Research Article

Photodegradation of Rhodamine B in Presence of CaO and NiO-CaO Catalysts

Tobias Kornprobst and Johann Plank

Chair for Construction Chemicals, Technische Universität München, Lichtenbergstraße 4, 85747 Garching bei München, Germany

Correspondence should be addressed to Johann Plank, sekretariat@bauchemie.ch.tum.de

Received 2 April 2012; Accepted 2 May 2012

Academic Editor: Leonardo Palmisano

Copyright © 2012 T. Kornprobst and J. Plank. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A CaO catalyst was prepared by mild calcination (650°C) of facilely precipitated $\text{Ca}(\text{OH})_2$ and compared to an NiO-CaO catalyst obtained from an $\text{Ni}(\text{OH})_2/\text{Ca}(\text{OH})_2$ coprecipitate as a precursor. Both catalysts degraded rhodamine B (RB) effectively when exposed to ultraviolet light but exhibited slower degradation under visible light conditions. Under UV light, CaO was more effective than NiO-CaO, while in visible light, the opposite was observed. A mechanistic study revealed no influence of the specific surface area of the catalysts on RB degradation, no adsorption of RB on the positively charged surfaces of the catalysts, and only incomplete degradation of RB. Consequently, both materials represent nonconventional photocatalysts.

1. Introduction

Photocatalytic processes deliver solutions for a number of environmental applications, such as water purification [1–3], reduction of air pollution [4, 5], or self-cleaning surfaces of building materials [6–8]. Also, in environmentally friendly energy production, which definitely is one of the key challenges for the next decades, photocatalytic processes exhibit considerable potential [9].

Conventional photocatalysis involves semiconductors such as TiO_2 , ZnO, titanates, and niobates [10–12]. Today, the largest commercial application of photocatalysts lies in the field of construction materials. There, more than 10,000 tons of TiO_2 photocatalysts are used annually in indoor wall paints and plasters for air purification [13], on roof shingles and in tile grouts possessing self-cleaning properties, and for road pavements, which reduce exhaust gas pollutants from car traffic [5].

Conventional TiO_2 (anatase), which is used in most commercial applications, requires sunlight to achieve the photocatalytic effect. For indoor applications, TiO_2 doped with carbon or nitrogen that can work with visible light has been developed [14, 15].

Recently, novel photocatalysts based on coupled metal oxides (e.g., ZnO/SnO_2) were introduced [16]. Also, an

NiO-CaO photocatalyst effective even under visible light conditions was presented [17, 18]. Obviously, a CaO-based photocatalyst would be highly interesting for building material applications because of its low cost and compatibility with cement binders. Here, we studied the photocatalytic activity of pure, mildly calcined CaO and compared our results with those reported earlier for the NiO-CaO catalyst.

2. Experimental

2.1. Chemicals. Titan dioxide (Aeroxide P25, Evonik Degussa GmbH, Essen/Germany) was used as received. All other chemicals (analytical grade) purchased from Merck KGaA, Darmstadt/Germany, were used without further purification. Deionised (DI) water obtained from a Nanopure system (Barnstead International, Dubuque, IA/USA) was used.

2.2. Catalyst Preparation

2.2.1. CaO. Under vigorous stirring, aqueous sodium hydroxide solution (4 mol/L) was combined with aqueous $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution (2 mol/L) at 1:1 volume ratio. After stirring for 30 min, the colourless precipitate was separated by centrifugation (10 min, 10,000 g), washed two times with DI water, dried at 110°C for 3 h, and then calcined at

650°C for 15 h in a platinum crucible. The colourless solid was stored carefully under air exclusion, ground thoroughly directly before use, and identified as CaO-2.

Additional catalysts were prepared from higher (5 mol/L) and lower (0.5 mol/L) concentrated calcium nitrate solutions, always using a molar ratio of NaOH : Ca(NO₃)₂ of 2 : 1. These products were labelled as CaO-0.5 and CaO-5.

2.2.2. NiO-CaO. For comparison, an NiO-CaO catalyst was prepared from 4 mol/L Ni(NO₃)₂·6H₂O and 4 mol/L Ca(NO₃)₂·4H₂O solutions (combined at volume ratio 1 : 1) by mixing with NaOH (8 mol/L) at molar ratio 2 : 1 under vigorous stirring as described in [18]. An aqueous sodium hydroxide solution was prepared in a 2 : 1 molar ratio relative to the concentration of metal ions in the above solution. Under vigorous stirring, the sodium hydroxide solution was added to the metal nitrates solution in a 1 : 1 volume ratio. All further processing was done as described above for the CaO catalyst.

