Bulgarian Chemical Communications, Volume 47, Number 1 (pp. 317–322) 2015

TiO_2 obtained from mechanically activated ilmenite and its photocatalytic properties

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Received December, 2014; Revised January, 2015

Mechanically activated $FeTiO_3$ concentrate, and TiO_2-the product after autoclave leaching of mechanically activated $FeTiO_3$ were characterized by XRD, specific surface area measurement (BET method) and Mössbauer spectroscopy (MS). The photocatalytic properties of the so obtained titania sample were evaluated in the oxidation reaction of photo-discoloring of Methyl Orange aqueous solution. The mechanical activation accelerated the dissolution of $FeTiO_3$ in sulfuric acid due to decreasing of the crystallite size and revealing the inner surface available for contact with the acid. A well-crystallized anatase TiO_2 phase was obtained with low content of impurities. The specific surface area was 28 m^2g^{-1}. The photocatalytic activity of TiO_2 obtained from mechanically activated ilmenite ore was found to be slightly lower than that of the commercially available TiO_2 P 25 Degussa photocatalyst.

Key words: mechanical activation, ilmenite, leaching, TiO_2, photocatalyst.

INTRODUCTION

Ilmenite ($FeTiO_3$) is an important material for the production of metallic titanium, titanium dioxide, titanium carbide and other titanium-based compounds. There are two industrial methods, that have been developed for the preparation of titania from ilmenite mineral: the pyrometallurgical and the hydrometallurgical one. The pyrometallurgical production of rutile includes some processes which are all extremely energy consuming processes [1]. The direct hydrometallurgical treatment of ilmenite ore produces synthetic rutile using hydrochloric acid [2]. The chlorination process involves high reaction temperature of above 1000 °C, which is also highly consuming process. The application of the industrial hydrometallurgical method leads mainly to rutile formation. In the present paper an environmentally friendly process is proposed based on mechanical activation of ilmenite ore concentrate. Mechanical activation generally increases the reactivity of solids and subsequent can induces chemical reactions, which take place spontaneously in activated systems and may appear even during milling or after milling are completed [3]. Milling operation changes the crystalline structure of mineral. The breakage of mineral crystal may cause defects on the crystal faces and increase in the reactivity of mineral [4]. The mechanically driven chemical process has a number of advantages over the conventional metal processing techniques [5]. The reaction kinetic conditions for the processing of mechanically activated ilmenite by means of direct hydrometallurgical conversion in autoclave to synthetic anatase at 150 °C with 30% H_2SO_4 were investigated by Achimovičová et al. [6].

In the following, we will study textural and structural properties of as-received and mechanically activated ilmenite and structural and photocatalytic properties of TiO_2-product after autoclave leaching of mechanically activated ilmenite.

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EXPERIMENTALS

Material

The investigations were carried out with ilmenite ore concentrate (>95% $FeTiO_3$, <5% SiO_2) of Russian origin (GMD, Mineral Trade Company). The chemical composition was as follows: 34.43% Fe, 30.02% Ti, 0.76% Si, 0.47% Mg, 0.42% Al, 0.34% Mn, 0.11% Zn, 0.09% Ca, 0.07% Cr, 0.06% Co, 0.03% Ba, 31.63% O and 1.57% insoluble residual.

Mechanical activation and leaching

The mechanical activation of ilmenite $FeTiO_3$ was performed in an industrial eccentric vibratory ball mill ESM 656-0,5 ks (Siebtechnik, Germany) in the air atmosphere and room temperature for 15 min with 300 g of $FeTiO_3$ per charge. The following conditions were: 5 L steel satellite milling chamber, steel balls having a diameter of 30 mm with a total mass of 17 kg, rotational speed of the eccenter 960 rpm. This type of mill was developed by Gock and Kurrer and is currently used in industry [7, 8].

Mechanically activated $FeTiO_3$ was leached in 2 L autoclave (Deutsch&Neumann, Germany) in air atmosphere under the following conditions: 200 g of $FeTiO_3$/L, 30% H_2SO_4, leaching time 60 min, temperature 150 °C, 16 w% of Fe-powder was added because of Fe^{3+} reduction in $FeTiO_3$ concentrate.

