been created in the titania. However, these Au/TiO_2 samples as well as SiO_2-supported Au were completely inactive for CO and acetone hydrogenation, and rates for ethylene hydrogenation were lower than those on the corresponding pure support. Thus the model proposed by Frost invoking only O vacancies as active sites for methanol synthesis on metals dispersed on Zn, Zr, and Th oxides [16] cannot explain the high activity of certain MSI catalysts such as Pt/TiO_2 and, based on a recent paper by Lambert and coworkers [57], this model may not even be appropriate for methanol synthesis catalysts.

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