Structure and Composition of the Nanocrystalline Phases in a MgO−TiO$_2$ System Prepared via Sol−Gel Technique

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Samples in the MgO−TiO$_2$ system were prepared via the sol−gel technique with titanium and magnesium ethoxides as precursors and HNO$_3$ as hydrolysis catalyst. The analyzed magnesia to titania weight ratios were 0.1:0.9, 0.5:0.5, and 0.9:0.1 (0.05, 0.5, and 4.0 MgO:TiO$_2$ molar ratios). Samples were characterized with X-ray powder diffraction, differential thermal analysis, and thermogravimetry. To quantify the concentration and the crystallography of the phases in the samples, their crystalline structures were refined by using the Rietveld method. In addition to periclase, anatase, and rutile, three intermediate compounds were observed: karooite (MgTi$_2$O$_5$), geikielite (MgTiO$_3$), and qandilite (Mg$_2$TiO$_4$). The formation of the above crystalline phases in the samples occurred after an exothermic reaction at 200 °C, and their dehydroxylation above 300 °C. Karooite was abundant only in titania-rich samples, while geikielite and qandilite concentrations were high in the samples with equal magnesia to titania weight percent. Phase concentrations depended on the annealing temperature of the sample and its MgO content. Magnesium was soluble in anatase, but not in rutile; the solubility, however, was low.

Introduction

Titania is a material that has many applications in industry. For example, it is the most used pigment in paintings and textiles.[1] Because of its electronic properties, titania is also used in the production of electrochemistry electrodes,[2] capacitors,[3] and solar cells.[4] Titania is also of interest in catalysis, where it can be the support, as in the catalyst used for oxidation of CO,[5] or the catalyst, for example, for cleaning water polluted with microorganisms. In latter case, titania photocatalyzes the oxidation of the organic and inorganic matter suspended in water.[6]

The properties of titania can be modified when it is mixed with another oxide. For instance, when it is mixed with SiO$_2$, the pure oxides segregate and for the high silica concentration the titania is dispersed, providing a large titania surface area.[7] When titania is doped with MgO, the magnesium ions substitute for titanium ions, creating defects that change its catalytic properties.[8] When the doping is made with PtO$_2$, the stabilized titania polymorph is rutile.[9]

If titania is mixed with CuO,[10] copper will form a solid solution with the structure of anatase and brookite, two of the titania polymorphs, although copper valences can be only 2+ or 1+. This fact induced us to investigate the solution of alkali and alkali-earth elements in titania. For example, we found that lithium forms solid solutions in anatase, brookite, and rutile,[11] while cal-

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cium only forms solid solutions in anatase and brookite.[12] The next study is to analyze the effect of magnesia on titania by cogelling magnesium and titanium alkoxides for different magnesia to titania weight ratios. To enrich the knowledge about MgO−TiO_2 system, we extended this study to high magnesia concentrations, which provided its intermediate compounds that can be formed via the sol−gel technique. MgO is a catalyst support that stabilizes transition metals and avoids their sintering and evaporation.[13] Magnesia is also the support in the catalysts for CO hydrogenation.[14]

To understand the properties of mixed oxides, it is necessary to have information about the different phases produced during the mixing: their concentrations, lattice parameters, average crystallite sizes, and their dependence on synthesis method and annealing conditions.

For the MgO−TiO_2 system, only one previous report is available in the literature.[8] In that investigation, samples are prepared by mixing magnesium oxide and titanic acid, producing a mixture of an amorphous phase, periclase, anatase, and rutile. Their synthesis method, however, does not favor a good reaction between atoms and produces inhomogeneous samples and metastable phases. To avoid these difficulties, we prepared the samples of MgO−TiO_2 system by using the sol−gel technique, at the MgO:TiO_2 weight ratios of 0.1:0.9, 0.5:0.5, and 0.9:0.1 (0.05, 0.5, and 4.0 molar ratios).

