

Chemical and Phase Transformations of Nanocrystalline Oxides in a Carbon Nanoreactor

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ABSTRACT

The application of nanocrystalline oxides as precursors for synthesis of new nanomaterials with the preservation of the dimensions of the initial nanoparticles is of considerable interest. A promising approach to the overcoming the problem of the sintering and growth of the nanoparticles during the solid-state chemical is the deposition of a coating on the surface of the precursor nanoparticles that would prevent their sintering. Current study was devoted to the investigation of the solid-state phase and chemical transformations of nanocrystalline TiO₂, MgO and Al₂O₃ coated with carbon. Such coating appeared to be penetrable by the molecules present in the gas phase. The anatase phase in all synthesized C@TiO₂ nanocomposites could be completely converted to TiOF₂ in the reaction with halocarbons. Overall, it is possible to deposit an intelligent carbon coating on the surface of the oxide nanoparticles that would prevent their sintering and make it possible to synthesize new nanomaterials.

Keywords: carbon nanoreactor, destructive sorption, halocarbons, nanocrystalline oxides

1 INTRODUCTION

Nanocrystals of common metal oxides such as MgO, CaO, ZnO, TiO₂, Al₂O₃, and Fe₂O₃, have been shown to be highly efficient and active adsorbents for many toxic chemicals including air pollutants, chemical warfare agents, and acid gases [1-8]. In most cases, destructive adsorption takes place on the surface of the nanocrystals, so that the adsorbate is chemically dismantled and thereby made nontoxic. In particular, aerogel-prepared (AP) nanocrystalline MgO has been shown to have small average particle size (~ 4nm), high surface area (> 500 m²/g) and high reactivity [1, 5]. At elevated temperatures, chlorocarbon reactions can be driven to stoichiometric proportions, especially if small amounts of transition metal catalysts are added.

The use of these nanocrystalline metal oxides is limited under conditions where liquid water or water vapor is present due to their tendency to adsorb water, and thereby be partially deactivated toward adsorption of the target pollutants. Although the target pollutants are usually subjected to conversion in the presence of water as well, relatively large amounts of water can mitigate against the

adsorption of the target adsorbate decreasing the efficiency of the destructive adsorbent. We have shown that coating destructive sorbent with an intelligent carbon layer significantly improves the stability of such nanocrystalline materials in the presence of water and the possible time of their storage in air in comparison with not coated nanoscale oxides without a considerable loss of activity [9]. For practical application of nanoscale oxides as destructive sorbents, it is extremely important that the carbon coating makes such materials hydrophobic.

In the current publication we shall discuss the specific features of the reactions of nanoscale MgO and TiO₂ with chlorofluorocarbons and the effect of carbon on the performance of the destructive sorbents.

2 EXPERIMENTAL

AP-MgO with the surface area of 385 m²/g was prepared by a sol-gel technique involving high-temperature supercritical drying described in detail earlier [4, 9]. The final preparation step was overnight evacuation at 500°C.

A flow reactor equipped with a McBain spring balance and an on-line gas chromatograph was used in the flow experiments. This made it possible to monitor both the composition of the products and the sample weight during the reaction. The sensitivity in the determination of the sample weight was 10⁻⁴ g. CF₂Cl₂ and CFCI₃ of “pure” grade and Ar of “ultra pure” grade were used in the experiments. The halocarbon was passed through the reactor with a volume rate of 3 L/h. MgO sample weight was 0.05-0.1 g. The samples were activated in argon flow at 500°C for 30 min.

The same flow reactor equipped with a McBain spring balance was used for “in situ” carbon formation. AP-MgO was placed in a quartz basket and placed on a spring. This allowed for measuring of the sample weight change and accurate determination of carbon percentage in the sample. Then, the sample was heated under a flow of argon, at 500 °C for 1 hour. After that butadiene used as a carbon source was added to the flow. The flow rates were: butadiene - 7.5 L/h; argon - 75 L/h. Initial carbon formation occurred at a rate of approximately 2 wt. % per hour. After the desired amount of carbon was obtained, the butadiene flow was stopped and the product was cooled to room temperature under an argon flow.

Two TiO₂ samples were used in the experiments: Degussa P-25 and Nanoactive TiO₂ (Nanoscale Materials). Before the experiments, the samples were calcined in an

argon flow at 500°C for 1 h. Then, the temperature was decreased to the desired reaction temperature, and the halocarbon flow was turned on. The standard reaction time was 30 min. Then, the sample was cooled in the argon flow to room temperature. The products were analyzed using a Shimadzu GCMS-QP5000 gas chromatograph mass spectrometer equipped with a 30 m Restec capillary column with XTI-5 phase. XRD studies were performed using a Bruker D8 instrument with $\text{CuK}\alpha$ monochromatic irradiation.

