CHEMICAL ENGINEERING TRANSACTIONS

VOL. 65, 2018

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Mario Costa

ISBN 978-88-95608-62-4; **ISSN** 2283-9216

DOI: 10.3303/CET1865088

Effects on the Combustion Characteristics and Denitrification of Modified TiO2 in the Combustion with Biomass and Coal

Shuqin Wang*, Xiao Zhang, Daqi Yin, Zhiping Han

Department of environmental Science and Engineering, North China Electric Power University, Baoding 071003, China
wsqhg@163.com

The V/Mn modified TiO2 samples were prepared by sol-gel method assisted by microwave. At the same time, the denitrification experiments were carried out in the tube furnace and the combustion characteristics of the samples were analyzed by thermogravimetric analyzer. The results showed that the denitrification efficiency of V-Mn-TiO2 was 10% and 15% higher than that of V-TiO2 and Mn-TiO2 respectively. The calcination temperature of the catalyst prepared by microwave assisted sol-gel process was 100oC lower than that of using sol-gel method but the two catalysts have the same efficiency. The BET analysis showed that the modified TiO2 can reduce the emission of NOX because of the larger specific surface area, adsorption and the pore volume. V-Mn-TiO2 could make effects such as reducing apparent activation energy in combustion, and it had a great influence on the early stage of coal burning. Without CaO, V-Mn-TiO2 made the ignition lowered than 33.2oC; mixed with CaO, V-Mn-TiO2 made the ignition lowered than 39.9oC. Thus the coal and biomass co-combustion were suitable for the first-order kinetic model. The results showed that modified TiO2 can help to make the fault coal available and reduce the emissions of NOX to achieve ultra-low emission standard.

1. Introduction

With the emergence of energy crisis and environmental issues, the development and utilization of biomass energy as a renewable energy source has become a research hotspot in recent years. The biomass and coal co-combustion is feasible for research because the technology is simple and the cost is low (Zhang et al., 2016; Koch, 2017; Sayin, 2017; Puglia et al., 2017; Malaguti et al., 2017; Zaccone et al., 2017).

Wang et al., (2017) analyzed the co-combustion characteristics of coal and biomass. Experiments showed that with rice husk, the combustion characteristics of single coal could be improved and with oxygen volume fraction increases, the co-combustion characteristics of mixed coal and biomass could be improved. Feng et al., (2016) analyzed the co-combustion characteristics and the emission of NO, the results of which showed that the atmosphere had little effect on the volatilization analysis and the biomass had a combustion-supporting effect. Junga et al., (2017) analyzed the co-combustion characteristics of coal and biomass. Zhong and Tang (2007) also found that biomass coke is more effective than coal char on the reduction of NO activity in a dropper furnace experiment. Wang et al. (2017) studied the NOx emission characteristics of different coal and biomass co-combustion in a dropper furnace experiment and analyzed the effects of different atmosphere, biomass mixing ratio and oxygen volume fraction. Wang et al. (2016) analyzed the NOx emissions under oxygen-rich combustion of coal combustion. Li et al. (2017) analyzed the effect of modified titanium dioxide on NO oxidation and flue gas composition. Wang et al. (2017 and 2016) studied the effects of pure TiO_2 on co-combustion desulfurization, denitrification of coal and biomass, and the photocatalytic activity of V-Mn-TiO_2 prepared by sol-gel method. A large number of previous studies has focused on the combustion characteristics of both biomass and coal, the influencing factors of co-combustion, and the emission characteristics of nitrogen oxides. Research on the denitrification using additives are relatively rare. Studies on titanium dioxide are mostly focused on the study of photocatalytic properties. The main preparation methods are sol-gel methods while other methods like the adsorption performance and the use of microwave assisted sol-gel process are rarely used. In view of this, the use of microwave assisted sol-gel method to prepare V-

Please cite this article as: Shuqin Wang , Xiao Zhang , Daqi Yin , Zhiping Han , 2018, Effects on the combustion characteristics and denitrification of modified tio2 in the combustion with biomass and coal, Chemical Engineering Transactions, 65, 523-528
DOI: 10.3303/CET1865088

Mn-TiO_2, and the study of the effects on the biomass and coal co-combustion characteristics and denitrification can lay a solid foundation for further application.