Samples were characterized with X-ray powder diffraction. To have a quantitative analysis, all crystalline structures were refined by using the Rietveld method, in which diffraction patterns are calculated by modeling the experimental arrangement and the crystalline structures. The parameters of the model are varied until the difference between calculated and experimental diffraction patterns is minimal.[15] For modeling a phase, its known crystalline structure is used as the starting point for the refinement. This structure has several variable parameters that can be refined: atom positions, Debye−Waller factor, unit cell parameters, and site occupancy. Phase concentrations and phase average crystallite sizes are parameters of the model that can be refined too. Samples were additionally characterized by using differential thermal analysis (DTA) and thermogravimetry (TG).

Experimental Section

Sample Preparation. To obtain 20 g of MgO−TiO_2 with the weight ratios of 0.1:0.9, 2.89 g of $Mg(OC_2H_5)_2$ (Aldrich 98%) was dissolved in 150 mL of ethanol (Baker 99.9%). To complete the dissolution of the magnesium alkoxide, 0.1 g of oxalic acid was added to the solution, which was stirred and refluxed at 70 °C. Under these conditions, to the solution was added 3.5 mol of HNO_3 (Baker 55.85% Vol. in water). Finally, to it was added drop by drop 35.9 mL of $Ti(OC_2H_5)_4$. This final solution was stirred and refluxed for 12 h. The amounts of alkoxides used to prepare the samples with the weight ratio of 0.5:0.5 were 14.48 g of magnesium alkoxide and 19.9 mL of titanium alkoxide. To prepare the sample with the MgO:TiO_2 weight ratio of 0.9:0.1, the amount of magnesium ethoxide was 26.07 g and that of titanium ethoxide, 3.9 mL. Before annealing the samples, they were dried in air for 24 h at 70 °C. The yields of the samples calcined at 400 °C for 12 h were 88, 82, and 93 wt % for the MgO:TiO_2 weight ratios of 0.1:0.9, 0.5:0.5, and 0.9:0.1, respectively.

X-ray Diffraction Analysis. Crystalline structures were analyzed with X-ray powder diffraction and refined via the Rietveld method with the DBWS-9411 code.[16] X-ray diffraction patterns were measured at room temperature with a Siemens D-5000 diffractometer using Cu K_α radiation on specimens prepared by packing sample powder into a glass holder. Intensity was measured by step scanning in the 2θ range between 10° and 110°, with a step of 0.02° and a measuring time of 2 s per point. Diffraction peak profiles were modeled with a pseudo-Voigt function that used the average crystallite size as a fitting parameter.[17] The standard deviations, given in parentheses, correspond to the variation of the last figures of the corresponding number. Since the standard deviations corresponded to refined parameters, they are not estimates of the analysis as a whole, but only of the minimum possible probable errors based on the normal distribution of the parameters.[18] Before X-ray analysis, samples were heated in air at 200, 400, 600, or 800 °C for 12 h.

DTA and TG Analysis. These analysis were carried out in a Dupont Model 950 thermoanalyzer with DTA and TG stages; samples were annealed in flowing air (1.8 L/h) from 25 to 1200 °C, at 20 °C/min.

Results and Discussion

When samples were annealed above 400 °C, they contained periclase, anatase, rutile, karooite ($MgTi_2O_5$), geikielite ($MgTiO_3$), and qandilite (Mg_2TiO_2) (Figures 1−3). This result differs from Tanabe's et al. report,[8] because they only produced periclase, anatase, rutile, and an amorphous phase.

To analyze quantitatively the crystalline phases, their crystalline structures were refined with the Rietveld method. Since this method requires knowledge of the crystallography for all relevant crystalline phases, anatase was modeled with a tetragonal unit cell that had the symmetry described by space group $I4_1/amd$; rutile was also modeled with a tetragonal unit cell but described by space group $P4_2/mnm$; the atom positions in these unit cells are published elsewhere.[19] The refined anatase lattice parameters a and c varied from 0.3704(3) to 0.37838(5) nm and from 0.9481(2) to 1.024(2) nm, respectively. The large c value compared with that of pure anatase,[19] $c = 0.9502(3)$ nm, suggests that magnesium was incorporated into the anatase lattice. For rutile, the refined lattice parameter a varied from 0.4590(1) to 0.4595(1) nm and c from 0.2957(2) to 0.2958(1). These values are similar to those observed in pure rutile,[19] 0.45896(1) and 0.29586(1) nm, indicating that magnesium was not dissolved in rutile lattice.