Characterization techniques

The specific surface area was measured by the low temperature nitrogen adsorption method using a NOVA Station A surface area analyzer (Quantachrome Instruments, USA). The phase composition identification was performed by X-ray diffractometry (XRD) with an X´Pert PW 3040 MPD diffractometer (Phillips, Germany) operating in the 2θ geometry with CuK_α radiation.

The Mössbauer measurements were performed with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer operating in a constant acceleration mode. A ^{57}Co/Rh source and a α-Fe standard were used for this purpose. The experimentally obtained spectra were fitted with CONFIT2000 software. The parameters of hyperfine interaction such as isomeric shift (δ), quadrupole splitting (Δ), effective internal magnetic field (B), line widths (Γ_{exp}), and relative weight (G) of the partial components in the spectra were determined.

The photocatalytic experiments were carried out on a semi-batch photoreactor (fixed charge of photocatalyst and dye solution + continuous air flow) with magnetic stirring (400 rpm). The suspension was prepared by adding the photocatalyst sample (100 mg) to 100 mL of MO solution ($1x10^{-5}$ M). In order to form slurry the mixture was sonicated for 5 min. The air flow was bubbled through the suspension by 2 frits forming tiny bubbles to ensure oxygen saturation. The suspension was stirred in the dark for 30 min to achieve an adsorption-desorption equilibrium under ideal mixing conditions and the illumination was switched on. This was considered to be the initial moment (t=0) of the reaction, occurring at room temperature. The suspension was irradiated by Philips 4 Watt TUV lamp (cold illumination). The UV-C monochromatic radiation has wavelength λ=254nm. The concentration of MO during the photocatalytic reaction was determined by monitoring the changes of the maximal absorbance peak of MO by fixed point measurement at wavelength 463 nm.

RESULTS AND DISCUSSION

The X-ray diffraction patterns revealed that the major phase of ilmenite concentrate was non-stoichiometric ilmenite $FeTiO_{3+x}$. The XRD patterns of the as-received and mechanically activated ilmenite concentrate demonstrate that the milling process causes the broadening and weakening of peaks (Fig. 1). The broadening and decrease in the intensity of the peaks can be related to decrease in the degree of crystallinity during the mechanical activation leading to rapid dissolution of milled ilmenite in diluted H_2SO_4 and formation of TiO_2 during hydrolytic reaction in the autoclave according to the reactions 1a) and 1b) summarized as reaction 2.

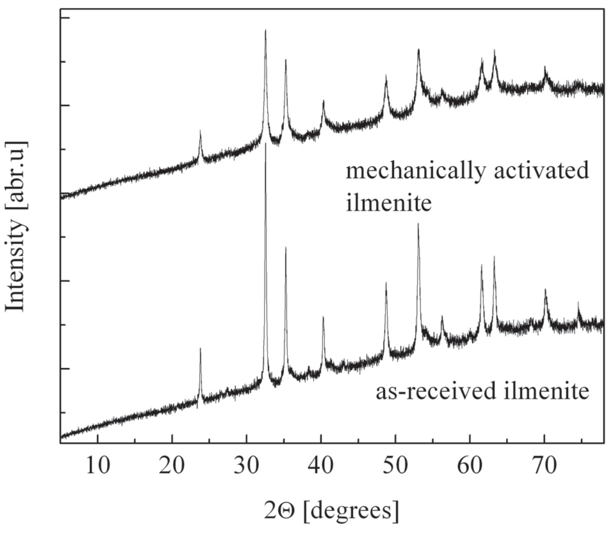

Fig. 1. XRD-patterns of as-received and mechanically activated ilmenite concentrate

$$FeTiO_3 + 2H_2SO_4 \rightarrow Fe^{2+} + 2SO_4^{2-} + TiO^{2+} + 2H_2O \quad (1a)$$

$$TiO^{2+} + 2SO_4^{2-} + H_2O \rightarrow TiO_2\downarrow + H_2SO_4 \quad (1b)$$

$$FeTiO_3 + 2H_2SO_4 \rightarrow Fe^{2+} + 2SO_4^{2-} + TiO_2\downarrow + H_2O \quad (2)$$

Fig. 2 illustrates that the TiO_2 contains anatase (JCPDS PDF 021-1272) and minor amount of rutile phase (JCPDS PDF 021-1276). The chemical composition of TiO_2 is the following: 52,1% Ti; 2,9% Fe; 0,86% Ca; 0,78% Si; 0,18% Al; 0,03% P; 0,03% Zr and 3,1% insoluble residual.

