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Effect of SiO_2, NaCl, Al_2O_3, and $FeCl_3$ on Phase Change Behavior of Supported and Unsupported TiO_2

PEKKA ESKELINEN

Kemira Oy, Pori 28840, Finland

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The anatase–rutile phase change temperatures in TiO_2 powders precipitated from aqueous $TiCl_4$ and the same deposited on muscovite and phlogopite micas were investigated. Doping with Al_2O_3, NaCl, and SiO_2 increased the phase change temperature of supported and unsupported TiO_2, but doping with $FeCl_3 \cdot 6H_2O$ decreased the beginning temperature of the phase change on unsupported TiO_2. The difference in phase change dependence on temperature between undoped TiO_2 supported by micas and unsupported TiO_2 was caused by diffusion of aluminum, silicon, and sodium ions from the mica substrate during the calcination step.

Introduction

The phase change temperature of anatase–rutile transformation has been studied extensively. The temperature range for transformation has been reported to vary from 350 to 1175°C depending on the method of preparation, titanium chemical used, and presence of impurities. A thorough review is given by Dassler *et al.* (*1*) and Shannon (*2*).

The anatase–rutile transformation temperature can be varied by doping with different compounds. These include SiO_2, Al_2O_3, Na_2O, and Fe_2O_3, which are also components of micas. SiO_2 (*3, 4*) and Al_2O_3 (*5, 6*) are known to retard or at least not accelerate the transformation, but Fe_2O_3 accelerates it (*6–8*). The role of Na^+ is found to be in some cases that of an accelerator (*8*) and in some cases an inhibitor (*8, 9*).

In our previous study it was shown that thin TiO_2 layers deposited on mica were more stable towards anatase–rutile transformation than the unsupported TiO_2 (*10*). The phase change took place on unsupported TiO_2 already between 750 and 800°C. The phase transition of TiO_2 films supported by phlogopite mica began at 850°C but the films supported by muscovite had anatase structure up to 1000°C. The phenomenon could not be exactly understood then but it was assumed that it could have been caused by ions diffused from mica into the TiO_2 layer. The probability for diffusion could be quite high given that Bach and Schroder reported that sodium diffused from a glass substrate through the overlaying TiO_2 films during thermal treatment at temperatures below 600°C (*11*).

In a later study the diffusion of mica cations through TiO_2 was proved by XPS measurements (*12*). The outermost layer of TiO_2 films contained several mica cations. These included as major components silicon, aluminum, and sodium and as minor components iron, magnesium, and potassium. Depth profiling by sputtering of TiO_2 films showed that concentrations of mica cations decreased fast below the outermost surface, but the concentrations did not go to zero even when entering the bulk film. Hence the whole film was doped with mica cations with highest concentrations at the surface. The total amount of these components was strongly dependent on calcination temperature but relative concentrations were depen-

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dent on the type of the mica. The diffusion of cations began above 600°C. The XPS analysis showed that typical surface cation composition for TiO_2 film supported by phlogopite was Ti 68.2%, Si 17.5%, Al 5.8%, Mg 4.8%, Na 2.5%, and Fe 1.3% and for TiO_2 film supported by muscovite Ti 67.7%, Si 14.2%, Al 7.8%, and Na 10.3%.

The aim of this study was to investigate the role of the cations diffused from the mica support to the differences of crystal structure transformations in unsupported and in TiO_2 supported by different micas.

2. Experimental

To avoid diffusion of mica cations into the TiO_2 layer during calcination, we coprecipitated SiO_2 and Al_2O_3 together with TiO_2 using the same method as earlier (*10*) but without mica. The raw materials for SiO_2 and Al_2O_3 were sodium silicate and sodium aluminate solutions, respectively. Sodium and iron were introduced into TiO_2 as chlorides in a water slurry, which was dried without filtration.

The behavior of TiO_2 films doped with SiO_2, Al_2O_3, NaCl, and $FeCl_3 \cdot 6H_2O$ was also investigated. SiO_2 and Al_2O_3 were codeposited together with TiO_2. TiO_2 layer thickness varied between 100 and 120 nm. The raw materials and deposition technique were the same as described earlier (*10*). The Al_2O_3 and SiO_2 were produced by adding sodium aluminate and/or sodium silicate solution constantly to the slurry when aqueous solution of $TiCl_4$ was added.

The analysis of the filtrate after the deposition step revealed that about 50% of Al_2O_3 and SiO_2 were codeposited with TiO_2. After drying, samples of different compositions were calcined in air at temperatures ranging from 700 to 1100°C. In order to be sure about the origin of sodium on the surface of dried powders their surface composition was determined by the XPS technique as described earlier (*12*). The analysis showed that neither sodium nor chlorine were present at detectable amounts after drying. Hence the samples were not contaminated by sodium originating from sodium hydroxide, aluminate, and silicate solutions used in the preparation step.