Periclase was modeled with a cubic unit cell that had the symmetry described by space group $Fm3m$, with the magnesium atom at the center of the cell and the oxygen atom at its corner. The observed periclase lattice

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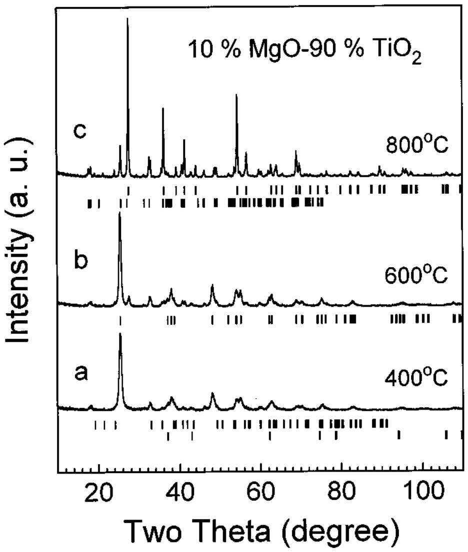

Figure 1. X-ray diffraction patterns of a sample with 10 wt % MgO/90 wt % TiO$_2$ after it was annealed at different temperatures: (a) 400 °C, (b) 600 °C, and (c) 800 °C. Under the curve of the sample annealed at 800 °C, the upper tick marks correspond to rutile and the lower to karooite. Tick marks under the middle curve correspond to anatase. Under the lowest curve the upper tick marks correspond to geikielite and the lower to MgO.

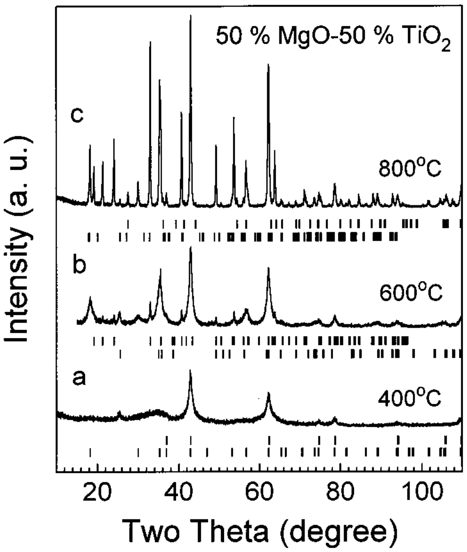

Figure 2. X-ray diffraction patterns of a sample with 50 wt % MgO/50 wt % TiO$_2$ after it was annealed at different temperatures: (a) 400 °C, (b) 600 °C, and (c) 800 °C. Under the curve of the sample annealed at 800 °C, the upper tick marks correspond to rutile and the lower to karooite. Under the middle curve, the tick marks correspond to geikielite. Under the lowest curve, the upper tick marks correspond to MgO and the lower to qandilite.

parameter *a* varied between 0.42100(1) and 0.4238(2) nm, which are similar values to those observed in pure periclase,[20] 0.421032(2) and 0.421022(2) nm, suggesting that titanium was not dissolved in its structure.

Karooite ($MgTi_2O_5$) was refined with an orthorhombic unit cell that had the symmetry described by space group *Bbmm*, and the atom positions given in Table 1. This phase appeared mainly in titania-rich samples (Table 2). Its lattice parameters *a*, *b*, and *c* varied between 0.9834(2) and 0.980(2) nm, 0.981(1) and 0.9998(2) nm, and 0.3731(2) and 0.3749(4) nm, respectively.