2. Materials and Methods

2.1 Proximate and ultimate analysis

The results of proximate analysis (by GB/T212-2001) and ultimate analysis (by GB214/T-2007) of Shanxi coal and Hebei corn cobs (the analysis method of biomass refer to the method of coal) has been shown in our previous research.

2.2 The performance test of catalyst

Thermal characteristics of samples are studied by using thermal analyzer, during which process the sample weight was about 5.00mg and heating rate was 50 °C /min. In the beginning of the experiments, a certain amount of experimental sample was transferred into a porcelain boat, following by positioning it to the center of a tubular furnace. Connected to the absorption bottle, it was feed for 3min, then turn on the temperature controller. The experimental samples were heated to 300 °C for 10min and then heated to 500°C for 5min through oxygen gas flow (When coal is burned separately, it does not stay at 300°C and burns for 5min only at 500°C) to expel the volatile and prevent deflagration. Ultimately, heating it to 850°C for 25min. he feed gas was supplied from oxygen gas cylinder with a volume flow at 40mL/min. The blending ratios of coal and corn cob was 8:2, the Ca/S ratio was 2.3 (calcium-based additives was CaO) and the dosage of catalytic was 8% during the thermal gravimetric analysis. Under the above conditions, samples were heated to 850°C with different catalysts and preparation conditions for denitrification performance experiments. The NO concentration was determined by using naphthyl ethylenediamine dinydrochloride spectrophotometric method and the efficiency calculation formula could be found in our previous study.

2.3 TiO_2 prepared by microwave assisted sol-gel process

Using tetrabutylitanate, glacial acetic acid, ethyl alcohol absolute, aluminium sulfate, ammonium metavanadate, manganese sulfate and high pure water as the starting materials, which were slowly stirred at 600w in a microwave synthesizer to get the sol. Then the sol was dried under microwave for 15 mins. Finally, the dried gel obtained was calcined at different temperature for 1-3h in close roaster to get the TiO_2 powder.

3. Results and Discussions

3.1 Denitration performance of co-combustion evaluation results

3.1.1 Effects of different catalyst types on the denitrification efficiency of co-combustion

The denitrification efficiency of metal co-doped titanium dioxide is higher than that of metal-doped titanium dioxide, which is shown in Table1.The catalyst is conducive to denitrification. Because of the synergistic effects of ions, the catalytic activity of TiO_2 was improved. Mn doping in V-Mn-TiO_2 is conducive to the formation of anatase TiO_2 by, restraining the growth of grains and increasing the specific surface area of the catalyst to increase the denitrification efficiency.

Table1: Effect of catalyst types on denitrification efficiency of co-combustion

Catalyst types	TiO_2	V-TiO_2	Mn-TiO_2	Al-TiO_2	V-Mn-TiO_2	Al-Mn-TiO_2	Al-V-TiO_2
Efficiency%	30.4	48	42.7	45.3	55.4	49.0	50.0

3.1.2 Effects of different preparation methods on the denitrification efficiency of co-combustion

The calcination temperature of the V-Mn-TiO_2 prepared by microwave assisted sol-gel process was 100 °C lower than that of using sol-gel method, but the two catalysts have the same efficiency and the same application in the V-TiO_2, which is shown in Table2. It can be seen that the microwaves participated in the reaction during the preparation of TiO_2, which may increase the strengthening effect of microwave heating. The microwave heating eliminates the temperature gradient in the reaction liquid, and the temperature in the reaction system is balanced so the physical and chemical reactions can be greatly sped up. In addition, there were hydroxyl, water and organic molecules on the surface of TiO_2. These molecules can directly transfer heat to the surface of the metal oxide under the action of microwave energy to accelerate the crystallization of the particles. Therefore, microwave heating can greatly shorten the reaction time.

Table2: Effect of microwave on denitrification efficiency

		500 °C	600 °C	700 °C	900 °C
V-Mn-TiO_2	microwave	48.7%	55.4%	43.2%	27.0%
	sol-gel	39.5%	48.0%	54.8%	28.9%
V-TiO_2	microwave	33.8%	51.0%	40.3%	28.9%
	sol-gel	34.2%	37.3%	46.6%	31.9%

3.1.3 Effects of different preparation conditions on the denitrification efficiency of co-combustion

The effects of different preparation conditions on the denitrification efficiency of co-combustion were shown in Table3. Based on previous studies, the amount of V doping was set as 1%. Mn doping can improve the catalytic oxidation ability by the co-doping of metals and can promote the formation of v-doped valence band, but the optimum doping amount of Mn was 1%. Once the optimal value was exceeded, the number of active sites in the catalyst would decrease and agglomeration would be caused. The particle size of the catalyst was increased, the specific surface area was decreased, and the denitrification efficiency was reduced.