Leaching of mechanically activated ilmenite with 30% H_2SO_4 lowers the flue gas pollution due to the low reaction temperature and it also reduces

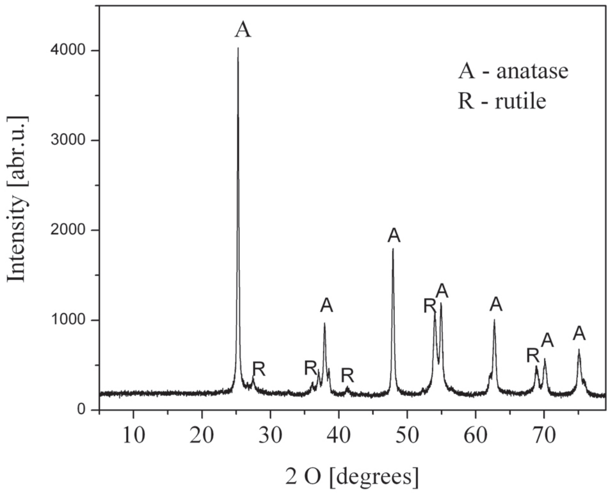

Fig. 2. XRD-pattern of the product after leaching of mechanically activated ilmenite concentrate

the waste acid release by partially recycling the diluted acid. The mechanical activation carried out by energetic milling in vibrational industrial mill accelerates the dissolution rate of ilmenite concentrate by increasing its chemical reactivity. The specific surface area of prepared anatase by leaching of mechanically activated ilmenite increases from 2 m^2/g for ilmenite concentrate to13 m^2/g for mechanically activated ilmenite ore and 28 m^2/g for titania.

Mössbauer spectroscopy is a very sensitive and versatile technique that can be used to supply information about the chemical, structural, magnetic and time-dependent properties of a material and is widely used to supplement the XRD analysis. The experimentally obtained Mössbauer spectra of the samples represent combinations of doublets or doublets and a sextet. The ^{57}Fe Mössbauer spectrum of as-received ilmenite concentrate is fitted with two doublets model. The results of fitting (Table 1) evidently have shown the presence of Fe ions in oxida-

