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A method for measuring the titania surface area on mixed oxides of titania and silica

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We have used temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of 2-propanol to characterize several silica, titania, and silica-supported titania samples. Upon evacuation, most of the 2-propanol desorbed intact from the silica samples. This is in contrast to the results on titania and on silica-supported titania, where a significant amount remained on the surface following evacuation, with a fraction of this reacting to propene and water. The coverages of 2-propanol are approximately proportional to the titania surface area, corresponding to between 2.4 and 6.1×10^{18} molecules/m^2 of titania, depending on the form of the titania. The results suggest that selective adsorption of 2-propanol may be useful for determining the surface area of titania in titania-silicates.

Keywords: Titania; silica; 2-propanol adsorption; temperature-programmed-desorption; surface-area-measurements

1. Introduction

The characterization of supported oxides is often difficult due to the fact that preparation conditions can strongly affect the properties of the resulting materials. For example, it is possible that a catalytic oxide may form a monolayer species over the support oxide under some preparation conditions but that the catalytic oxide will crystallize into large particles under other preparation conditions [1–4]. Solid solutions of the two oxides may form when still other synthesis procedures are used. A great deal can be learned about mixed oxides using transmission electron microscopy [5] or Raman spectroscopy; however, even with these sophisticated techniques, the simple question of what fraction of the surface area is covered by each oxide may be difficult to answer. While H_2 or CO chemisorption are used extensively to determine the surface areas of many supported-metal catalysts, it is usually difficult and sometimes impossible to determine the surface area of the active component for supported oxides.

In recent adsorption studies of aluminas [6,7], an observation has been made which could be useful for characterizing the surface area of some mixed oxides. In temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of isopropanol, it was observed that, on various aluminas, between 1×10^{14} and 2×10^{14} molecules/cm^2 reacted to form propene and water. The type of alumina used, whether α, δ, or γ, and the level of impurities changed the temperature at which the simultaneous formation of water and propene occurred; but the number of molecules which reacted on a surface-area basis was relatively constant. In contrast to this, no reaction of isopropanol was observed on two pure silicas which were examined. This would suggest that it might be possible to use selective adsorption to distinguish the surface area of one component in the presence of another.

In the present study, we have chosen to test this idea on silica-supported titania. Titania silicates could have important applications for catalysis, and the preparation conditions can affect the structure and surface areas of the materials which are formed [5]. Previous studies of 1-propanol dehydration on silica, titania, and silica-supported titania indicated that titania is much more active than pure silica and that the monolayer form of titania on silica exhibits specific dehydration rates which are essentially identical to those on bulk titania [5]. Furthermore, two of us (SS and AKD) have produced well-defined samples of silica-supported titania in which the surface area and structure of the titania have already been characterized by a variety of techniques.

In this study, we will demonstrate that TPD-TGA of 2-propanol is useful for estimating the titania surface area in these mixed oxides. 2-propanol associated with the titania can be distinguished from 2-propanol on the silica, and the coverage of 2-propanol which is associated with the titania is approximately proportional to the titania surface area. In addition, the results are similar when the titania is present as a monolayer phase on silica or as bulk anatase.

2. Results and discussion

The titania sample used in this study was anatase (Degussa P-25) with a surface area of 65 m^2/g. Two different silica samples were examined, both with and without titania. The first was a commercial Cabosil HS-5 (from the Cabot Corporation) with a surface area of 300 m^2/g; the second sample consisted of nonporous spherical particles prepared by the method of Stober and Fink [8]. This model silica was in the form of uniform spheres, 130 nm in diameter. Titania was incorporated onto both silicas by adding 0.5 g of silica to a solution of titanium(IV) *t*-butoxide (0.4 g; 1.2 mmol) in THF under dry nitrogen. Excess alkoxide was then washed from the samples with THF, and the samples were then calcined in oxygen at 773 K. The resulting samples were characterized extensively using X-ray diffraction, Raman spectroscopy, TEM, 1-propanol dehydration kinetics, and methanol oxidation kinetics, with the results having been presented elsewhere [5]. For purposes of this study, it is only important to notice that titania covered the silica surfaces uniformly so that the surface area of titania could be estimated. On both silicas, the titania was present as a monolayer phase and no bulk forms of titania were observed in either TEM or Raman spectroscopy. We calculated the monolayer capacities based on the density of the (110) plane of rutile, which has been calculated to be 1.37×10^{-3} g/m^2 [5]. On the model silica spheres, the average weight percent titania from EDS was 1.1, compared to the theoretical monolayer capacity of 4.0% for 130 nm spheres. On Cabosil HS-5, the titania coverage was only 3 wt%, compared to a theoretical monolayer coverage of 29%. Since the titania on the model silica spheres covers a larger fraction of the surface area than it did on Cabosil HS-5, these two samples provide a good test of the effect of uncovered silica near titania species.

