International Journal of Chemical Engineering and Applications, Vol. 2, No. 1, February 2011
ISSN: 2010-0221

Reaction Configuration Critical Effect in Activated Carbon Desulfurization Process on the Condition of Desorbing by Water

Yi LIU

***Abstract*—Mechanism of activated carbon desulfurization under the condition of desorbing by water is researched according to the result of adsorbing performance experiment using different adsorbents. A new theory is proposed to explain the oxidation process of sulfur dioxide and the formation of the effective adsorption sites when water exists. Argument is presented that effective adsorption sites are produced only at a certain reaction space that can provide appropriate distances and configurations between reactant molecules. Analysis and estimation of reaction space in the whole reaction process are done on the basis of Zawadzki's desulfurization theory. Studies show that the aperture distribution of adsorbent is a crucial factor in the adsorption process and effective adsorbing reaction space will be generated when aperture width is over 1.0nm.Results of this study will lead a correct choice of the suitable activated carbon for flue gas desulfurization and effectively increase activated carbon's adsorption capacity for SO_2.**

***Index Terms*—activated carbon; adsorption; reaction space; sulfur dioxide.**

I. INTRODUCTION

The mechanism of activated carbon desulfurization is investigated extensively in recent years. The intensity of potential energy field is considered to be the determinant of adsorption performance in the past. Nevertheless, some studies show that the activated carbon with large average aperture and relatively weak potential energy field has better adsorption performance when water is used in desorption process. The method of desorbing by water is a constantly -used desorption method with less material loss and lower energy consumption. We must attention the mechanism of activated carbon desulfurization when water exists. As water interferes with the chemical reaction, the process must be more complicated.

It might also be noted, in the process of activated carbon desulfurization, the occurrence of the reaction must rely on certain places. These places are provided by abundant pore structures of activated carbon. Similar to the molecular siege effect of the physical adsorption, chemical adsorption process need such places as well. However, the places of the chemical adsorption process should contain all molecules involved in this process and must be different to that of the physical adsorption. In this paper, a new theory is proposed to draw water into adsorption process trying to explain the oxidation process of SO_2 and the formation of the effective adsorption sites.

II. EXPERIMENTAL

A series of experiments are done to determine the adsorption performance of 5 kinds of activated carbons on which have different aperture distribution under the conditions when water exists or doesn't exist. In these experiments, flue gas is simulated in the light of the same percent content of actual flue gas from boiler. Flow rates of air, vapor and SO_2 are measured and controlled respectively by flowmeters of different ranges. The mass of each kind of activated carbon is 1.5kg. Volume ratios of water vapor and SO_2 are 10% and 3×10^{-3} respectively. Air temperature in the adsorption device is measured with thermocouples and self-compensated potentiometer and is adjusted to 80℃ by a converter. Volume ratio of water vapor is 10%. QGS—08B infrared SO_2 analyzer is used at the intake of simulative flue gas to verify the concentration of SO_2. SO_2 concentration after adsorbing is reported by MSI SO_2 analyzer at real time. Flow velocity of air is regulated to 1.1m/s. After adsorption, 6L distilled water is poured uniformly from the dripping device on top of the adsorption device to desorb adsorbate from adsorbent. Desorption time is 3 min.

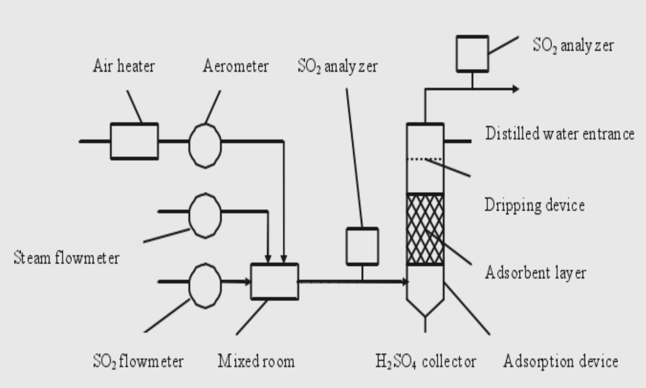


Figure 1. Experimental system

Adsorption capacity of each adsorbent can be calculated according to the penetrating time. Γ_1 and Γ_2 are the mass of adsorbed SO_2 under the conditions when water doesn't

---

Manuscript received February 6, 2011.