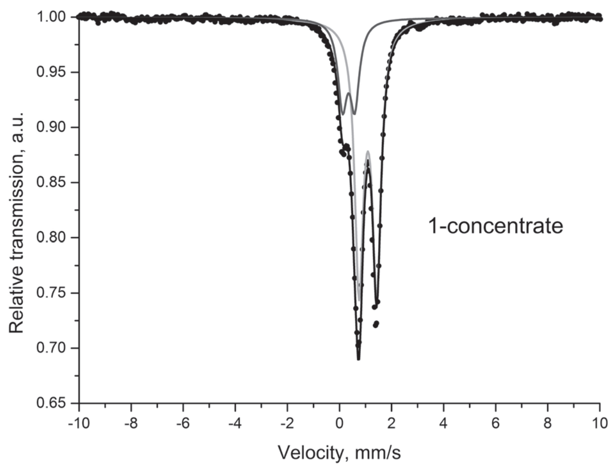

Fig. 3. Mössbauer spectrum of ilmenite concentrate

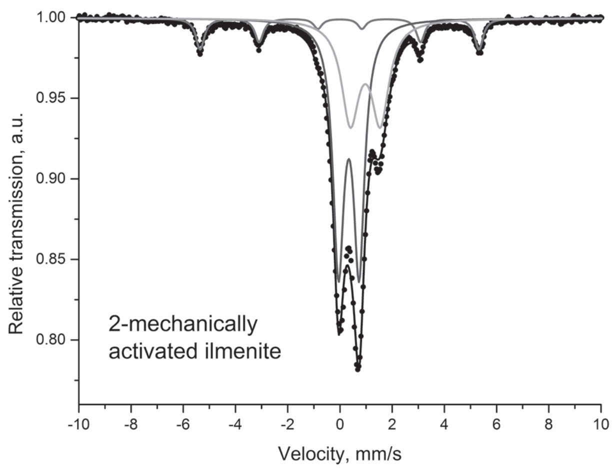

Fig. 4. Mössbauer spectrum of mechanically activated ilmenite concentrate

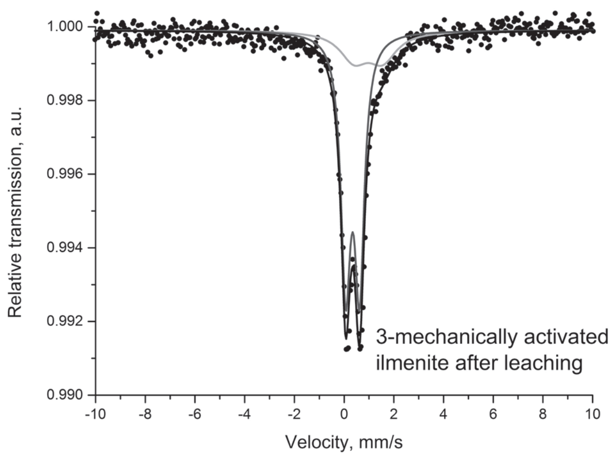

Fig. 5. Mössbauer spectrum of TiO_2 – product after leaching of mechanically activated ilmenite

Table 1. Calculated parameters of Mössbauer spectra of the investigated samples

Sample	Components	δ, mm/s	Δ, mm/s	B, T	Γ_{exp}, mm/s	G, %
Ilmenite concentrate	Db1 – $Fe_{1+x}Ti_{1-x}O_3$ – Fe^{3+}	0.35	0.47	–	0.43	25
	Db2 – $Fe_{1+x}Ti_{1-x}O_3$ – Fe^{2+}	1.09	0.68	–	0.40	75
Mechanically activated ilmenite	Sx – α-Fe – Fe^0	0.00	0.00	33.2	0.39	11
	Db1 – $Fe_{1+x}Ti_{1-x}O_3$ – Fe^{3+}	0.34	0.79	–	0.51	54
	Db2 – $Fe_{1+x}Ti_{1-x}O_3$ – Fe^{2+}	0.97	1.15	–	0.81	35
TiO_2 – product after leaching of mechanically activated ilmenite	Db1 – $Fe_{1+x}Ti_{1-x}O_3$ – Fe^{3+}	0.34	0.56	–	0.47	75
	Db2 – $Fe_{1+x}Ti_{1-x}O_3$ – Fe^{2+}	0.97	1.15	–	1.36	25

tion states Fe^{3+} and Fe^{2+}. The calculated parameters of doublets correspond to nonstoichiometric ilmenite $Fe_{1+x}Ti_{1-x}O_3$. The relative weight of Fe^{3+} component (G) is 25%.

The spectrum of the mechanically activated concentrated ilmenite ore is fitted with a model comprising two doublets and one sextet. The hyperfine parameters of the components, obtained as a result of the processing (Table 1), are indicative of the presence of Fe in various oxidation states: Fe^0, Fe^{2+} and Fe^{3+}. The parameters of the sextet component are corresponding to the phase of α-Fe and it has a relative weight of 11%. The parameters of the two doublet components of the spectra are in correspondence with those of the non-stoichiometrical ilmenite. The Mössbauer spectrum of mechanically activated ilmenite after extraction of the iron represents a doublet having very low intensities of the absorption lines. The parameters of the doublet components, are in correspondence with those of the non-stoichiometric ilmenite, however the ratio Fe^{3+}/Fe^{2+} is 3/1. Quite lower values are noticeable for the quadrupole splitting of the component Db1 – Fe^{3+}, which is due to a residual of less defective particles of ilmenite in the sample after the treatment for leaching of iron.

Methyl orange (MO), a representative of the azo dye family, is a source of pollution, which releases toxic and potentially carcinogenic substance into the waterways. The photocatalytic activity of sample in MO reaction of oxidative degradation was studied in solution using anatase, prepared by leaching of mechanically activated ilmenite. The photocatalytic degradation of MO was investigated by determining the remaining concentration of MO at various time intervals (Fig. 6). The C/C_0 vs irradiation time curves showed differences. 93% of MO was removed after 120 min irradiation of TiO_2 – product after leaching of mechanically activated ilmenite. Under the same conditions, the mechanical activated ilmenite sample can degrade MO over 38%, which could be expected in advance due to its lower surface area (Table 2). 99% of the MO removal is obtained using P 25 Degussa TiO_2 photocatalyst. The TiO_2 – product after leaching of mechanically activated ilmenite showed slightly lower photocatalytic activity than that of commercially available P 25 Degussa TiO_2 photocatalyst. A smaller particle size and a larger surface area would facilitate the increase of