For the TPD and TGA experiments, approximately 20 mg of sample was placed in the sample pan of a microbalance and the system was evacuated with a turbomolecular pump to a base pressure of approximately 1×10^{-7} Torr. Samples were first heated to 825 K in vacuum, cooled to 295 K, and then exposed to 2-propanol by admitting 15 Torr of the vapor until no further weight changes were observed in the catalyst. The samples were then evacuated for ≈ 1 h to remove some of the weakly adsorbed alcohol, and the temperature was ramped at 20 K/min. The desorption products were monitored using a mass spectrometer which was attached directly to the vacuum chamber. The only products observed in desorption were 2-propanol ($m/e = 45$, with additional peaks at $m/e = 41$ and 17), propene ($m/e = 41$), and water ($m/e = 17$ or 18). All of the alcohol was completely removed in the TPD-TGA measurement, and the final sample weights were equal to the initial values within our abilities to measure them. Due to static charging, particularly with the silica samples, there was some uncertainty in the TGA results; but this does not change any of the conclusions reached in this study. Further details on the equipment and adsorption procedures have been discussed elsewhere [9].

The TPD-TGA results for 2-propanol from each of the samples are shown in figs. 1–3, with the coverages summarized in table 1. For the silica samples, the TGA results are shown as thinner lines in figs. 2 and 3. Since the amount of 2-propanol remaining on these samples was very small, the TGA curves for the silica can be used as measure of the effect of sample charging on the TGA results. On the Cabosil HS-5, there was a small amount of propene desorption above 650 K, corresponding to no observable weight change; however, no other features were observable in TPD. For the Degussa P-25, anatase sample, shown in fig. 1, the coverage of 2-propanol after evacuation was ≈ 15 mg 2-propanol/g of catalyst. Using the BET surface area of this sample (65 m^2/g), this coverage