The X-ray diffraction patterns were recorded with a Philips PW 1840 diffractometer. As a measure of the anatase–rutile transformation the intensity ratio of anatase (100) and rutile (101) reflections was used.

3. Results and Discussion

3.1. Crystal Structure of Unsupported TiO_2

First the effects of SiO_2, Al_2O_3, and NaCl on anatase–rutile transformation temperature were studied separately. The results are shown in Table I. The degree of transformation was monitored by measuring the intensity ratio of anatase (101) reflection to rutile (100) reflection. Hence the ratio for pure anatase is ∞ and for pure rutile the ratio approaches zero.

The anatase–rutile transformation of undoped TiO_2 began below 750°C and was almost complete at 800°C. Doping with SiO_2 and Al_2O_3 retarded the transformation. The

TABLE I

THE INTENSITY RATIO OF ANATASE (101) REFLECTION TO RUTILE (100) REFLECTION OF UNSUPPORTED TiO_2 DOPED WITH DIFFERENT COMPOUNDS

Dopant added (%)	Temperature (°C)			
	750	800	850	900
None	0.46	0.006	0	0
1.5 SiO_2	∞	6.6	0.3	0.2
3.0 SiO_2	∞	∞	∞	2.4
1.5 Al_2O_3	3.1	0.10	0	0
3.0 Al_2O_3	8.6	0.5	0.04	0
0.14 NaCl	0.06	0.09	0	0
0.60 NaCl	0.06	0.05	0	0
1.0 NaCl	0.1	0.2	0.03	0.002
2.1 NaCl	0	0.2	0.01	0.003
3.2 NaCl	∞	∞	∞	∞
6.3 NaCl	∞	∞	∞	∞

Note. The amounts of dopant compounds are expressed in wt%.

retarding effect was stronger when concentration of dopant was increased. The retarding effect caused by NaCl was detected only at high doping level.

NaCl influenced most strongly the phase transformation when the doping level was high enough. The transformation did not proceed at all when addition of NaCl was 3.2% or higher. Lower doping levels did not have any effect on the transformation. Hence the effect of NaCl is very sensitive to the actual concentration of this compound. Iida and Ozaki have reported that doping with Na_2CO_3 (1.2 wt%) retards the transformation (*8*). According to their results the transformation began only when temperature exceeded 800°C. At 900°C the amount of rutile was only 14 wt% for Na_2CO_3 doped TiO_2 and 82 wt% for undoped TiO_2. The difference between results of Iida and Ozaki and results obtained in this study can be explained as due to the use of a different preparation method and different raw materials. In their study TiO_2 was prepared by decomposing ammonium titanium sulphate and it is known that sulphate retards the anatase–rutile transformation (*5, 9, 13*). On the other hand, Mackenzie has reported that 1.3 wt% addition of Na_2CO_3 enhances the transformation at 1000°C and the conversion is 25.4% relative to the undoped sample. On the other hand, 0.53% addition of NaF is reported to result 85.6% conversion (*6*). The above-mentioned results indicate clearly that the effect of sodium is very strongly dependent at least on the accompanying anion. Hence, it is not possible to compare the results obtained in this study straight to those obtained by other authors. However, one can conclude that the effect of sodium compounds to anatase–rutile transformation remains somewhat unclear, but in our experiments sodium chloride retarded the transformation when the addition was 3.2% or higher.

SiO_2 had also a strong retarding effect on the anatase–rutile transformation. At the highest doping level (3%) the transformation began only when temperature exceeded 850°C. This is in accordance with results obtained by Hishita and Hirai (*4*). They have reported that SiO_2 inhibits anatase–rutile transformation by covering the surface of TiO_2.

TABLE II

THE ANATASE–RUTILE RATIO OF UNSUPPORTED TiO_2 DOPED SIMULTANEOUSLY WITH DIFFERENT COMPOUNDS

	Temperature (°C)			
Dopant (%)	750	800	850	900
1.5 SiO_2	∞	6.6	0.3	0.2
1.2 SiO_2; 0.3 Al_2O_3	∞	4.8	1.0	0.5
1.2 SiO_2; 0.3 Al_2O_3; 1.4 NaCl	∞	∞	∞	∞
1.2 SiO_2; 0.3 Al_2O_3; 2.8 NaCl	∞	∞	∞	22
1.2 SiO_2; 0.3 Al_2O_3; 1.9 $FeCl_3$	95	11	2.1	0.8
1.2 SiO_2; 0.3 Al_2O_3; 3.9 $FeCl_3$	51	2.2	0.4	0.1
0.9 SiO_2; 0.6 Al_2O_3	∞	17	0.5	0.2
0.9 SiO_2; 0.6 Al_2O_3; 1.4 NaCl	∞	∞	∞	∞
0.9 SiO_2; 0.6 Al_2O_3; 2.8 NaCl	∞	∞	∞	18
0.9 SiO_2; 0.6 Al_2O_3; 1.9 $FeCl_3$	254	8.5	2.4	1.0
0.9 SiO_2; 0.6 Al_2O_3; 3.9 $FeCl_3$	59	2.3	1.0	0.2

Note. The amounts of dopant compounds are expressed in wt%.

