

PAPER • OPEN ACCESS

Flue Gas Desulfurization by Using Calcined Dolomite

To cite this article: S Baslayici *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **614** 012015

View the [article online](#) for updates and enhancements.

You may also like

- [Insight into the Effect of the Continuous Testing and Aging on the \$\text{SO}_2\$ Sensing Characteristics of a YSZ \(Yttria-stabilized Zirconia\)-Based Sensor Utilizing \$\text{ZnGa}_2\text{O}_4\$ and Pt Electrodes](#)
Xidong Hao, Xishuang Liang and Geyu Lu
- [Protective Efficiency of the Oil Composition Coatings Against Carbon Steel Atmospheric Corrosion in the \$\text{SO}_2\$ Presence](#)
Natalia Shel, Vladimir Vigdorovich, Liudmila Tsygankova et al.
- [Spatio-temporal assessing of natural vegetation regulation on \$\text{SO}_2\$ absorption coupling ecosystem process model and OMI satellite data](#)
Fen Zhao, Peng Yang, Renqiang Li et al.

Flue Gas Desulfurization by Using Calcined Dolomite

S Baslayici^{1,2}, M Bugdayci³, A Turan³, L Oncel⁴ and E Acma¹

¹Istanbul Technical University, Faculty of Chemistry and Metallurgy, Metallurgical and Materials Eng. Dep., 34469, Istanbul

²Istanbul Medipol University, Vocational School, Construction Technology Dep., 34810, Istanbul, Turkey

³Yalova University, Chemical and Process Engineering Department, Yalova, 77100, Turkey

⁴Sinop University, Faculty of Engineering and Architecture, Department of Metallurgical and Materials Engineering, 57000, Sinop, Turkey

Abstract. SO₂ emissions has begun to cause serious problems in industrialized countries. Today, various methods are used for removal of SO₂ gas. SO₂ gas is an important raw material for production of sulfuric acid. However, SO₂ content of flue gas must be over 6% to produce sulfuric acid commercially. Flue gases, which don't have enough amount of SO₂ to produce sulfuric acid commercially are harmful to the environment and human health and they must be filtered. In this study, calcined dolomite was used to remove SO₂ in flue gas which doesn't have enough SO₂ to produce sulfuric acid but have high emission values. Pyrite was used as SO₂ source and SO₂ removal efficiency of dolomite was determined for different experimental parameters. SO₂ capturing system was thermodynamically modeled and SO₂ capturing efficiency was determined as 77.81% in the experiments.

1. Introduction

The increasing population of the world and industrialization leads to an increase in energy needs. Use of fuels with sulfur content has been increasing to meet the rising energy demand. Emission of air-pollutant gases has been rising for that reason [1].

Sulfur dioxide (SO₂) is known as the most important air-pollutant gas. Main reasons that causes arising of SO₂ are natural sources and human activities. Microbial activities, volcanic eruptions, combustion of sulfur-containing fossil fuels, molten sulfur ores and oil refineries are among the causes of SO₂ formation. [2-6].

SO₂ is highly soluble in water and SO₂ in flue gas is used as raw material in sulfuric acid production. On the other hand, SO₂ content of flue gas must be over 6% to produce sulfuric acid commercially. It is necessary to filter the flue gases containing SO₂ which do not have enough SO₂ amount for production of sulfuric acid commercially. It may cause serious irreversible damage if they are released directly into the nature. [7-11]. SO₂ gas pollutes the nature and it also increases the risk for cardiovascular diseases and lung cancer [12-14].

Sulfur dioxide is a colorless, sour-scented, fireproof and stifling gas. Taste of SO₂ can be detected when its concentration reaches to 785 µgr/m³ and SO₂'s smell can be detected when its concentration reaches to 1305 µgr/m³ in the atmosphere. Sulfur dioxide is present in volcanic gases and its level is high in industrialized regions. SO₂ is formed with combustion of sulfur-containing coals. This gas is condensed as a colorless liquid when cooled to -10 °C and it is solidified in white crystalline form when cooled to -73 oC [1, 15].



Researchers have been working on developing cost-effective systems for decreasing levels of air pollutant gases like sulfur dioxide (SO₂), nitrogen oxide (NO_x) and carbon monoxide (CO) [16-18]. In industry, gas-liquid reactions and gas-solid reactions are used for desulfurizing. Gas-liquid reactions are obtained by using activated carbon and liquid alkali materials (lime slurry and ammonia) [1, 17]. In other situations, catalysts (generally vanadium pentoxide) are used to turn SO₂ into sulfuric acid but these processes produce SO₂ gas as by product [19].