The optimal calcination time for achieving high efficiency was 3h. It not only provides the required energy by relying on the calcination temperature, but also provides a suitable calcination time to maintain the energy to replace the complex center ions in the crystal lattice as the manganese ion enters the TiO_2 lattice and the manganese and vanadium ions form lattice defects when preparing the V-Mn-TiO_2.Therefore, the calcination time of 3h during the preparation of the V-Mn-TiO_2 was sufficient. Prolonging the calcination time would lead to the increase of the catalyst particle size and indicate that the specific surface area will decrease and the denitrification efficiency will decrease.The optimal temperature for achieving high efficiency was 600 °C. It will accelerate the transformation of rutile TiO_2 at a high temperature and the catalytic activity decreased; And the deformation of the catalyst channels and micropores, reduced effective channel and area will make the adsorption capacity of NOx decreased and the denitrification efficiency reduced.

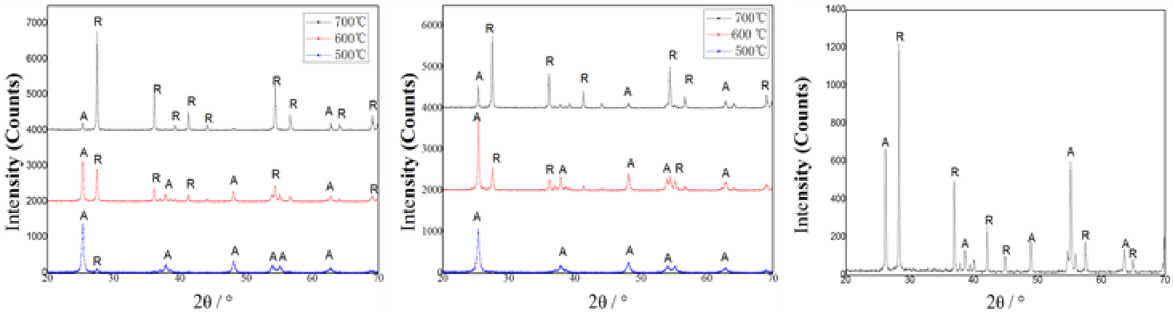
Table3: Effect of preparation conditions on denitrification efficiency for V-Mn-TiO_2.

Doping amount of Mn	Efficiency%	Time	Efficiency%	Temperature	Efficiency%
0.5%	31.7	2h	42.5	500°C	48.7
1.0%	55.4	3h	55.4	600°C	55.4
1.5%	45.6	4h	43.0	700°C	43.2

3.2 Characterization analysis of different TiO_2

3.2.1 XRD analysis

It can be seen from Figure1 that with Mn doping, the formation of v-doped valence band can be improved. At the same calcination temperature, V-TiO_2 doping Mn showed higher percentage of anatase and higher surface area, and the adsorption capacity increased.



(a)V-TiO_2 (assisted by microwave) (b) V-Mn-TiO_2 (assisted by microwave) (c) V-Mn-TiO_2 (sol-gel)

Figure1: XRD Patterns of different TiO_2

V-Mn-TiO_2 has a sharper diffraction peak than V-TiO_2 and the crystal were integrity. As the calcination temperature increased from 500°C to 700°C, the ratio of anatase decreased sharply. The increase of calcination temperature and the excess energy destroyed the common O-O in the TiO_2 crystal lattice, resulting in the reduction of the number of common edges. Due to the space conformation, the number of the polygons of anatase TiO_2 was two more than that of the rutile type. Therefore, the increase of calcination temperature could promote the transformation from anatase to rutile, during which the anatase-rutile mixed crystal structure was formed. The anatase TiO_2 was more active than rutile TiO_2 and the existence of mixed-type titanium dioxide was more stable so that it is not easy to be deformed in high-temperature combustion denitrification, and it maintains good adsorption performance and improves the denitrification efficiency. Too high calcination temperature would make the catalyst particle size larger, resulting in a reduction of the catalyst surface area and of the denitrification efficiency, so the best calcination temperature of TiO_2 in sol-gel method assisted by microwave was 600 °C. The result is agreed with that in section 3.1.