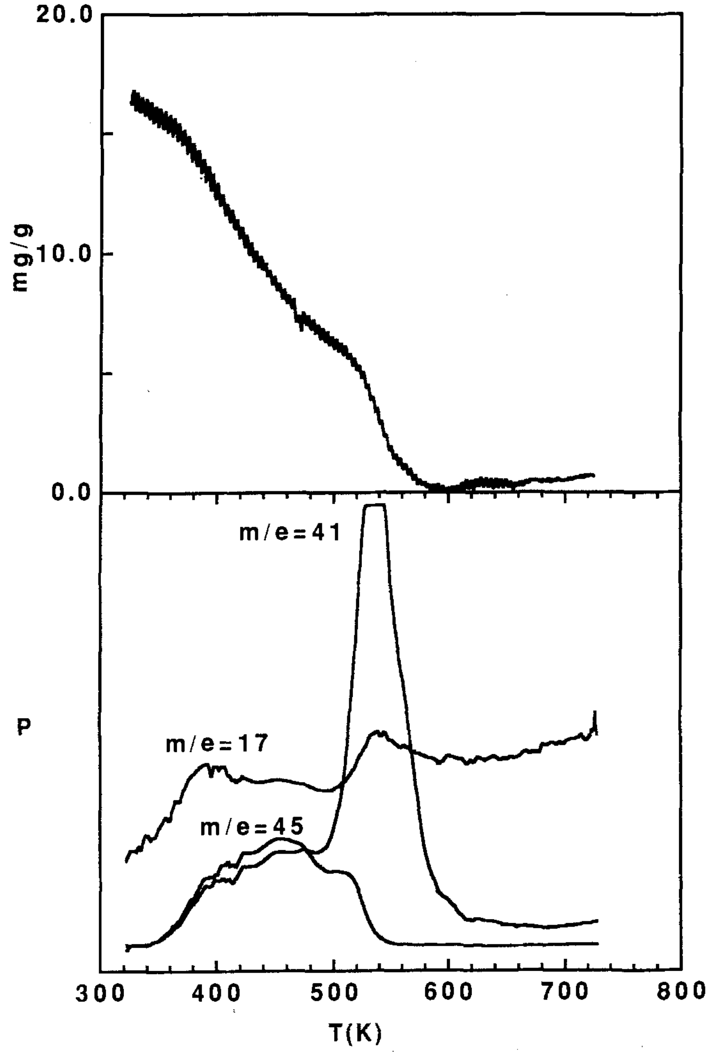

Fig. 1. TPD-TGA results for 2-propanol from anatase (Degussa P-25). The peaks in the TPD correspond to 2-propanol (*m*/*e* = 45, 41, and 17), propene (*m*/*e* = 41), and water (*m*/*e* = 17).

corresponds to 2.4×10^{18} molecules/m^2. The features in the TPD for this sample showed unreacted 2-propanol desorbing from a broad feature extending up to 500 K. Above 500 K, most of the 2-propanol reacted to propene and water, with some of the water desorbing from a featureless increase in the water background. The amount of 2-propanol which reacted was 5.7 mg 2-propanol/g, or 0.9×10^{18} molecules/m^2. The amounts of 2-propanol desorbing from both reacted and unreacted features in the TPD are very close to the values observed for 2-propanol from alumina samples [6,7] and approach what one would expect for a monolayer of 2-propanol based on size of the 2-propanol molecule. These

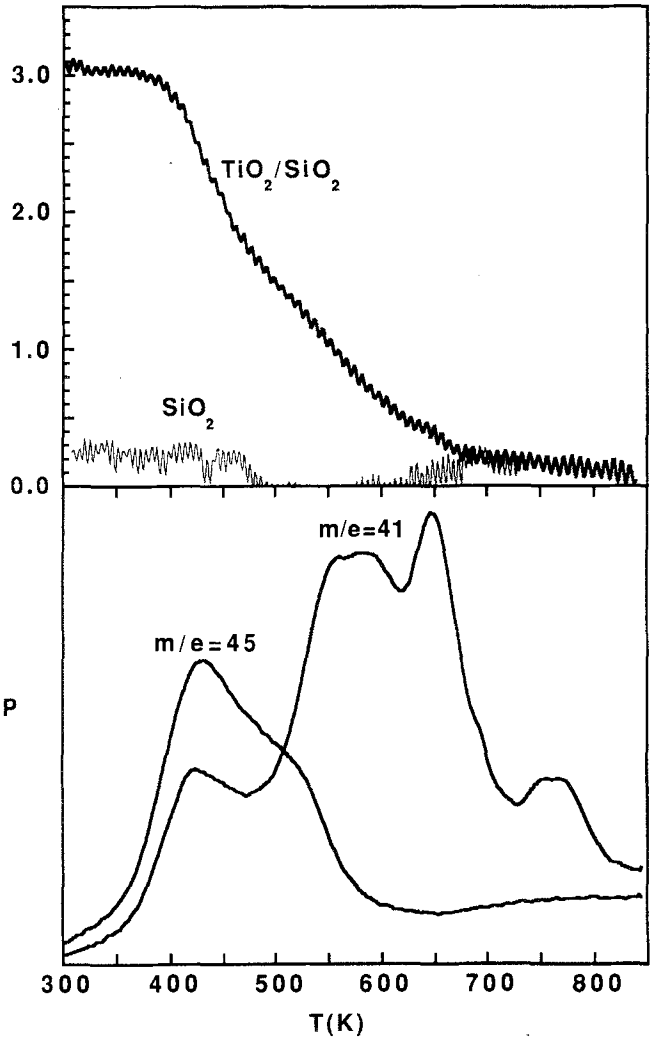

Fig. 2. TPD-TGA results for 2-propanol from the model silica spheres with 1.1% titania. The lower curve in the TGA was obtained on the silica spheres without titania.

results are virtually identical to those reported in a previous study of alcohol adsorption on titania and suggest that the 2-propanol is interacting with most of the titania surface [10].