Main inorganic sorbent used in this process is calcite but in order to utilize large dolomite reserves in Turkey, dolomite is used as inorganic sorbent in this study. Results obtained from experimental studies were compared to the previous literature, where calcite and active carbon are used.

2. Experimental

In the experimental studies, pyrite ore from Kure region of Turkey was used as SO₂ source. Chemical composition of pyrite ore is given in Table 1 and XRD analysis result of pyrite ore is shown in Figure 1.

Table 1. Chemical composition of pyrite

Sample	Fe,%	S%	Cu%	Mg%	Ca%	SiO ₂ %	K%
Pyrite	38,18	41,67	0,58	0,38	0,77	9,33	0,02

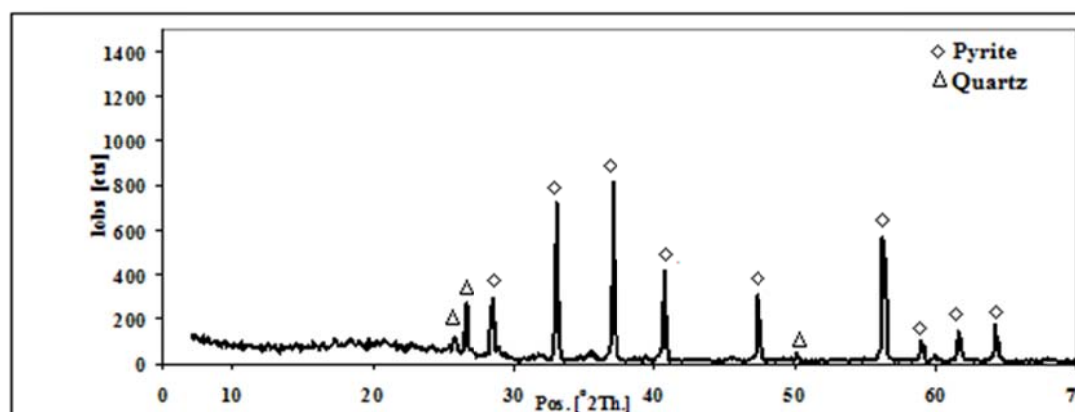


Figure 1. XRD analysis of Pyrite ore.

Mineralogical examinations show that pyrite (FeS₂), quartz (SiO₂) and hydronium jarosite ((H₃O)Fe₃(SO₄)₂(OH)₆) minerals were present in the pyrite concentrate. Main mineral of pyrite concentrate was pyrite and there were trace amount of chalcopyrite, covellite, marcasite, bornite, sphalerite, digenite and various silica minerals. According to particle size measurements, mean particle size of pyrite was 41 μm.

Calcined dolomite used in experimental studies was Kutahya Yaylababa dolomite and it was procured from Kumas Magnezit Sanayi Corporation. Chemical analysis of Yaylababa dolomite is shown in Table 2. Calcined dolomite's mean grain size was 42 μm.

Table 2. Chemical analysis of dolomite.

Sample	Loss on Ignition	CaO%	MgO%	FeO%	Al ₂ O ₃ %	SiO ₂ %	Na ₂ O%
Dolomite	9.52	57.59	31.00	0.12	Trace	1.07	0.0086

Thermo Scientific XSeries 2 ICP-MS was used for chemical analyses of the samples. Bruker D8 Advance was employed for XRD analyses and mineralogical examinations. Roasting operation were carried out in a tube furnace working with 220V electricity. Samples were grinded with ring mill and dehumidified in Binder drying-oven. Samples particle size were measured with Malvern Mastersizer 2000.

In the roasting experiments, ceramic boat was weighed initially and it was weighed again after filling with pyrite. Pyrite was roasted in furnace and weight loss caused by roasting was measured by weighing. Roasting process was carried out with different times and optimum roasting time was determined. Various air flow rates were used in SO₂ capturing experiments. SO₂ emissions were measured after roasting process for every air flow rate used. SO₂ emission measurements after roasting process were repeated for different flow rates with using dolomite for capturing SO₂ gas. Then, SO₂ capturing results were compared.