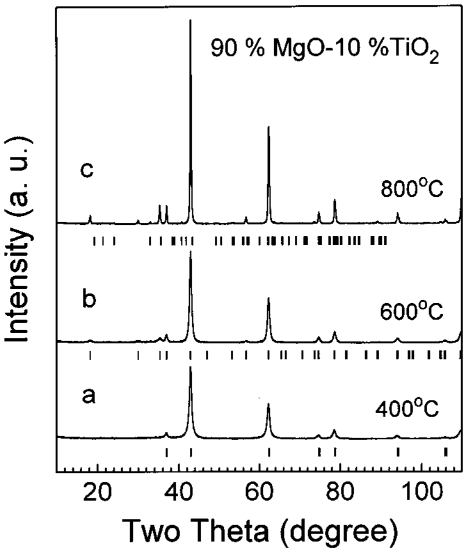

Figure 3. X-ray diffraction patterns of a sample with 90 wt % MgO/10 wt % TiO$_2$ after it was annealed at different temperatures: (a) 400 °C, (b) 600 °C, and (c) 800 °C. The tick marks under the curve of the sample annealed at 800 °C, correspond to geikielite; those under the middle curve correspond to qandilite, and the tick marks under the lowest curve correspond to MgO.

Table 1. Karooite ($MgTi_2O_5$), Space Group *Bbmm*: Atomic Fractional Coordinates[a]

atom	site	*x*	*y*	*z*
Mg	4c	u_x	0.25	0.00
Ti	8f	v_x	v_y	0.00
O(1)	4c	w_{1x}	0.25	0.00
O(2)	8f	w_{2x}	w_{2y}	0.00
O(3)	8f	w_{3x}	w_{3y}	0.00

[a] The initial values were $u_x = 0.19$, $v_x = 0.135$, $v_y = 0.56$, $w_{1x} = 0.73$, $w_{2x} = 0.045$, $w_{2y} = 0.11$, $w_{3x} = 0.31$, $w_{3y} = 0.095$.

Geikielite ($MgTiO_3$), which appeared in all samples (Table 2) and is the magnesium analogue to ilmenite ($FeTiO_3$),[21] was modeled with a trigonal unit cell described by space group $R\bar{3}$ and the atom positions reported in Table 3. Its lattice parameters *a* and *c* varied between 0.5048(3) and 0.50516(7) nm, and 1.3888(8) and 1.3896(1) nm, respectively. In nature, geikielite always appears in rutile and spinel minerals.[22]

Qandilite (Mg_2TiO_4) was modeled with a spinel structure. The unit cell is cubic with the symmetry described by space group *Fd*3*m*, the atom positions given in Table 4, and lattice parameter *a* varying between 0.8435(3) and 0.848(3) nm. This phase was absent in the samples with low magnesium content (Table 2).

Figure 4 shows a typical Rietveld refinement plot for the MgO−TiO$_2$ system. It corresponds to a sample with the MgO:TiO$_2$ weight ratio of 0.1:0.9 that was annealed at 800 °C; it contained anatase, rutile, karooite, geikielite, and periclase.

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Table 2. Phase Concentrations as a Function of Annealing Temperature and Oxide composition

sample	*T* (°C)	rutile (wt %)	anatase (wt %)	$MgTi_2O_5$ (wt %)	$MgTiO_3$ (wt %)	Mg_2TiO_4 (wt %)	MgO (wt %)
10% MgO/90% TiO_2	400		83.8(4)	14.4(4)	1.2(1)		1.5(1)
	600	8.0(2)	70.6(4)	16.4(3)	2.8(1)		2.2(1)
	800	59.5(3)	10.9(3)	23.0(4)	4.5(1)		2.1(1)
50% MgO/50% TiO_2	400		0.4(1)		16.1(9)	4.6(6)	78.8(8)
	600		1.3(1)		3.9(1)	29.3(4)	65(8)
	800	2.2(1)	0.5(1)	5.1(3)	26.7(4)	17.4(3)	48.1(8)
90% MgO/10% TiO_2	400						100
	600				0.5(1)	5(1)	94.5(1.4)
	800				0.66(3)	5.3(2)	94.1(6)

Table 3. Geikielite ($MgTiO_3$), Space Group R$\bar{3}$: Atomic Fractional Coordinates[a]

atom	site	*x*	*y*	*z*
Mg	6c	0.00	0.00	u_z
Ti	6c	0.00	0.00	v_z
O	18f	w_x	w_y	w_z

[a] The initial values were $u_z = 0.358$, $v_z = 0.142$, $w_x = 0.305$, $w_y = 0.015$, $w_z = 0.250$.