Yi LIU is from School of Energy and Power Engineering, Yangzhou University, Yangzhou 225127 China phone: 086-514-87340706; fax: 086-514-87971315; e-mail: liu19740808@ sina.com.cn

exist or exists. Relative adsorption capacity (Φ_1、Φ_2) is defined as the ratio of the mass of adsorbed SO_2 to the mass of the adsorbent.

III. RESULTS AND DISCUSSION

A. Experimental results

Table I shows external surface area (a_w), specific surface area (a_s), aperture peak value (r_{peak}) of each kind of activated carbon and the results of the experiments. Difference can be observed when we use water to desorb activated carbon. When water doesn't exist, adsorption process is a physical process on the whole. Large adsorption capacity comes from the mechanism of multi-layer adsorption. However, under the condition that water exists, the adsorption performance improves when the external surface area is greater, but the specific surface area is independent of the adsorption performance. The reason lies in that when water exists, inner surface area of activated carbon is occupied by water molecule, effective adsorption sites can only form at adsorbent's external surface.

TABLE I. ADSORPTION CHARACTERISTIC OF 5 KIND OF ACTIVATED CARBON UNDER THE CONDITIONS WHEN WATER DOESN'T EXIST OR EXISTS

	MHY10	**MHY30**	**MHY40**	**MHY60**	**MHY100**
$a_w(m^2/g)$	0.012	0.004	0.003	0.002	0.002
$a_s(m^2/g)$	920	750	870	730	710
$r_{peak}(nm)$	0.8-1.0	1.0-2.0	0.8-1.0	1.0-3.5	1.0-4.0
Γ_1 (g)	48.5	30.4	41.5	10.3	9.7
Φ_1(%)	3.23	2.03	2.77	0.68	0.64
Γ_2(g)	5.7	6.5	1.4	1.7	1.8
Φ_2(%)	0.38	0.43	0.09	0.11	0.12

Result can also be found from Table I that the adsorption performance is tied up with the aperture distribution of the adsorbent. When water exists, the adsorption capacity is quite small at the time $r_{peak}<1.0$nm.This brings out a fact that effective adsorption sites will not be generated inside micropores. To understand the truth of the phenomenon, it is essential to analyze the mechanism of the reactions about how to change SO_2 into H_2SO_4.

B. Critical dimension effect

When an adsorption process is only physical process, single molecule will enter the pore of activated carbon and be adsorbed. When the critical dimension of the molecule is slightly smaller than the diameter of the pore, molecular siege effect will take place and potential energy field will increase greatly which promote the adsorption process.

In accordance with the relative position between the pores and the graphite micro-crystal plane, the pores of the activated carbon can be divided into two kinds: interlayer pores and intergranular pores.

The average distance between two activated carbon crystal layers is slightly larger than the distance between two graphite layers. The value of it is about 0.344nm. Interlayer pores come into being inside these layers of which are regarded as a kind of sub-micropores. Molecular siege effect will take place for water molecule whose critical dimension is 0.27nm. Thus, water absorptivity of microporous activated carbon is far better than that of mesoporous activated carbon.

Activated carbon is a kind of amorphous carbon. In its activation technology, a part of the carbon atoms at the edge of the graphite micro-crystal are burned up and intergranular pores are enlarged. The average dimension of intergranular pores will be larger when more carbon atoms are burned up. Thus, intergranular pores of activated carbon can be divided into macropores, mosopores and micropores.