Titrimetric method was used in SO₂ analysis. In this method, gases released from the flue were kept in the hydrogen peroxide solution which was in the washing bottle and it was converted to sulfuric acid. Concentration of SO₂ was determined by titration with a base with a known normality.

100 ml. of a 1% H₂O₂ solution was filled in each of the two gas washing bottles, which were coupled in series. Gas exited from the flue was transferred to first gas washing bottle. SO_x was oxidized to acid by H₂O₂ in the washing bottle. SO_x gas, which didn't react in the first washing bottle moved to second washing bottle and reacted with H₂O₂. After the process was completed, solutions in two washing bottles were titrated with alkali (1N Na₂CO₃) and equivalent SO₂ quantity in the flue gas was determined. Reactions took place in this process are given in Equation 1 and Equation 2.



Total reaction is shown in equation 3.



Acid's titration reaction is given in Equation 4.



SO₂ concentration in the gas mass is calculated as shown in Equation 5. Here, N is normality of the base and S is base consumption (ml).

$$\text{SO}_2 \text{ (mg/l)} = (32 \cdot N_{\text{Na}_2\text{CO}_3} \cdot S_{\text{Na}_2\text{CO}_3}) / \text{volume of air (l)} \quad (5)$$

SO₂ capturing experiments were started after determining the roasting conditions in the first experimental set. Calcined dolomite was used to capture SO₂ in this experimental set. Different air flow rates were used in SO₂ capturing experiments. Initially, SO₂ formation amounts were determined for every air flow rate used. Then, dolomite was used to capture SO₂, and capturing efficiencies were compared. The amount of dolomite was determined by weighing the empty boat and then weighing the boat filled with dolomite. The resulting products were weighed and compared with roasting experiments' results.

3. Results and Discussion

In the experimental studies, quantity of theoretical air requirement for roasting of pyrite was calculated initially. Studies were carried out with two times, four times, six times and eight times of the theoretical air quantity. According to Equation 6; in order to obtain 0.0651 mole S, 0.31 mole of air is required. Table 3 represents roasting experiments' conditions.

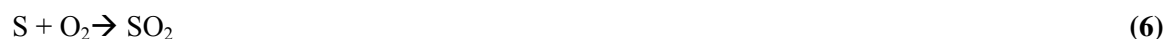
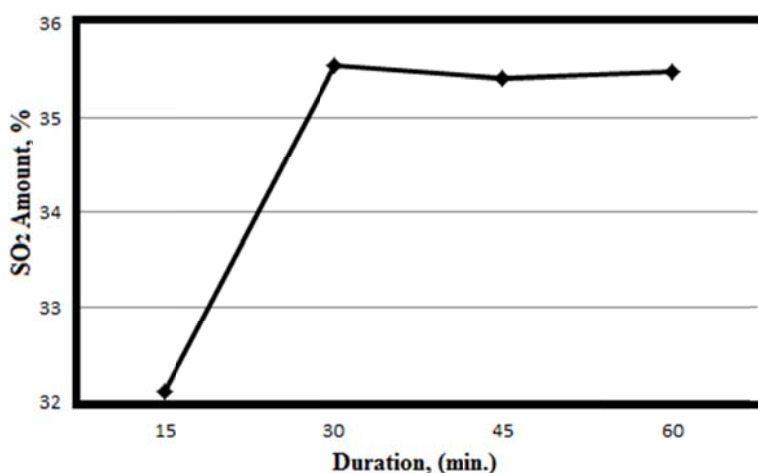


Table 3. Roasting experiments' conditions.

Exp. No	Duration (min.)	Flow Rate (l./min.)	Weight Before Roasting (g.)	Weight After Roasting (g.)	Difference (g.)	SO ₂ Amount (mg/l.)	
1	15	1	5.79	3.93	1.86	32.15	
2			5.78	3.93	1.85	32.08	
3			5.30	3.60	1.70	32.10	
Avg.15				5.62	3.82	1.80	32.11
4	30		5.34	3.44	1.89	35.52	
5			5.25	3.39	1.86	35.47	
6			5.33	3.43	1.90	35.68	
Avg. 30				5.30	3.42	1.88	35.55
7	45		5.17	3.34	1.83	35.44	
8			5.32	3.43	1.88	35.36	
9			5.31	3.42	1.88	35.47	
Avg. 45				5.26	3.39	1.86	35.42
10	60	5.34	3.44	1.89	35.53		
11		5.29	3.41	1.87	35.45		
12		5.17	3.33	1.83	35.50		
Avg. 60			5.26	3.39	1.86	35.49	

Experiments were repeated three times for all roasting conditions and average values were calculated. Roasting experiments showed that 1 l./min. air flow rate and 2 times of the theoretical air quantity was not enough to complete the roasting process. Roasting efficiency was increased to 100% with four times of the theoretical air quantity used and it was determined that using more air in the process was not necessary.