3.2.2 BET analysis

Table 4 showed that the specific surface area, adsorption capacity and pore volume of V-Mn-TiO_2 were larger than that of V-TiO_2, while the average pore of V-Mn-TiO_2 were smaller than that of V-TiO_2. The addition of Mn can further inhibit the growth of particle size and increase the specific surface area of the catalyst. The effective ionic radius of V^{5+} and Mn^{2+} was 0.054 nm and 0.067 nm respectively. The doping process may introduce lattice defects, and the effective ionic radius of Ti^{4+} was 0.061nm. As V and Mn replace Ti, the interionic attraction became larger, making the original distance between Ti and O became shorter, and reducing the particle size. The specific surface area, adsorption capacity and pore volume of V-Mn-TiO_2 were larger than that of V-TiO_2, which leads to the improvement of denitrification efficiency. Thus the denitrification efficiency of metal co-doped TiO_2 was higher than that of single-doped TiO_2.

The BET showed that the specific surface area, adsorption capacity and pore volume of V-Mn-TiO_2 in sol-gel method assisted by microwave calcined at 600 °C were better than that in sol-gel method at 700 °C and more favorable for adsorption. Therefore, the microwave assisted sol-gel method can reduce the calcination temperature, reducing the aging time by half. The result is the agreement with that in section 3.1.

Table 4: Data of surface structure by BET

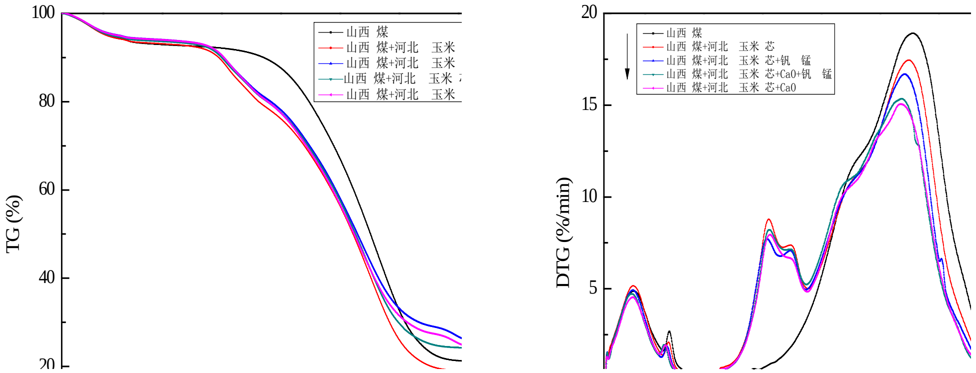
Samples	$S_{BET}/(m^2\cdot g^{-1})$	r_P/nm	V_m/ ($cm^3\cdot g^{-1}$ STP)	$V_P/(cm^3\cdot g^{-1})$
V-TiO_2(1%, 500 °C, 3h)	2.90	37.88	0.70	0.028
V-TiO_2(1%, 600 °C, 3h)	5.49	21.63	1.29	0.030
V-TiO_2(1%, 700 °C, 3h)	1.75	35.37	0.42	0.016
V-Mn-TiO_2(Mn1%, 500 °C, 3h)	16.34	8.20	3.82	0.034
V-Mn-TiO_2(Mn1%, 600 °C, 3h)	26.93	7.14	6.29	0.048
V-Mn-TiO_2(Mn1%, 700 °C, 3h)	7.44	16.24	1.72	0.030
V-Mn-TiO_2(Mn1%, 700 °C, 3h) Sxol-gel method	18.17	7.48	4.17	0.034

3.3 Combustion performance

3.3.1 Thermogravimetric analysis

The ignition temperature of each sample with additives shown in Figure 2 was reduced. The ignition temperature of biomass was lower than that of coal and the pyrolysis process was faster. Biomass contained a large amount of oxides of alkali metals, alkaline earth metals, rare earths, and transition metals. These interactions with inorganic substances can reduce the apparent activation energy, ignition temperature and accelerate the coal combustion rate. By accelerating the coal combustion in the process of various bond breaking, the volatilization rate of coal was improved and the final ash content was also reduced.