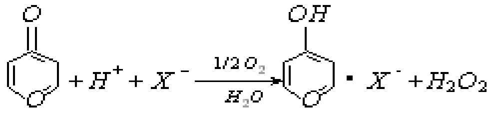
For some macropores whose diameters are more than 50nm, the proportion of the inner surface area to the total surface area is tiny and few reactant molecules can reach reaction sites at the inner surface of the aperture walls. Under the condition of desorbing by water, macropores are mostly served as passages to transport reactant molecules.

For some micropores whose diameters are less than 0.5nm, reactant molecules can't enter them. Thus, adsorption process can't take pace inside it.

For mesopores and a part of macropores whose diameters are between 0.5nm and 50nm, reactant molecules can enter them and the distances of aperture walls to mostly reactant molecules are not too far. Therefore, only the intergranular pores in this range can become effect adsorption sites.

As SO_2 molecule is a kind of covalent molecule, the critical dimension of it contains the dimension of each atom and each bond length. Because the bond length of the two S-O bonds inside SO_2 molecule is 0.143nm, the radius of S atom forming single σ bond is 0.104nm, so the critical dimension of SO_2 molecule is about 0.49nm.This dimension is relatively small and is close to the aperture of the micropore inside activated carbons. From Table I we can see, average particle diameters of MHY30 and MHY40 are approximate, but adsorption performance of MHY40 who has smaller aperture peak value is better when water doesn't exist. Thus, microporous activated carbon has already been widely used on the condition of thermal desorption.

In recent years, the mechanism of activated carbon desulfurization was investigated extensively. Several theories trying to explain the process about the formation of H_2SO_4 were advanced [1]–[7]. However, the importance of water was given only in Zawadzki's theory [8]–[10]. Functions of pyrone structure and non-localized π electrons in the oxidation process are proposed in this theory. When water exists, pyrone structure and non-localized π electrons can both react with H_2O, so that H_2O_2 is produced. H_2O_2 is such a strong oxidizing agent that can turn SO_2 into H_2SO_4. Chemical equations of above process are as follow:



(1)

$$O_2^- + 2H_2O + e^- \rightarrow H_2O_2 + 2OH^- \tag{2}$$

$$SO_2 \cdot H_2O + H_2O_2 \rightarrow 2H^+ + SO_4^{2-} + H_2O \tag{3}$$

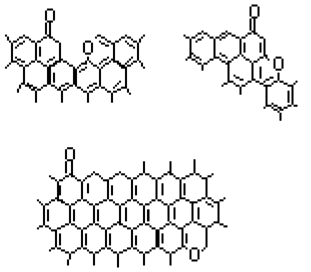


Figure 2. Pyrone structure

Now we have an analysis from the point of the sites where adsorption process can take place. From above, we can find that effective adsorption sites can be generated at two places: the edge of the six-membered rings where pyrone structures exist and the interlayers of the six-membered rings where the electrons are non-localized. These places are both located in the surface of the apertures. Furthermore, the sites where adsorption can take place must be large enough to contain all the molecules involved in all reaction processes. Thus, some tiny apertures will not become effective adsorption sites. In this paper, the theory of adsorbing reaction space is put forward to explain the adsorption process of activated carbon desulfurization [11].

C. *Reaction configuration analysis*

1) *Critical dimension of multi-molecules configuration*

In conformity to the concept of a single molecule's critical dimension, critical dimension of a multi-molecules configuration is defined as the equivalent diameter of the configuration's boundary including electron clouds. The critical dimension of a multi-molecules configuration is much larger than that of a single molecule. Because of the uncertainty of molecules' movement, we can only have the approximation of it [12]–[15].

2) *Formation of H_2O_2*

Known from the reaction equation, the formation of one H_2O_2 molecule needs one O_2 molecule and two H_2O molecules. Geometric configurations of these three molecules are shown in Fig. 3.