On the silica-supported titanias, the TPD results are more complex; but one again observes unreacted 2-propanol leaving the surface below 500 K, with substantial amounts of propene desorbing above 500 K. Propene desorbs from three peaks on the silica-supported titanias at ≈ 570, 650, and 770 K. The feature at 570 K is close to the same temperature at which propene is formed on the anatase. We suggest that the peak at 650 K is associated with titania in the monolayer phase and may be shifted to higher temperatures compared to bulk

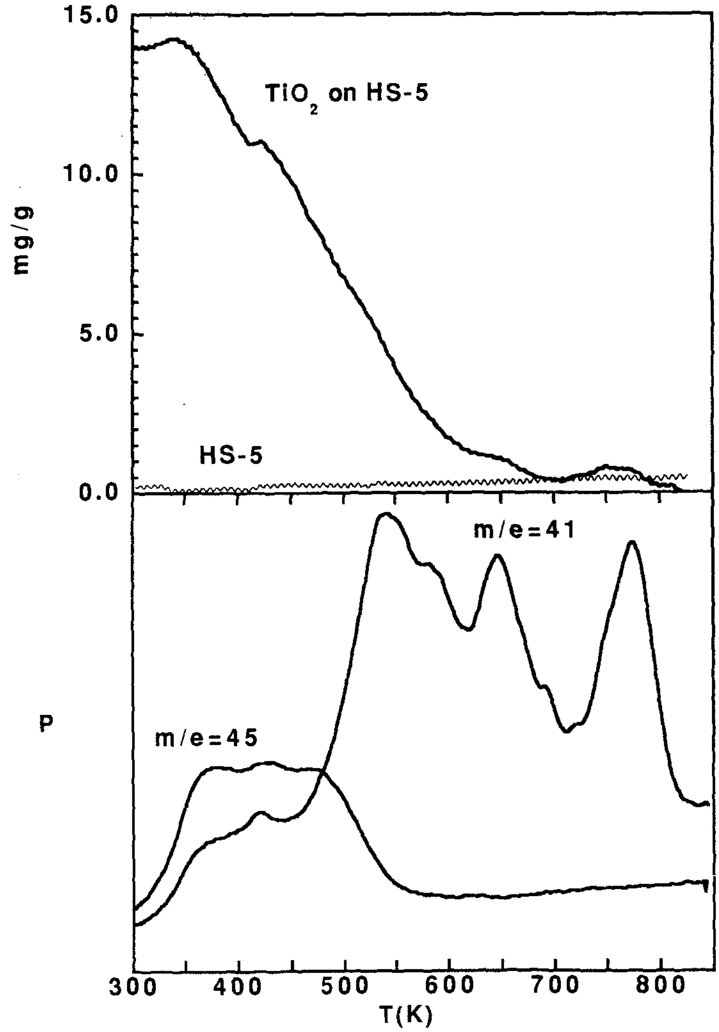

Fig. 3. TPD-TGA results for 2-propanol from Cabosil HS-5 with 3% titania. The lower curve in the TGA was obtained on the Cabosil HS-5 without titania.

Table 1
Adsorption stoichiometries for 2-propanol following adsorption at 298 K and evacuation for 1 h

Sample	Total 2-propanol		Reacting 2-propanol	
	(mg/g)	(molecules/m^2)	(mg/g)	(molecules/m^2)
TiO_2 (Degussa P-25)	15.0	2.4×10^{18}	5.7	0.9×10^{18}
model SiO_2 spheres	< 0.3			
TiO_2 on model spheres	3.1	3.9×10^{18}	1.2	1.5×10^{18}
Cabosil HS-5	< 0.2			
TiO_2 on Cabosil HS-5	13.5	6.1×10^{18}	7.8	3.6×10^{18}

titania due to differences inherent in the monolayer form of titania. The peak at 770 K corresponds to only a very small amount of 2-propanol and is similar to what is observed on pure silica.