Figure 2 shows effect of roasting time on SO₂% formation. It is seen in the figure that amount of SO₂% was increased exponentially when roasting time was increased from 15 minutes to 30 minutes. SO₂% amount remained nearly constant when roasting time exceeded 30 minutes. Table 3 and Figure 2 shows that optimum roasting conditions of pyrite is 30 minutes of roasting time and 1 l./min. of air flow rate.

**Figure 2.** Change of SO₂% amount versus time.

After roasting experiments, SO₂ capturing system was thermodynamically modeled via FactSage 6.2 database. Figure 3 illustrates standard free energy of dolomite and pyrite concentrates changing with temperature. Figure 3 shows that dolomite will be sulphated and pyrite will be oxidized at 600 °C.

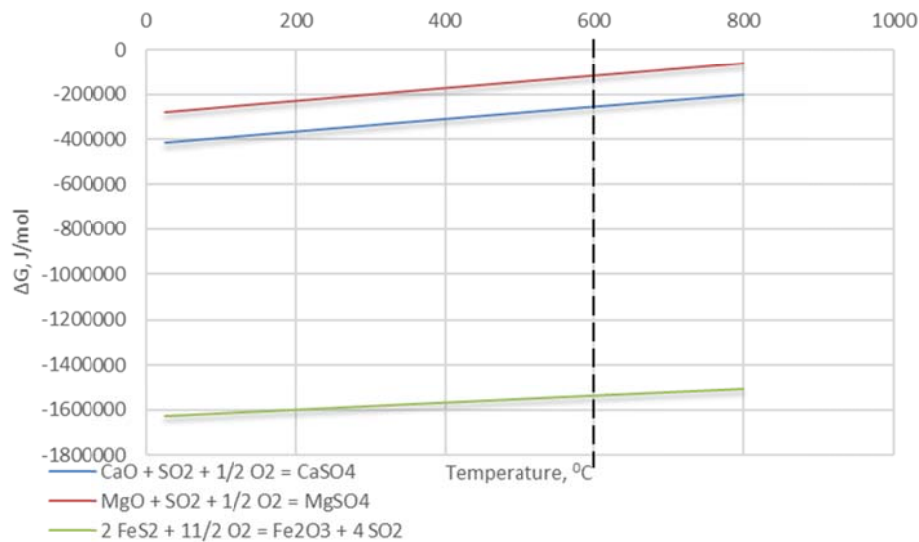


Figure 3. Standard free energy of dolomite-pyrite system changing with temperature.

Two boats were used in SO₂ capturing experiments. Pyrite concentrate was charged in the first boat and dolomite was charged in the second boat. Table 4 presents experimental parameters and results of SO₂ capturing experiments. SO₂ capturing amount versus time curve, which was created by using data in Table 4 is shared in Figure 4.

In SO₂ capturing experiments, better results were obtained at low air flow rates. Contact time between solid and gas is increased at low air flow rates. Contact surface area, which is needed for occurring of reactions remain same but contact time is increased with using low air flow rates. Therefore, flue gas desulfurization efficiency increases at low air flow rates. The optimum SO₂ capturing result was obtained as 77.76% when 0.4 l. /min. air flow rate was used.

Effect of temperature on SO₂ capturing efficiency was investigated by using different temperatures with constant air flow rate. Results showed that temperature didn't have a significant effect on capturing efficiency. On the other hand, high temperatures were used in experimental studies and it doesn't provide information about low temperatures like room temperature. Figure 4 shows that SO₂ capturing efficiency increased insignificantly from 77.76% to 77.81% with increasing temperature. According to these data, flue gas desulfurization efficiencies of the companies using sulphurous fuel will show insignificant changes due to the narrow temperature range of the flue gases.