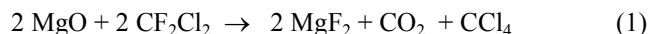
3 RESULTS AND DISCUSSION

3.1 Effect of carbon coating on MgO reaction with CF_2Cl_2

CF_2Cl_2 is a colorless and odorless gas, which is chemically very inert and has a high thermal stability. It appeared to react with nanoscale MgO at temperatures as low as 325°C to give a significant gain of the sample weight as evidenced by kinetic curves presented in Figure 1. The presence of an obvious induction period, after which an intense gain of the sample weight starts, is the most distinctive and interesting feature of the kinetic curves.

The induction period phenomenon is reproduced with 100% probability, and its duration is reproduced with ca. 5-10% accuracy when all conditions are kept the same. The existence of an induction period on the kinetic curve must be connected with gradual accumulation of certain active sites or defects on the MgO surface, which eventually lead to complete transformation of the nanoparticles. As soon as enough active sites are accumulated, intense bulk substitution of oxygen by fluorine starts. Note that the weight gain stops at values close to 40% indicating the end of the reaction. The maximum theoretical weight gain corresponding to complete transformation of the oxide to fluoride is 55%. This indicates that about 80% transformation is actually achieved in our experiments.

The main products resulting from the AP-MgO reaction with CF_2Cl_2 are MgF_2 , CO_2 and CCl_4 [10] formed according to overall reaction (1). The former is identified as the only solid phase according to the XRD and HRTEM data. CCl_4 appears to result from CF_2Cl_2 exchange reaction with partially chlorinated MgO/MgF₂ surface.



We have earlier shown that carbon-coated AP-MgO has improved stability in the presence of water and the possible storage time in air in comparison with not coated nanoscale MgO [9]. Our EPR investigation of the active basic sites present on the surface of AP-MgO partially covered with carbon showed that samples containing 10% carbon or less retain significant amounts of open active sites that are available for destructive adsorption reactions [11]. So, it was interesting to study how the introduction of such

carbon coating affects the AP-MgO reactivity with respect to destructive adsorption of halocarbons.

Unexpectedly we observed that the carbon coating improves the reactivity of AP-MgO in destructive adsorption of CF_2Cl_2 . Its reaction with AP-MgO is characterized by a prolonged induction period that is nearly 1 h long at 400°C (Fig. 1). The addition of only 1 wt.% carbon significantly shortens the induction period, while induction period over 10% C/AP-MgO was 3 times shorter than over AP-MgO. Similar results were obtained in the reaction with another halocarbon CFCl_3 .

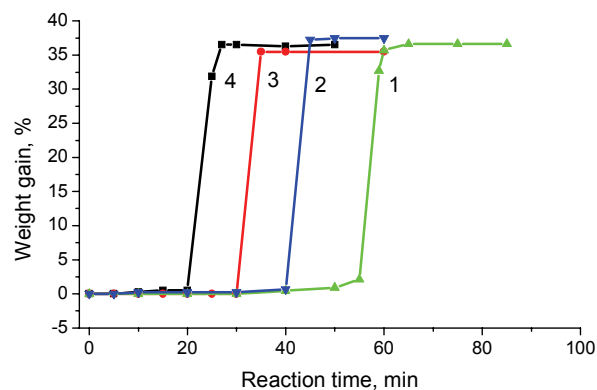
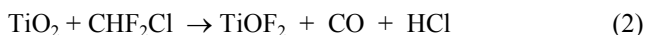


Figure 1. Kinetic weight gain curves of AP-MgO (1), 1% C/AP-MgO (2), 3% C/AP-MgO (3) and 10% C/AP-MgO (4) treated with CF_2Cl_2 at 400°C.

3.2 Phase selectivity in solid-state transformation of nano- TiO_2 to TiOF_2

The phase composition of the oxide nanoparticles appeared to be another parameter having a significant effect on such reactions. Relatively easily the phase composition and size of the nanoparticles can be regulated for titanium dioxide. We have studied reaction of nanocrystalline TiO_2 samples with CHF_2Cl resulting in the formation of a new chemical compound titanium oxyfluoride:



The reaction was studied in the flow of the halocarbon at different temperatures. Its kinetics appeared to be significantly dependent on the size of TiO_2 nanoparticles and their crystalline phase. Figure 2 presents the XRD spectra characterizing the solid products of the reaction of Degussa P-25 TiO_2 with CHF_2Cl at different temperatures. The initial TiO_2 sample (spectrum 1) consists of a mixture of anatase (~75%) and rutile (~25%) with the particle size about 25 nm. The reaction with CHF_2Cl leads to the formation of a new solid product identified by XRD as TiOF_2 and decrease in the intensity of anatase lines (spectra 2 and 3). Note that even after complete transformation of anatase the lines of rutile remain unchanged (spectrum 3).