Table 4. Qandilite (Mg_2TiO_4), Space Group *Fd*3*m*: Atomic Fractional Coordinates[a]

atom	site	x	y	z
Ti	8a	0.00	0.00	0.00
Mg	16d	0.625	0.625	0.625
Ti	8a	0.00	0.00	0.00
O	32e	*u*	*u*	*u*

[a] *u* varied between 0.26446 and 0.27242.

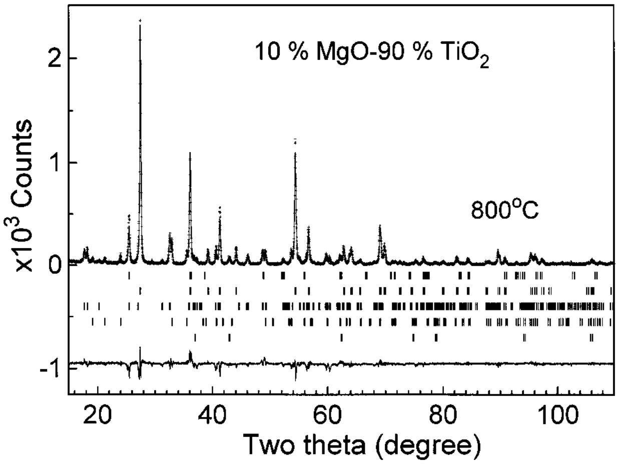

Figure 4. Rietveld refinement plot of a sample with 10 wt % MgO/90 wt % TiO_2 and annealed at 800 °C. Experimental data are represented with crosses; the calculated diffractogram and its difference with the experimental one are indicated with continuous lines. From top to bottom, tick marks correspond to anatase, rutile, karooite, geikielite, and periclase.

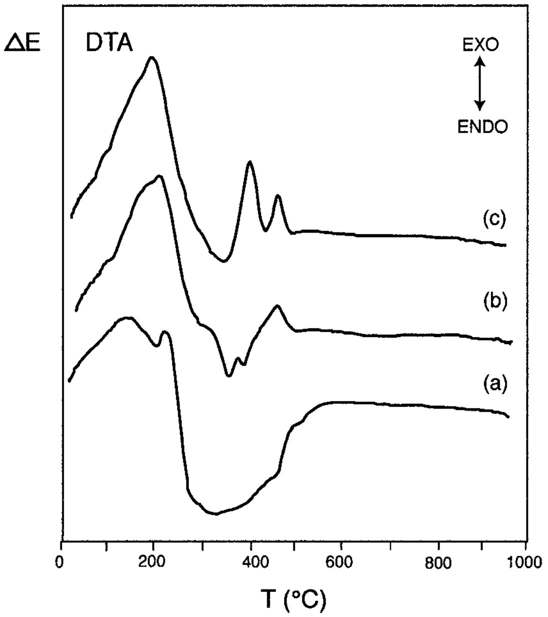

Figure 5. DTA curves of MgO−TiO_2 system: (a) for 10 wt % MgO/90% TiO_2, (b) 50 wt % MgO/50% TiO_2, and (c) 90 wt % MgO/10% TiO_2.

We want to note that for the quantitative phase analysis, we only considered the crystalline phases and excluded any amorphous ones. This observation is especially important for the samples annealed at low temperatures (Figure 2a) which had an X-ray diffraction pattern with a large background caused by the presence of amorphous material.

Samples with 10 wt % MgO and 90 wt % TiO_2. The fresh samples were composed of an amorphous phase and magnesium oxalate hydrate, $MgC_2O_4{\cdot}2H_2O$, which was identified in the X-ray diffraction pattern. This oxalate was produced by the oxalic acid added during the synthesis to improve the solubility of the magnesium and disappeared when samples were annealed at 200 °C. When these samples were annealed, they produced a strong exothermic reaction at 143 °C and a weak one at 232 °C (Figure 5a) and had a sample weight loss of 10.9% (Figure 6a). Because the oxalate disappeared when the sample was annealed at 200 °C, the strong exothermic peak can be associated to its reaction with the amorphous phase. An endothermic reaction occurred at 280 °C together with a additional sample weight loss of 15.9%. Another endothermic reaction was initiated at 340 °C and finished above 500 °C, producing a weight loss of 12.8%. In this temperature range, the most abundant phase was anatase (Figure 1a and Table 2), which was transformed into rutile as the temperature was increased. Therefore, most of the sample weight loss observed in this temperature range must be associated with the anatase dehydroxylation that occurs when it is transforming into rutile.[19]

When samples were annealed at 400 °C, they contained 83.8(4) wt % anatase, 14.4 (4) wt % karooite, 1.2(1) wt % geikielite, and 1.5(1) wt % MgO, indicating that the solubility of magnesium in anatase was low. This contrasts with the results obtained when titania is doped with calcium,[12] because calcium is soluble in anatase at concentrations as high as 10 wt %.