When all results are taken into consideration, filtering with dolomite is suitable for plants with average emission values lower than 1285 μg per hour, 485 μg per day and 214 μg per year. Mangun et al. obtained 82% SO₂ capturing efficiency by using active carbon but large dolomite reserves in Turkey make dolomite a good alternative to active carbon. In this study, SO₂ which is captured by dolomite can be converted into sulfuric acid [20]. Mathieu et al.'s study showed that SO₂ can be captured by using calcite but regeneration of captured SO₂ is not possible in this method. Therefore, using dolomite instead of calcite is advantageous [21].

Table 4. Conditions and results of SO₂ capturing experiments.

Exp. No	Temperature, °C	Flow Rate, lit./min	Weight Before Roasting, g.	Weight After Roasting, g.	SO ₂ Amount, mg./lt.	SO ₂ Capture, %
1			1.07	0.68	25.60	-
2			1.07	0.69	26.67	-
3	600	1.0	1.09	0.70	25.60	-
Avg.			1.07	0.69	25.95	-
4			1.00	0.64	7.46	71.25
5			1.21	0.77	7.46	71.25
6	600	1.0	0.99	0.64	6.93	73.29
Avg.			1.06	0.68	7.28	71.93
7			1.06	0.68	33.33	-
8			1.15	0.73	33.33	-
9	600	0.8	1.05	0.68	32.67	-
Avg.			1.08	0.69	33.11	-
10			1.07	0.69	8.67	73.81
11			1.09	0.70	8.67	73.81
12	600	0.8	1.02	0.66	9.33	71.82
Avg.			1.06	0.68	8.89	73.14
13			1.16	0.75	44.44	-
14			1.04	0.66	44.89	-
15	600	0.6	1.10	0.71	44.89	-
Avg.			1.10	0.70	44.59	-
16			1.10	0.71	10.67	76.15
17			1.00	0.64	11.11	75.16
18	600	0.6	1.02	0.65	10.22	77.15
Avg.			1.04	0.66	10.66	76.15
19			1.06	0.68	64.00	-
20			1.12	0.71	64.00	-
21	600	0.4	1.01	0.65	64.00	-
Avg.			1.06	0.68	64.00	-
22			1.02	0.67	14.67	77.07
23			1.11	0.70	14.67	77.07
24	600	0.4	0.99	0.63	13.34	79.15
Avg.			1.04	0.66	14.22	77.76
25			1.05	0.67	64.00	-
26			1.05	0.68	61.34	-
27	700	0.4	1.05	0.68	64.00	-
Avg.			1.05	0.67	63.11	-
28			1.09	0.70	14.67	76.75
29			1.11	0.68	13.67	78.34
30	700	0.4	1.03	0.66	13.67	78.34
Avg.			1.07	0.68	14.00	77.81

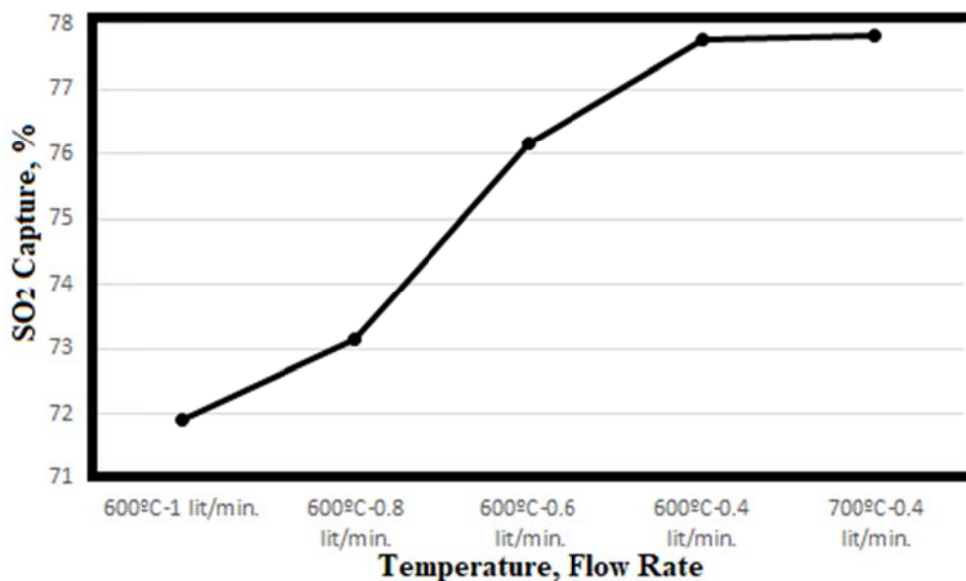


Figure 4. Effect of temperature and air flow rate on SO₂ capturing amount.