CaO can reduce the dissociation energy of oxygen and activation energy, and strengthen the combustion of coal when carbon was burned. The combustion of coal in air belongs to the gas-solid two-phase reaction. There were an electromotive force between two reactants at the two-phase contact point. Titanium has the property of transition metal, that is, its d empty orbit. The orbital formed of d,s or p by the hybridization has the directionality, which leads to the weakening of the bonds between the reactant molecules, the longer bonds and the easier activation of the bonds. Thus the energy barrier between the reactants and the activation energy of the reactants can be reduced, which lowered the ignition point. The burning temperature increased with the CaO because CaO made the SO_2 formed by coal combustion to form $CaSO_3$ or $CaSO_4$, which was fixed on the surface of the carbon particles and blocked the pores, resulting in a decrease in the combustion performance of the coal. This effect made internal porosity decreased and burning temperature increased.



(a) TG curve of the sample (heating rate: 50°C/min) (b) DTG curve of the sample (heating rate: 50°C/min)

Figure 2: Thermogravimetric analysis

3.3.2 Kinetic analysis

The heating rate was 50°C/min. The DTG curve (Figure2) representing the effects of additives on the co-combustion of biomass and coal in the thermogravimetry experiment showed that the maximum mass loss rate, and its corresponding temperature are shown in Table5.

Table5: The maximum mass loss rate and its corresponding temperature (%/min)

samples	Devolatilization appears of biomass		Devolatilization appears of coal		Stage of coal combustion	
	Maximum mass loss rate	Temp (°C)	Maximum mass loss rate	Temp (°C)	Maximum mass loss rate	Temp (°C)
Shanxi coal	——		——		18.92	556.5
Shanxi coal+Hebei corn cob	2.09	139.2	8.79	311.1	17.45	549.2
Shanxi coal+Hebei corn cob +V-Mn-TiO_2	1.85	137.1	7.71	307.7	16.68	541.9
Shanxi coal+Hebei corn cob +CaO	1.93	135.7	7.94	316.5	15.10	538.3
Shanxi coal+Hebei corn cob +CaO+V-Mn-TiO_2	1.96	135.2	8.22	313.4	15.36	536.9

According to the maximum rate of weight loss of coal combustion and the corresponding temperature shown in Table 5, the curve of reaction conversion with temperature before and after peak is calculated and it can be shown that with Hebei corn cob, V-Mn-TiO_2 and CaO, the conversion rate increases, indicating that their participation was beneficial to the combustion of Shanxi coal. The conversion with V-Mn-TiO_2 and CaO was lower than that only with Hebei corn cob, because the V-Mn-TiO_2 was not react, and CaO was non-flammable. Therefore, Shanxi coal and Hebei corn cob co-combustion can promote combustion, and the pre-peak conversion rated rapidly while post-peak conversion rate slowly, indicating that the combustion of coal combustion in the early stage burning faster. Ash and other wrapped in the carbon surface reduced carbon particles with the outside, resulting in slow conversion rate because of the reduction of flammable substances in the later stage. According to DTG curve and Coats-Redform equation, the pre-peak and post-peak activation energies of the coal combustion stage and the correlation coefficients of the fitted equations. The correlation coefficient of the fitting equation is equal or greater than 0.99, indicating that linear regression fitting is reasonable and the combustion reaction is suitable for first-order reaction kinetics model. The activation energy of Shanxi coal and corn cob co-combustion is lower than that of Shanxi coal combustion in both stages, indicating that biomass and coal co-combustion can promote combustion, which is consistent with the burning rule obtained by thermogravimetric analysis. When calcium oxide and catalyst were added, the activation energy was reduced, reducing the difficulty of combustion reaction. Coal and biomass co-combustion with calcium oxide desulfurization the titanium dioxide can make the activation energy lower than that of Shanxi coal burned separately in the early and late combustion stage by 12.41kJ/mol and 6.16kJ/mol respectively. Without calcium oxide, the desulfurization decreased by 11.34kJ/mol and 4.57kJ/mol. Therefore, it has bigger influence on the pre-combustion stage than on the post- combustion stage.