The retarding effect of Al_2O_3 was clearly weaker than that of SiO_2, although it did retard the transformation. The retarding effect of Al_2O_3 in the temperature range from 708 to 870°C has also been reported by Rao *et al.* (*5*). On the contrary Mackenzie found no retarding or enhancing effect when TiO_2 was doped with Al_2O_3 (*6*).

In order to simulate the effects of thermally induced diffusion of mica cations on supported TiO_2, pure TiO_2 was doped simultaneously with SiO_2 and Al_2O_3. The difference in the chemical composition of phlogopite (SiO_2 47%, Al_2O_3 11%) and muscovite (SiO_2 48%, Al_2O_3 34%) was taken into account by doping TiO_2 with two SiO_2/Al_2O_3-ratios. SiO_2 and Al_2O_3 doped TiO_2 was doped further with $FeCl_3 \cdot 6H_2O$ or NaCl. The results are presented in Table II.

The effects of simultaneous doping of TiO_2 with SiO_2 and Al_2O_3 is quite similar to

TABLE III

COMPOSITION AND CRYSTAL STRUCTURE OF THIN TiO_2 FILMS SUPPORTED BY PHLOGOPITE AND DOPED WITH DIFFERENT COMPOUNDS

Thickness of TiO_2 film (nm)	NaCl (%)	Al_2O_3 (%)	SiO_2 (%)	$FeCl_3$ (%)	Crystal structure
100					anatase and rutile
100	2.8				anatase
100	5.6			1.9	anatase
100				3.9	anatase
120					anatase and rutile
120		1.5			anatase
120		3.0			anatase
120		6.0			anatase
120			1.5		anatase
120			3.0		anatase
120		0.5	1.0		anatase
120		1.0	2.0		anatase

Note. The calcination temperature range is 850–900°C. The amounts of dopant compounds are expressed in wt% from TiO_2.

the doping with those compounds separately. The most interesting observation is that the addition of NaCl into the SiO_2 and Al_2O_3 doped TiO_2 retards rutile formation markedly, although the addition of NaCl is only 1.4%. At this addition level transformation is totally inhibited, but when the amount of NaCl is increased to 2.8% and the temperature up to 900°C, a small amount of rutile could be detected in the samples.

The promoting effect of $FeCl_3$ was quite clear. The conversion was enhanced at both SiO_2/Al_2O_3-ratios. The amount of rutile was increased steadily when calcination temperature and/or the amount of $FeCl_3$ was increased.

3.2. *Crystal Structure of TiO_2 Films*

In order to gain more valid information about the role of the cations diffusing from the mica substrate into TiO_2 films, doped TiO_2 films were prepared as shown in Table III. By doping TiO_2 films supported by phlogopite with NaCl, SiO_2, and Al_2O_3 a better simulation to TiO_2 films supported by muscovite can be achieved than by doping powdered TiO_2. If doping with NaCl and Al_2O_3 could be detected to stabilize anatase structure of TiO_2 films supported by phlogopite, it would suggest that diffusion of aluminum and/or sodium compounds is the origin for differences in anatase–rutile transformation behavior between thin TiO_2 films supported by phlogopite and muscovite micas. The role of iron oxide in phase transformation was intended to be cleared by doping TiO_2 films by $FeCl_3 \cdot 6H_2O$.

The anatase–rutile transformation of the undoped TiO_2 films supported by phlogopite began between 800 and 850°C. At 950°C the amount of rutile could be approximated from intensities of anatase (100) and rutile (101) reflections to be about 40% for TiO_2 films with a thickness of 120 nm.

The behavior of Al_2O_3, NaCl, and/or SiO_2 doped films was totally different from the behavior of undoped films. In the temperature range studied there was no evidence of a rutile structure in the TiO_2 films (see Table III). Even at the lowest doping level the films were 100% anatase. The influence of prolonged heating for 6 hr at 900°C on the degree of phase tansformation of Al_2O_3 doped films was studied at different doping levels. However, no clearly measurable change in the TiO_2 structure was observed.