No reaction of rutile with CHF_2Cl was observed even when the reaction temperature was increased to 400°C .

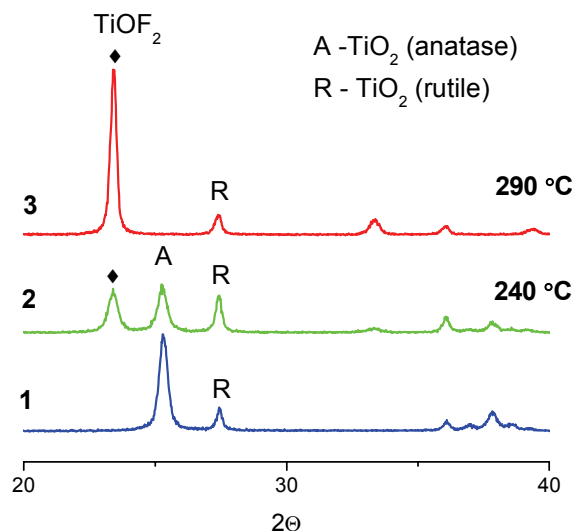


Figure 2. XRD spectra of Degussa P-25 TiO_2 before reaction (1) and after reaction with CHF_2Cl at 240°C (2) and 290°C (3).

The observed phase selectivity phenomenon vividly shows that the crystalline phase of titania nanoparticles has a major effect on their reactivity. This reaction can be used for preparation of pure nanoscale rutile phase for use as a photocatalyst.

Using Nanoactive TiO_2 prepared by sol-gel technology it is possible to prepare sample with different particle size and phase composition by simply varying the heat treatment temperature. For example, after calcination at 500°C for 1 h the average size of nanoparticles according to the XRD data is about 15 nm, and anatase is the only identified crystalline phase. Its reaction with CHF_2Cl at temperature as low as 240°C results in almost complete TiO_2 transformation to TiOF_2 . This temperature is 50°C lower than the temperature required for complete conversion of 25 nm anatase nanoparticles. Thus, similar to reactions of halocarbons with MgO , a decrease of the TiO_2 particle size allows for a significant decrease of the temperature necessary for complete conversion of solid phase nanoparticles.

According to the XRD data, the particle size of reaction product TiOF_2 is similar to that of the nanoparticles of the initial TiO_2 . The surface area of the material also does not change much. These results prove that such reactions can be used for synthesis of new halogenated nanocrystalline materials using nanocrystalline oxide as precursors.

3.3 Effect of carbon on the solid-state transformations of TiO_2 and Al_2O_3

Current study was devoted to the investigation of the solid-state phase and chemical transformations of nanocrystalline TiO_2 and Al_2O_3 with carbon coatings obtained by CVD method and by decomposition of polyvinyl alcohol. In all cases the carbon coating acting as a carbon nanoreactor prevented the sintering of the nanoparticles and helped to stabilize their size. The dimensions of the anatase nanoparticles in such C@TiO_2 nanocomposites could be stabilized at 10-12 nm. Almost no rutile was observed by XRD even after calcination at 750°C (Fig. 3, curve 3). This is due to the thermodynamic stability of the anatase phase at small particle size. Meanwhile, pure TiO_2 without the carbon coating was almost completely transformed to rutile under the same conditions (Fig. 3, curve 2)..

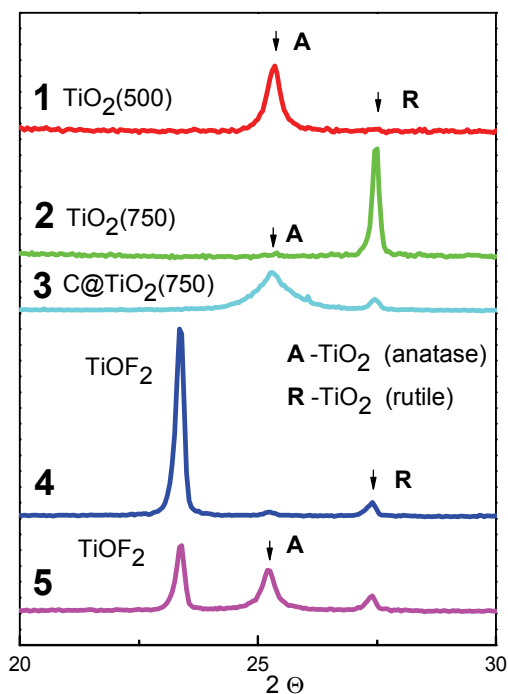


Figure 3. XRD patterns registered for nanocrystalline TiO_2 (1,2) and C@TiO_2 (3-5) after heating at 500° (1) and 750°C (2,3), after reaction of C@TiO_2 with CF_2Cl_2 at 330°C (4) and following hydrolysis at 310°C (5).