2.3. Catalyst Characterization. Powder X-ray diffraction (XRD) measurements were carried out on a D8 Advance diffractometer (Bruker AXS, Karlsruhe/Germany) with Bragg-Brentano geometry, equipped with a two-dimensional Vantec-1 detector (Bruker AXS).

Scanning electron microscopy (SEM) was performed on an XL30 ESEM FEG microscope (Philips/FEI Company, Eindhoven/Netherlands) equipped with an energy dispersive X-ray detector (EDX) for elemental analyses (New XL30, EDAX Inc., Mahwah, NJ, USA).

Specific surface area of the catalysts was determined by BET method (N₂, Nova 4000e, Quantachrome Instruments, Boynton Beach, FL, USA). Prior to measurement, all samples were heated for 2 h to 200°C.

Surface charge of particles (zeta potential) was measured on a Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, England). The catalysts were dispersed in DI water ($c = 10^{-2}$ g/L) by sonication for 10 min. Averages of 3 independent measurements were taken.

2.4. Testing of Photoactivity. Photodegradation activity was tested by monitoring the degradation of 10^{-5} mol/L aqueous rhodamine B (RB) solution. Rhodamine B was chosen as model compound because of its high stability in native light, while methylene blue (MB), which was used in a similar study before [17, 18], is strongly degraded even in the absence of any photocatalyst (Figure 1). Therefore, it is not suitable for photodegradation studies under visible light conditions.

For the photo degradation experiments, the solid catalysts were dispersed in RB solution by sonication for 10 min. Catalyst dosages used were 10 mg/mL for CaO and NiO-CaO, and 1 mg/mL for TiO₂. As reference, an RB solution holding no catalyst was employed.

For studies under visible light conditions, 50 mL of each catalyst suspension were transferred to a standard 100 mL beaker and placed in a sunlight simulation chamber (Suntest CPS+, Atlas MTS, Linsengericht, Germany) equipped with a window glass filter to cut off UV light of low wavelength.

FIGURE 1: Time-dependent degradation of methylene blue and rhodamine B under visible light conditions in absence of photocatalysts.

Irradiation intensity was set to 750 W/m² to ensure high reaction rates.

For studies under UV light, the catalyst suspensions were transferred into glass petri dishes (5.3 cm × 1.4 cm) and a UV lamp (NU-8 KL, Benda Laborgeraete, Wiesloch/Germany) was placed directly on top. The UV lamp possesses 2 tubes, which produce UV light at 254 nm and 365 nm (8 W each) and can be operated independently.

At specific irradiation times, samples were taken from the suspension, the catalyst was removed by centrifugation (3 min, 20.000 g), and the RB concentration was determined by absorbance measurements in quartz glass cuvettes (SpectroFlex 6100 photometer, WTW GmbH, Weilheim/Germany) at 554 nm, where RB shows a maximum in light absorption. A calibration curve was developed, showing linear relationship between RB concentration and absorbance. Averages of three independent measurements were recorded.

2.5. pH-Dependent Charge of RB. RB solutions (10^{-3} mol/L) were prepared, and the pH value was adjusted with Ca(OH)₂ in a range of 7–12.7. Measurements of the streaming potential were performed on a particle charge detector (Mütek PCD-03, BTG S.A, Eclépens/CH).

2.6. Adsorption Studies. RB adsorption on the catalysts was performed by filling RB solutions (concentrations $5 \cdot 10^{-7}$ – $1.2 \cdot 10^{-4}$ mol/L) into 20 mL glass vials, followed by addition of catalyst (weight ratio catalyst/solution 1 : 10) and sonication for 10 min. The samples were stored in darkness for 1 h to equilibrate; thereafter, the solid was separated by filtration (0.2 µm syringe filter). Pure RB reference solution was treated in the same way. The concentration of unadsorbed RB present in the supernatant was determined from absorbance measurements using the calibration curve from above. From this, the amount of RB adsorbed (in mg/gram catalyst) was calculated.