4. Conclusion

The world's energy requirement has been increasing because of the development in technology and industries. High SO₂ emissions caused by use of fuels with sulfur content must be reduced. SO₂ emission values are high in Turkey and it continues to increase despite the downward trend in developed countries. SO₂ emission values of Turkey should be reduced in the short term and the long term.

Because of the harmful effects of SO₂ gas on nature and human health, flue gases which don't have enough amount of SO₂ to produce sulfuric acid commercially but above the limits set by the authorities must be filtered.

In experimental studies, mineralogical analysis of Yaylababa dolomite was performed initially. Then, thermodynamic calculations were carried out and it was seen that dolomite can capture SO₂ gas. Experiments showed how theoretical calculations were working in practice.

Roasting conditions of pyrite concentrate were determined by experiments. The optimum air quantity required was calculated theoretically and determined in practice. It was seen that using four times of the theoretical air quantity was enough and there was no need to use more air. Optimum conditions vary according to the content of the concentrate and it can be specified as two to four times the theoretical amount of air.

In the experiments, SO₂ capturing efficiency of dolomite was reached to 77.76% at optimum conditions. However, it is predicted that efficiency value may decrease in small amounts at high air flow rates.

5. References

- [1] Baslayici S 2014, Flue Gas Desulphurization by Using Calcined Dolomite, MSc Thesis, Istanbul Technical University, Turkey.
- [2] Li N, Wang Z and Zhang Z 2018, *Environ Sci Pollut Res* 25 (35) 35099-35108.
- [3] Fowler D and Unsworth M H 1977, *Quart. J. R. Met. SOC* 105 767-783.
- [4] Hu K, Bai G, Li W, Yan H, Hu, Li L and Zhang H 2014, *Plant Growth Regul* 75 (1) 271-280.
- [5] Li P, Wang X, Allinson G, Li X, Stagnitti F, Murray F and Xiong X 2011, *Environ Sci Pollut Res* 18 (7) 1090-1097.
- [6] Majernik O and Mansfield T A 1970, *Nature* 227 377-378.

- [7] Blakemore F B, Davies C and Isaac J G 1999, *Appl Energy* 62 (4) 283-295.
- [8] Fenger J 2009, *Atmos Environ* 43 (1) 13-22.
- [9] Harnisch J, Borchers R and Fabian P 1995, *Environ Sci Pollut R* 2 (4) 229-232.
- [10] Shepherd M A, Haynatzki G, Rautiainen R and Achutan C 2015, *J Air Waste Manag Assoc* 65 (10) 1239-1246.
- [11] Taieb D and Brahim A B 2013, *C R Chim* 16 (1) 39-50.
- [12] Zhang D, Liu J, Jiang C, Li P and Sun Y 2017, *Sens Actuators B Chem* 245 560-567.
- [13] Chaudhary V, Kaur A 2015, *Polym. Int.* 64 (10) 1475-1481.
- [14] Liu X Y, Zhang J M, Xu K W and Ji V 2014, *Appl Surf Sci* 313 405-410.
- [15] Azimi M, Feng F and Yang Y 2018, *Sustainability* 10 (2) 367.
- [16] Miller M J 1986, *Environ Prog Sustain Energy* 5 (3) 171-177.
- [17] Wark K, Warner C F, Davis W T 1998 *Air Pollution: Its Origin and Control* 3rd Edition, (California: Addison-Wesley), p. 573.
- [18] Nersesian R L 2007, *Energy for the 21st Century: A Comprehensive Guide to Conventional and Alternative Sources*, (New York: M. E. Sharpe) New York, p. 456.
- [19] Bauer G, Güther V, Hess H, Otto A, Roidl Roller O H, Sattelberger S, Köther□Becker S, and Beyer T 2017 *Vanadium and Vanadium Compounds* (In Ullmann's Encyclopedia of Industrial Chemistry), (Online: Wiley□VCH), p. 22.
- [20] Mangun C L, Debaar J A and Economy J 2001, *Carbon* 39 1689–1696.
- [21] Mathieu Y, Tzanis L, Soulard M, Patarin J Vierling M and Molière M 2013, *Fuel Processing Technology* 114 81–100.