Meanwhile, such coating appeared to be penetrable by the molecules present in the gas phase. The anatase phase in all synthesized C@TiO_2 nanocomposites could be completely converted to TiOF_2 in the reaction with CHF_2Cl and CF_2Cl_2 halocarbons (Fig. 3, curve 4). The analysis of the reaction product by HRTEM coupled with EDX detected TiOF_2 nanoparticles with typical dimensions 10-15 nm inside the

carbon coating. Their size was close to that of the initial anatase nanoparticles. Intriguingly, this reaction was phase-selective. Only anatase nanoparticles were converted, whereas rutile, if present in the precursor, was totally inactive. The synthesized TiOF_2 nanoparticles could be converted to an interesting nanostructured anatase by hydrolysis in humid air (Fig. 4).

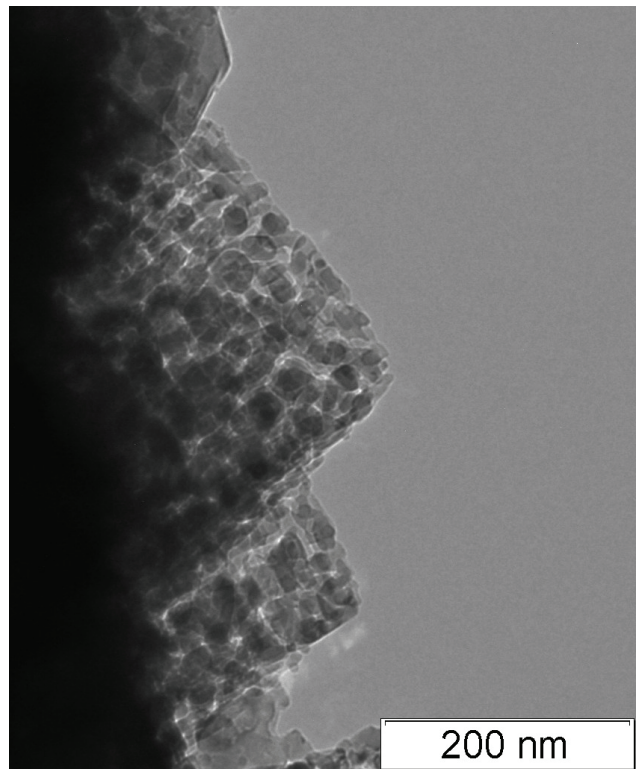


Figure 4. HRTEM image of nanostructured anatase prepared by TiOF_2 hydrolysis in humid air.

Similar results were also obtained for the phase transformations ($\gamma \rightarrow \theta \rightarrow \alpha$) in $\text{C@}\gamma\text{-Al}_2\text{O}_3$ nanocomposites. The nanoparticles inside the carbon shell are resistant to sintering until very high temperatures (1000°C for Al_2O_3). It was shown that such method can be used to synthesize a carbon film on the surface of Al_2O_3 nanoparticles without substantial changes of the initial oxide morphology. The phase transformations of such $\text{C@}\gamma\text{-Al}_2\text{O}_3$ core-shell samples from gamma to delta and, then, alpha alumina phase were studied by laser-induced luminescence, XRD, TEM and adsorption methods up to 1150°C . It was shown that the carbon coating prevents sintering of the Al_2O_3 nanoparticles and as a result prevents the corundum phase from being formed at such temperatures even in low concentrations.

4 CONCLUSIONS

We have demonstrated that nanocrystalline oxides can be used as precursors for synthesis of novel halogenated nanocrystalline materials. Of special interest are composite

materials consisting of carbon-coated nanocrystalline oxides. Such permeable carbon coating not only provides high stability of the destructive sorbents under atmospheric conditions, but in some cases shown in this publication considerably increases their reactivity.

The carbon coating deposited on the oxide nanoparticles prevents their sintering and makes it possible to synthesize new nanomaterials with nanoparticle dimensions close to those of the initial oxide precursors. The preservation of the small size of the oxide nanoparticles inside such carbon nanoreactor is a key factor preventing the phase transformation in the studied C@TiO_2 and $\text{C@}\gamma\text{-Al}_2\text{O}_3$ nanocomposites.

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