FIGURE 2: SEM micrographs of synthesized catalysts: (a) CaO-0.5, (b) CaO-2, (c) CaO-5, and (d) NiO-CaO (magnification: 10,000x).

3. Results and Discussion

3.1. Catalyst Characterization. Powder XRD confirmed high purity of CaO as prepared (no signals for CaCO_3 and only minor amounts of Ca(OH)_2 resulting from air humidity were detectable). For NiO-CaO, a mixture of bunsenite (NiO) and CaO at a molar ratio of 1 : 1 (EDX atom percentage: Ni 25%, Ca 23%, O 52%; calculated: Ni 25%, Ca 25%, O 50%;) was found, while the XRD diagram of TiO_2 shows ~90% anatase and ~10% rutile.

SEM micrographs of CaO show particles exhibiting an extremely smooth, glassy surface similar to that of sintered ceramics (Figure 2). This distinguishes the material obtained from this specific process from conventional CaO produced by standard calcination of CaCO_3 at temperatures $\geq 850^\circ\text{C}$. There, in spite of many attempts utilising a broad range of preparation conditions (temperatures and calcination times), we never obtained a material exhibiting this glassy, annealed surface. Only minor photodegradation of RB was observed for the CaO samples produced from this conventional calcination at $850\text{--}1400^\circ\text{C}$. Variation of the $\text{Ca(NO}_3)_2$ concentration significantly influences the particle sizes of the CaO catalyst. At increased concentrations, particle size increases correspondingly (Figure 2).

In contrast to CaO, the NiO-CaO catalyst shows a relatively coarse surface structure. There, nanoparticles are dispersed across the surface (Figure 2(d)).

The specific surface areas (N_2 , BET) of the catalysts were as follows: CaO-2, CaO-5, and NiO-CaO $< 1 \text{ m}^2/\text{g}$ (which is very low for catalysts), CaO-0.5 $4.2 \text{ m}^2/\text{g}$, and TiO_2 $49 \text{ m}^2/\text{g}$.

TABLE 1: Zeta potentials of aqueous suspensions of the catalysts.

Catalyst	Zeta potential [mV]	pH value of suspension
CaO-2	+12.4	12.7
NiO-CaO	+24.7	12.7
TiO_2	−9.1	7.0

Surface charges (zeta potential) of the catalyst suspensions ($c = 10 \text{ g/L}$) were determined at their native pH, as is shown in Table 1. The surface charges of CaO and NiO-CaO are highly positive, while TiO_2 exhibits a negative zeta potential.

3.2. Activity of Catalysts. At first, the catalyst samples holding RB were exposed to normal room light conditions by placing them on a lab bench indoor. Under these conditions, none of the catalysts showed any effectiveness, even after several hours of storage.

Next, the samples were exposed to visible light of much higher intensity by utilising the Suntest chamber equipped with a window glass filter (Figure 3). There, TiO_2 showed the best performance. Complete degradation of RB was achieved within less than 60 min. CaO-2 and NiO-CaO only showed a minor degradation, with the activity of NiO-CaO being slightly higher compared to that of CaO-2.

The high effectiveness of undoped TiO_2 in the previous experiment indicated the presence of a certain amount of light in the near UV range. Thus, additional experiments in UV light of different wavelengths were conducted in order

FIGURE 3: Photodegradation of RB solutions holding different catalysts, exposed to visible light in an irradiation chamber: light intensity 750 W/m².

FIGURE 4: Photodegradation of RB solutions holding different catalysts, exposed to UV light wavelengths 254 and 365 nm.

to study the performance of the catalysts under various UV light conditions.

First, combined irradiation at wavelengths of 254 and 365 nm (Figure 4) was performed. As expected, the most effective catalyst was TiO₂, which achieved complete degradation within 40 minutes. The CaO-2 catalyst degraded RB within 120 min. Opposite to this, the NiO-CaO catalyst was unable to fully degrade RB within 120 min. It achieved only ~60% reduction of the initial RB concentration. This compares with 25% degradation for the sample holding no catalyst. Still, in this experiment both NiO-CaO and CaO-2 exhibited a highly increased performance compared to visible light conditions.

FIGURE 5: Photodegradation of RB solutions holding different catalysts, exposed to near UV light (wavelength 365 nm).