Rutile and karooite concentrations were increased significantly, when samples were annealed at 800 °C, while those of geikielite and periclase did not change.

Table 5. Average Crystallite Size as a Function of Annealing Temperature and Oxide Composition

		d (nm)					
sample	*T* (°C)	rutile	anatase	Ti_2MgO_5	$MgTiO_3$	Mg_2TiO_4	MgO
10% MgO/90% TiO_2	400		19(2)	43(4)	62(6)		193(19)
	600	45(5)	25(3)	43(4)	62(6)		193(19)
	800	63(6)	125(13)	43(4)	62(6)		193(19)
50% MgO/50%TiO_2	400		109(11)		13(1)	8(1)	9(1)
	600		472(8)		79(8)	15(2)	12(2)
	800	63(6)	472(48)	43(4)	74(7)	56(6)	51(3)
90% MgO/10% TiO_2	400						14.4(4)
	600				20(2)	11(3)	20.3(1)
	800				63(6)	42(7)	61(1)

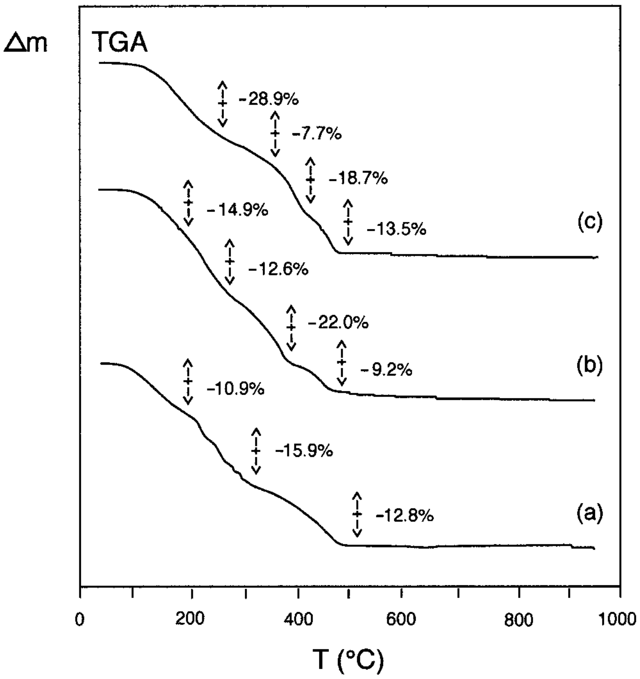

Figure 6. TG curves of $MgO-TiO_2$ system: (a) for 10 wt % MgO/90% TiO_2, (b) 50 wt % MgO/50% TiO_2, and (c) 90 wt % MgO/10% TiO_2.

Since karooite required magnesium for its formation and MgO concentration was constant, the only source of magnesium must be anatase. This provides indirect proof that magnesium was soluble in anatase. Magnesium ions substitute for titanium cations, in a similar way as copper ions,[9] lithium ions,[11] calcium ions,[12] and tin ions[23,24] substitute for titanium ions in anatase when titania is doped with their oxides.

For this magnesia to titania weight ratio, all phases were nanocrystalline (Table 5), except periclase, which was the minority phase (Table 2). The average crystallite sizes of anatase and rutile were larger when annealing temperature increased. The nanocrystalline character of the phases gives rise to large specific surface areas that could be attractive for catalysis.