Iron(III) chloride doping of thin TiO_2 films supported by phlogopite mica seemed to have no detectable effect on the crystal structure of the films. This may be caused by slower diffusion of iron in the TiO_2 film compared to the smaller cations (Na, Al, and Si) (*13*).

In order to enhance the rutile formation calcining experiments at 1100°C were performed. This caused an unpredicted phase change. TiO_2 reacted with phlogopite mica, which was clearly seen in the X-ray diffraction patterns measured from the samples calcined in the temperature range 700–1100°C (see Fig. 1). At 700°C the diffraction pattern consists of peaks from anatase TiO_2 and phlogopite mica. When the temperature was increased to 900°C peaks of rutile TiO_2 also became visible. At 1100°C peaks attributable to TiO_2 and phlogopite disappeared totally. The only crystalline

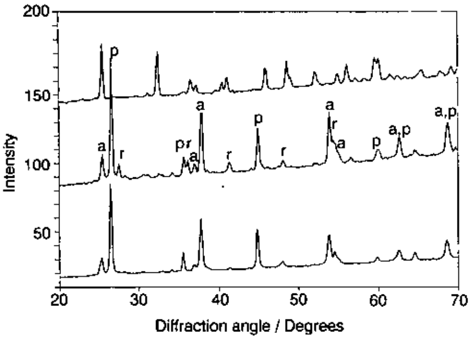

FIG. 1. X-ray diffraction patterns of thin TiO_2 films supported by phlogopite (a is anatase, r is rutile, and p is phlogopite). Bottom, film calcined at 700°C for 1 hr. Visible diffraction maxima are due to anatase TiO_2 and phlogopite mica. Center, film calcined at 900°C for 6 hr. Visible diffraction maxima are due to anatase and rutile TiO_2 and phlogopite mica. Upper, film calcined at 1100°C for 6 hr. Diffraction maxima of anatase and rutile TiO_2 and phlogopite mica are not visible. Measured diffraction maxima can be related to magnesium titanate, Mg_2TiO_4.

phase that could be identified as a result of the solid state reaction was magnesium aluminum titanate. No crystalline compounds containing SiO_2, Al_2O_3, or K_2O could be identified. Phenomenon may be due to noncrystalline nature of the unreacted part of the mica structure. A similar result has been reported by Roy, who has shown that when pure phlogopite was heated at 1000°C then the only crystalline phase was spinel, $MgAl_2O_4$ (*14*). Hence, no crystalline compounds containing SiO_2 and K_2O were detected. This result gives a possible explanation to the nonexistence of other crystalline phases in TiO_2–phlogopite system.

The codeposition of Al_2O_3, NaCl, and/or SiO_2 had a pronounced retarding effect on the TiO_2 phase transformation on thin TiO_2 films supported by phlogopite mica. TiO_2 films could be stabilized totally to anatase structure which remained up to 950°C. Hence the reason for partial rutile formation in thin TiO_2 films supported by phlogopite is the lack of the stabilizing sodium compound and/or Al_2O_3 in this system. However, the influence of the sodium compound is believed to be determining, because the differences in sodium and aluminum surface concentrations of TiO_2 films supported by muscovite and phlogopite favor this conclusion (*13*). When the calcination temperature was 850°C, the surface concentration of sodium on samples based on muscovite was 10 cation%, but in the samples based on phlogopite the sodium concentration was only one tenth of that. Also the aluminum content of the surface of the TiO_2–phlogopite system (5 cation%) was 30% lower than its value in the TiO_2–muscovite system.

4. Conclusions

The anatase–rutile transformation of undoped TiO_2 took place between 750 and 800°C. Doping with Al_2O_3, Na_2O, and/or SiO_2 increased the phase change temperature. On the other hand, doping with $FeCl_3 \cdot 6H_2O$ seemed to lower the phase change temperature of TiO_2 doped with Al_2O_3 and SiO_2.

The anatase–rutile phase change temperature of TiO_2 supported by micas was higher than that of unsupported TiO_2. This was caused by the diffusion of aluminum, silicon, and sodium ions from the mica substrate during calcination step. The difference between the phase change behavior of TiO_2 supported by phlogopite and muscovite could be related to the strong retarding influence of sodium compounds on the anatase–rutile transformation.

The crystal structure changes of the doped TiO_2 films supported by phlogopite behaved in the similar manner as those of the unsupported TiO_2. Hence the small difference in the crystal structure of muscovite and phlogopite did not have any effect on the crystal structure of TiO_2 supported by either micas. All differences resulted from chemical effects.

Preparation of rutile films supported by the micas would be possible if the diffusion of sodium, silicon, and aluminum can be hindered or TiO_2 can be deposited readily in the rutile form using appropriate complexing agents for Ti^{4+}. This must be confirmed by further studies.

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