Exposure to 254 nm UV light only produced the same results as above. The order of effectiveness was the same for all catalysts tested.

Next, the samples were irradiated under near UV light (wavelength 365 nm) only (Figure 5). Under those conditions, the CaO-2 and NiO-CaO catalysts exhibited a much reduced effectiveness, while TiO₂ still performed well. The results from this experiment compare well with those from visible light experiments.

The experiments allowed to conclude that the CaO-2 and NiO-CaO catalysts effectively degrade RB only when exposed to high energy ultraviolet light (254 nm). Therefore, they can degrade pollutants only under UV light conditions, while their visible light activity is comparatively low. Also, lower UV irradiation energy (365 nm) generally decreases their effectiveness significantly. Generally, pure CaO was found to be more effective than NiO-CaO under UV light conditions. Contrary to a previous report [18], only minor visible light activity was found for NiO-CaO and almost none for the CaO catalyst.

The results from above pose the question whether CaO and NiO-CaO are indeed photocatalysts. Thus, the mechanism underlying the photoactivity of CaO was studied.

3.3. Influence of Particle Size on Photoactivity of CaO. Classic semiconductor photocatalysis requires adsorption of the substrate on the surface of the photocatalyst to allow for photo-induced electron transfer processes, which lead to the formation of radicals and ultimately to complete degradation of the substrate. According to this specific mechanism, the degradation rate will increase with the specific surface area of the catalyst.

CaO samples possessing different specific surface areas (CaO-0.5, CaO-2 and CaO-5) were applied to aqueous RB solutions and exposed to the 254 and 365 nm UV light source. Surprisingly, all CaO samples exhibited the same degradation effectiveness. No influence of the catalyst's

FIGURE 6: pH-dependent streaming potential (charge) of rhodamine B in aqueous solution ($c = 10^{-3}$ mol/L), pH adjusted with $\text{Ca}(\text{OH})_2$.

surface area was apparent. Obviously, this CaO is not a photocatalyst as was reported in an earlier publication [18]. Also, this result clearly contradicts the mechanism known from conventional semiconductor photocatalysis.

3.4. Adsorption Studies. To investigate the mechanism of photodegradation, the adsorption behaviour of RB on CaO-2 was determined and compared with that on TiO_2 .

First, the charge amount of the RB molecule at pH 7–12.7 was determined (Figure 6). pH 7 represents the pH occurring in the TiO_2 catalyst suspension, while 12.7 is the pH of the CaO-2 slurry. At pH = 7, a strongly positive charge was found for RB, which decreased with increasing pH to a very slightly negative charge at pH 12.7. The isoelectric point was found to lie at pH 12.6.

The adsorption isotherms for RB on CaO-2 and TiO_2 , respectively, are shown in Figure 7.

TiO_2 , which possesses negative surface charge at pH 7 (Table 1), can adsorb considerable amounts of cationic RB. Up to a concentration of $\sim 5 \cdot 10^{-6}$ mol/L, RB is quantitatively depleted from the solution. At higher RB concentrations, the isotherm levels to a plateau, representing the state of saturated adsorption.

For CaO-2, however, no adsorption was detected. Obviously, at pH 12.7 the anionic character of RB is not high enough to adsorb on the positively charged surface of CaO-2.

The absence of adsorption strongly dispels a mechanism similar to that underlying conventional photocatalysis. Additionally, measurements of the carbon content (TOC) in the supernatant of RB solutions decoloured by CaO-2 still confirmed high organic loading, which was not the case for TiO_2 . Thus, only a partial degradation takes place, which involves decomposition of the chromophore present in the dye. This signifies that the photo-induced process observed here is completely different from conventional semiconductor photocatalysis.

FIGURE 7: Adsorption isotherms for RB on CaO-2 and TiO_2 catalysts.

4. Conclusion

CaO and NiO-CaO catalysts prepared by mild calcination of precipitates obtained from NaOH and $\text{Ca}(\text{NO}_3)_2$ or $\text{Ni}(\text{NO}_3)_2/\text{Ca}(\text{NO}_3)_2$ solutions effectively degrade rhodamine B when exposed to ultraviolet light. CaO was found to be more effective than NiO-CaO. However, contrary to previous reports, both catalysts exhibit only poor performance under visible light conditions. Our study suggests that photodegradation of rhodamine B by CaO and NiO-CaO does not follow the well-known adsorption-electron transfer process involving semiconductors. More likely, a photochemical process initiated by the presence of the metal oxides occurs. Its mechanism will be the subject of further investigation.