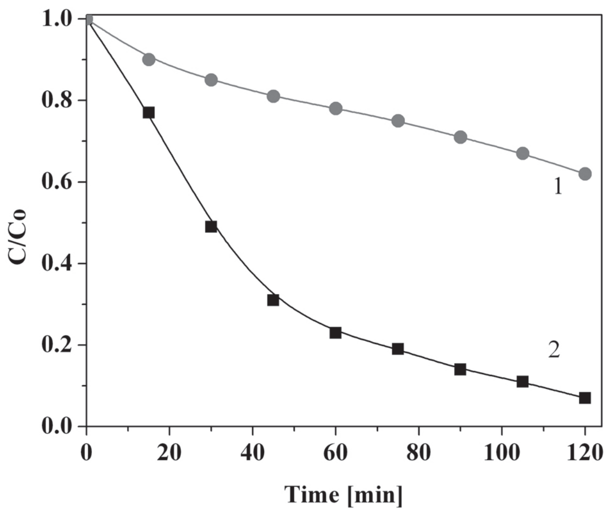

Fig. 6. The UV-C light photocatalytic oxidative degradation of Methyl Orange with mechanically activated ilmenite (1) and TiO_2 – product after leaching of mechanically activated ilmenite (2)

Table 2. Textural properties of samples

Sample	Surface area, m^2g^{-1}	Pore volume cc g^{-1}
Ilmenite concentrate	2	
Mechanically activated ilmenite	13	0,0087
TiO_2	29	0.0187

the photogenerated electrons [9]. The mechanical activation of ilmenite increased the surface area, which provided greater number of adsorption sites for MO. The highly crystalline anatase shows high activity due to the reduced number of defect sites which minimizes the electron-hole recombination.

CONCLUSSIONS

(i) The mechanical activation of ilmenite ore concentrate reduces the crystallite size as the lattice strain increased due to a slight compression of the unit cell. The combination of these factors resulted in a much more reactive surface than bulk ilmenite in the leaching process.

(ii) A substantial increase in the quadrupole shift in the Mössbauer spectrum of mechanically activated concentrate is observed as well as an increase in the width of the line of Db-Fe^{2+}, that is probably due to increase in the number of crystalline defects as a result of the milling.

(iii) The photocatalytic activity of anatase prepared by leaching of mechanically activated ilmenite ore concentrate was found to be slightly lower than that of the commercially available TiO_2 nanoparticles powder Degussa P 25 but it is also is high.

Acknowledgments: *The present investigations are financially supported by the Bulgarian National Science Research Fund under contract DNTS/SLOVAKIA 01/3, bilateral cooperation project between the Bulgarian Academy of Sciences and Slovak Academy of Sciences and project VEGA 2/0027/14.*

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TiO_2, ПОЛУЧЕН ОТ МЕХАНИЧНО АКТИВИРАН ИЛМЕНИТ И НЕГОВИТЕ ФОТОКАТАЛИТИЧНИ СВОЙСТВА

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Постъпила декември, 2014 г.; приета януари, 2015 г.

(Резюме)

Механично активиран $FeTiO_3$ концентрат и TiO_2 – продукт, получен след автоклавно извличане на механично активиран илменит са характеризирани с рентгенофазов анализ, измерване на специфичната повърхност (метод БЕТ) и Мьосбауерова спектроскопия. Фотокаталитичните свойства на получения титанов диоксид бяха определени в окислителната реакция на фотообезцветяване на воден разтвор на метил оранж. Механичното активиране ускорява разтварянето на $FeTiO_3$ в сярна киселина, дължащо се на понижаване размера на кристалитите и разкриване на вътрешната повърхност за контакт с киселината. Беше получена добре изкристализирана фаза анатаз с ниско съдържание на примеси. Специфичната повърхност на получения продукт беше 28 m^2g^{-1}. Фотокаталитичната активност на TiO_2, получен от механично активиран минерал илменит, беше малко по-ниска от тази на комерсиално достъпен TiO_2 P 25 Degussa фотокатализатор.