Samples with 50 wt % MgO and 50 wt % TiO_2. The fresh samples were a mixture of the precursors and an amorphous phase that was stable even when the sample was heated at 200 °C. When fresh samples were annealed, they showed an exothermic reaction at 208 °C (Figure 5b), causing a sample weight loss of 27.5% (Figure 6b). Their annealing at higher temperatures gave rise to three more endothermic reactions at 300, 361, and 393 °C, which produced an additional weight loss of 22%.

The samples annealed at 400 °C were a mixture of 78.9(8) wt % periclase, 16.1(9) wt % geikielite, 4.6(6) wt % qandilite, and 0.4(1) wt % anatase (Figure 2a and Table 2). Their annealing from 400 to 500 °C caused an exothermic reaction and a weight loss of 9.2% (Figures 5b and 6b), and the transformation of periclase into qandilite (Table 2). For temperatures between 500 and 800 °C, the TG and DTA curves were almost temperature independent, which shows that the transformations occurred slowly with temperature. The samples annealed at 800 °C contained nearly 50 wt % periclase, and the other half of the sample distributed among karooite, geikielite, and qandilite (Figure 2c and Table 2).

For the present MgO concentration, all phases, except anatase, the minority phase, were nanocrystalline with average crystallite sizes that became larger when the annealing temperature was increased (Table 5).

Samples with 90 wt % MgO and 10 wt % TiO_2. Although these samples were magnesium rich, when they were annealed at 200 °C, brucite, the typical phase obtained at this temperature in pure magnesia, was not observed. The samples annealed at this temperature produced a diffraction pattern similar to the one reported for pure MgO prepared by using the sol–gel technique with acetic acid as hydrolysis catalyst.[20]

The fresh samples showed an exothermic peak at 200 °C (Figure 5c) produced by the reaction between their phases, which gave rise to a weight loss of 28.9% (Figure 6c). Between 260 and 400 °C, the samples presented an endothermic reaction, which produced nanocrystalline MgO, and an additional weight loss of 18.7% caused by the dehydroxylation of the sample (Figure 3a and Table 2).

Since MgO was the only crystalline phase observed when the sample was annealed at 400 °C (Table 1), the titanium in the sample must be either dissolved in the crystalline structure of MgO or forming a compound with magnesium and oxygen. Because the lattice parameters of MgO were equal to those obtained in pure periclase, the solution of titanium in its crystalline structure must be discarded. If titanium was in qandilite, this phase would have a crystallite size so small that its diffraction pattern was hidden in background. The titanium in the sample appeared when it was annealed at 600 °C (Figure 3b), because the sample was composed of 94.5(1.4) wt % periclase, 0.5(1) wt % geikielite, and 5(1) wt % qandilite with an average crystallite size of only 11(3) nm, which supports the assumption that it is present with a very small average crystallite size in the sample annealed at 400 °C.

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The partial transformation of MgO into qandilite and geikielite was associated with the exothermic peaks observed at 420 and 483 °C (Figure 5c) and the weight loss of 13.5% produced by the further sample dehydroxylation (Figure 6c). Since the qandilite concentration was larger that the one of geikielite, the exothermic peak observed at 420 °C, which is larger than the peak at 483 °C, can be associated with the formation of qandilite. The exothermic peak at 483 °C should then be associated to the formation of geikielite. No more transformations of the sample were observed at temperatures above 600 °C. In this temperature range, the effect of annealing was mainly to increase the average crystallite size (Table 5 and Figure 3c).

Conclusions

In the samples of the $MgO-TiO_2$ system prepared with the sol−gel technique, additional to the stable phases of magnesia and titania, periclase, anatase, and rutile, three intermediate compounds were produced: karooite ($MgTi_2O_5$), geikielite ($MgTiO_3$), and qandilite (Mg_2TiO_2) in concentrations that depended on MgO to TiO_2 weight ratio and the annealing temperature of the sample. Prior to the formation of the intermediate compounds, the samples showed an exothermic reaction at 200 °C, and a continuous dehydroxylation above 300 °C. Magnesium was soluble in anatase, but not in rutile. Its solubility, however, was lower than the one observed for calcium. Karooite was abundant only in titania-rich samples, and geikielite and qandilite in the samples with equal magnesia to titania weight ratio. Almost all phases were nanocrystalline, which generates samples with large surface areas that would be of interest in catalysis.

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