The most interesting conclusions from these results come from analyzing the amounts of 2-propanol which desorb. Using the monolayer density given above for determining the titania surface areas of the silica-supported samples, the amounts of 2-propanol which desorb are 3.9×10^{18} molecules/m^2 (1.5×10^{18} molecules/m^2 of which react) on the model silica spheres and 6.1×10^{18} molecules/m^2 (3.6×10^{18} molecules/m^2 of which react) on the Cabosil HS-5. While these coverages are higher than those obtained on the anatase, they are in the same range. Given that only 10% of the surface on the Cabosil HS-5 sample is covered with titania, it is unlikely that significant spillover is occurring from the titania onto the silica phase. The variation in the coverages obtained on the various samples are probably due to the fact that the titania is not as densely packed on the supported titanias, leading to less steric hindrance between adsorbed molecules of 2-propanol. The higher 2-propanol coverage on the Cabosil HS-5 sample compared to that obtained on the model spheres may also be due to the higher titania surface density on the model spheres.

While differences in the specific surface coverages of 2-propanol on the three samples are not insignificant, we suggest that they are relatively small given the extreme differences between the types of samples studied. The monolayer phase on silica is amorphous in X-ray diffraction, has a unique vibrational spectrum in Raman spectroscopy, and exhibits a selectivity for methanol oxidation which bulk titania does not [5]. Even with these differences between the titania samples, the specific coverages of 2-propanol, both reacted and unreacted, are similiar, ranging from $(2.4–6.1) \times 10^{18}/\text{m}^2$ for the total adsorption coverage and $(0.9–3.6) \times 10^{18}/\text{m}^2$ for the amount which reacts. It should be noted that there are also significant changes in adsorption stoichiometry for CO on supported-metal catalysts and that these must be accounted for in order to estimate particle sizes from dispersion measurements [11]. While a highly accurate measure of the titania surface area from TPD-TGA of 2-propanol would probably require advanced knowledge of the form of titania, we suggest that a comparison of similar samples will provide useful information about differences between samples and can give a reasonable estimate of surface areas.

It must be acknowledged that there are significant complications associated with the use of TPD on porous samples [12,13]. The pumping speed or carrier-gas flow rate, sample size, specific surface areas, and other experimental parameters will affect results due to the coupling between readsorption and diffusion during the desorption process. For desorption from larger samples, using less rigorous evacuation procedures, it is likely that some 2-propanol will remain on silica as well as on titania. However, it should be possible to use the reactivity of titania for dehydration of 2-propanol in order to distinguish the 2-propanol which is adsorbed on titania. The fact that propene does not adsorb on titania under the conditions of our experiment suggests that the rate of propene evolution in the TPD is the decomposition rate for the 2-propanol. By monitoring a reaction product which cannot readsorb, readsorption and complications associated with it can be minimized. Furthermore, it appears that silica is not capable of catalyzing this decomposition below 650 K; therefore, the best measure of the titania surface area would probably be obtained from measuring the amount of 2-propanol which reacts to propene and water below this temperature. Certainly, calibration using known samples would provide the best method for calibrating adsorption procedures.

While we have concentrated on one particular catalytic system, it is easy to envision extending the concepts to other supported oxides. All one really needs is for one component to exhibit significantly different adsorption properties for a particular adsorbate. Given the low reactivity of silica for alcohols, it would appear that this concept could be easily extended to other silica-supported oxides. Extension of this concept to other supports will probably require a more extensive search for a selective adsorbate.

3. Conclusions

TPD-TGA measurements with 2-propanol on titania silicates appear to be a very useful method for determining the surface areas of the titania component. The amount of 2-propanol which adsorbs is proportional to the surface area of the titania, while 2-propanol interacts very weakly on the silica.

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