References

- [1] M. R. Hoffmann, S. T. Martin, W. Y. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.
- [2] A. Matilainen and M. Sillanpää, "Removal of natural organic matter from drinking water by advanced oxidation processes," *Chemosphere*, vol. 80, no. 4, pp. 351–365, 2010.
- [3] K. Pirkanniemi and M. Sillanpää, "Heterogeneous water phase catalysis as an environmental application: a review," *Chemosphere*, vol. 48, no. 10, pp. 1047–1060, 2002.
- [4] M. M. Ballari, Q. L. Yu, and H. J. H. Brouwers, "Experimental study of the NO and NO_2 degradation by photocatalytically active concrete," *Catalysis Today*, vol. 161, no. 1, pp. 175–180, 2011.
- [5] M. Hunger, G. Husken, and H. J. H. Brouwers, "Photocatalytic degradation of air pollutants—from modeling to large scale application," *Cement and Concrete Research*, vol. 40, no. 2, pp. 313–320, 2010.

- [6] G. Bolte, "Innovative building materials—reduction of pollutants with TioCem," *ZKG International*, vol. 62, no. 1, pp. 63–70, 2009.
- [7] S. Guo, Z. Wu, and W. Zhao, "TiO₂-based building materials: above and beyond traditional applications," *Chinese Science Bulletin*, vol. 54, no. 7, pp. 1137–1142, 2009.
- [8] M. Hunger, G. Husken, and J. Brouwers, "Photocatalysis applied to concrete products," *ZKG International*, vol. 61, no. 10, pp. 76–84, 2008.
- [9] D. Arney, T. Watkins, and P. A. Maggard, "Effects of particle surface areas and microstructures on photocatalytic H₂ and O₂ production over PbTiO₃," *Journal of the American Ceramic Society*, vol. 94, no. 5, pp. 1483–1489, 2011.
- [10] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [11] M. Miyauchi, M. Takashio, and H. Tobimatsu, "Photocatalytic activity of SrTiO₃ codoped with nitrogen and lanthanum under visible light illumination," *Langmuir*, vol. 20, no. 1, pp. 232–236, 2004.
- [12] Y. Lai, M. Meng, Y. Yu, X. Wang, and T. Ding, "Photoluminescence and photocatalysis of the flower-like nano-ZnO photocatalysts prepared by a facile hydrothermal method with or without ultrasonic assistance," *Applied Catalysis B*, vol. 105, no. 3–4, pp. 335–345, 2011.
- [13] S. Laufs, G. Burgeth, W. Duttlinger et al., "Conversion of nitrogen oxides on commercial photocatalytic dispersion paints," *Atmospheric Environment*, vol. 44, no. 19, pp. 2341–2349, 2010.
- [14] E. A. Konstantinova, A. I. Kokorin, S. Sakthivel, H. Kisch, and K. Lips, "Carbon-doped titanium dioxide: visible light photocatalysis and EPR investigation," *Chimia*, vol. 61, no. 12, pp. 810–814, 2007.
- [15] S. Sakthivel, M. Janczarek, and H. Kisch, "Visible light activity and photoelectrochemical properties of nitrogen-doped TiO₂," *Journal of Physical Chemistry B*, vol. 108, no. 50, pp. 19384–19387, 2004.
- [16] W. Cun, Z. Jincai, W. Xinming et al., "Preparation, characterization and photocatalytic activity of nano-sized ZnO/SnO₂ coupled photocatalysts," *Applied Catalysis B*, vol. 39, no. 3, pp. 269–279, 2002.
- [17] L. Song and S. Zhang, "A simple mechanical mixing method for preparation of visible-light-sensitive NiO–CaO composite photocatalysts with high photocatalytic activity," *Journal of Hazardous Materials*, vol. 174, no. 1–3, pp. 563–566, 2010.
- [18] L. Song, S. Zhang, B. Chen, and D. Sun, "Highly active NiO–CaO photocatalyst for degrading organic contaminants under visible-light irradiation," *Catalysis Communications*, vol. 10, no. 5, pp. 421–423, 2009.