4. Conclusion

The characterization of the samples showed that V-Mn-TiO_2 is more stable and the efficiency is higher than V-TiO_2 in combustion denitrification. With Mn doping the mixed-type, titanium dioxide is more stable and it inhibits the growth of grains to make the surface area of V-Mn-TiO_2 larger than that of V- TiO_2.

Microwave can speed up the reaction, shorten the aging time and lower the preparation temperature.

The modified titanium dioxide can reduce the ignition point of co-combustion with Hebei corn cob and Shanxi coal so as to promote complete combustion whether with CaO desulfurization or not. But with CaO desulfurization, the combustion-supporting effect is more obvious.

The modified titanium dioxide catalyst is used in the co-combustion with biomass and coal, which is suitable for the first-order reaction kinetic model. The catalyst has a great influence on the pre-reaction activation energy of the co-combustion which is conducive to the stage of devolatilization.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant No.51476056).

Reference

Feng T., Wang L.F., Lan Y., 2016, Study on co-combustion characteristics and NO release laws of biomass and coal blends at constant temperatures in oxygen-enriched atmosphere, North China Electric Power, 11, 36-42.

Koch H.J., 2017, Quantum biology: unit membrane reduces entropy due to wave particle duality, NeuroQuantology, 15(1), 42-44, DOI: 10.14704/nq.2017.15.1.1010

Li J.F., 2017, Biological origin of consciousness and a physical model of human brain, NeuroQuantology, 15(3), 89-93, DOI: 10.14704/nq.2017.15.3.1102

Malaguti V., Lodi C., Sassatelli M., Pedrazzi S., Allesina G., Tartarini P., 2017, Dynamic behavior investigation of a micro biomass CHP system for residential use, International Journal of Heat and Technology, 35(S1), S172-S178, DOI: 10.18280/ijht.35Sp0124

Puglia M., Pedrazzi S., Allesina G., Morselli N., Tartarini P., 2017, Vine prunings biomass as fuel in wood stoves for thermal power production, International Journal of Heat and Technology, 35(S1), S96-S101, DOI: 10.18280/ijht.35Sp0113

Sayin U.H., 2017, A bio-electrical tornado in the hippocampus: mechanisms of temporal lobe epilepsy, NeuroQuantology, 15(1), 92-103, DOI: 10.14704/nq.2017.15.1.1014

Wang S.Q., Liu M.Z., Sun L.L., 2017, Study on the mechanism of desulfurization and denitrification catalyzed by TiO2 in the combustion with biomass and coal, Korean Journal of Chemical Engineering, 34(6), 1882-1888, DOI: 10.1007/s11814-017-0051-z

Wang S.Q., Liu M.Z., Yao J.F., 2016, Characterization of V and Mn co-doped TiO2 and its visible light photocatalysis study, Oxidation Communications, 841-849.

Wang T.X., Kuang S.W., Fang Q.Y., 2017, Experimental study on co-firing characteristic of coal/biomass blends in O2/CO2 atmosphere, Thermal Power Generation, 46(4), 16-21.

Wang T.X., Kuang S.W., Fang Q.Y., 2017, NOx emission characteristics of coal and biomass co-firing in O2/CO2 atmosphere, Coal Conversion, 40(2), 36-41.

Wang Y., Huang X.H., Lu X., 2016, Experimental study of NOx emissions from coal combustion under oxyful condition, Chinese Journal of Environmental Engineering, 10(7), 3751-3755.

Zaccone R., Sacile R., Fossa M., 2017, Energy modelling and decision support algorithm for the exploitation of biomass resources in industrial districts, International Journal of Heat and Technology, 35(S1), S322-S329, DOI: 10.18280/ijht.35Sp0144

Zhang L., Zhang T.D., Gao R., Tang D.Y., Yang J.Y., Fu T.L., Zhan Z.L., 2016, Phenol adsorption property of high specific surface areas biomass based porous carbon materials, Mathematical Modelling of Engineering Problems, 3(4), 157-161. DOI: 10.18280/mmep.030401

Zhong B.J., Tang H., 2007, Catalytic NO reduction at high temperature by deashed chars with catalysts, Combustion & Flame, 49(1), 234-243, DOI: 10.1016/j.combustflame.2006.04.004.