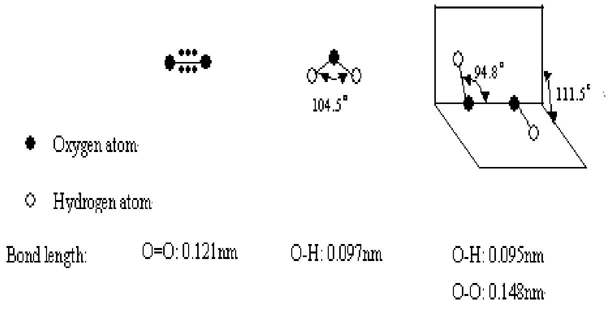


Figure 3. Geometric configurations of O_2, H_2O and H_2O_2

When an electron is received by O_2, O_2^- will be generated whose bond length is 0.128nm. O_2^- brings out strong proto affinity to break one of the O-H bonds from H_2O and obtain one hydrogen atom. Thus, HO_2 is produced. HO_2 is not so steady which can capture another non-localized π electron and converts into HO_2^-. HO_2^- can also break a O-H bond from H_2O. After one hydrogen atom has been received, H_2O_2 is finally produced.

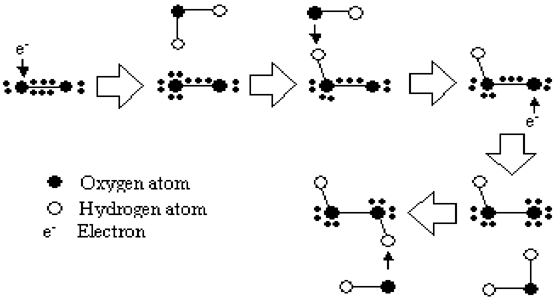


Figure 4. The form process of H_2O_2

From Fig. 4,it can be found that the orientations of two H_2O molecules are different. When bonds are formed, the plane angle of them is 111.5°. Accordingly, H_2O_2 will be generated only when one of the O-H bonds of the H_2O molecule is adjacent and approximately vertical to the covalent bond of the O_2, at the same time another alike configuration is in existence at another orientation.

Multi-molecules configuration of these reactions is shown as Fig. 5. From Fig. 5,we can see the formation of H_2O_2 is involved with a certain space. The minimum dimension of the space is estimated by the method of quantum chemistry.

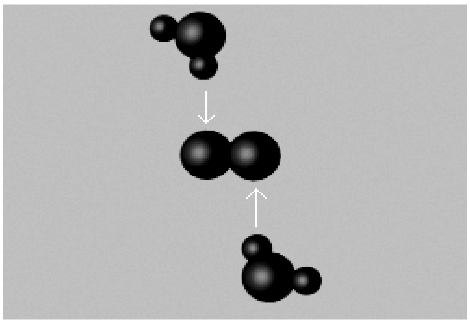


Figure 5. Molecule configuration system for producing H_2O_2

Consulted from "atomic and ionic radius list", we know atomic radius of H forming single σ bond is 0.037nm and atomic radius of O forming single σ bond is 0.066nm.Those who need a specification is, the atomic radius refers to covalent radius inside the same molecule, but not van der Waals radius defined from the distance from different molecules. By estimating the critical dimension of above molecule configuration system, we can draw that the aperture width should be greater than 0.6 nm at least in order to produce effective reaction space.

3) *Formation of* H_2SO_4

There are two S-O σ bonds and one non-localized π bond which has three cores and four electrons inside SO_2 molecule. When water exists, following reactions will take place:

$$SO_2 + H_2O \Leftrightarrow H_2SO_3 \qquad (4)$$

$$H_2SO_3 \Leftrightarrow H^+ + HSO_3^- \quad (K_1 = 1.54\times 10^{-2}) \qquad (5)$$

$$HSO_3^- \Leftrightarrow H^+ + SO_3^{2-} \quad (K_2 = 1.02\times 10^{-7}) \qquad (6)$$

According to the equilibrium constants of above reactions, we can know SO_3^{2-} is the main existence form in alkaline environment. SO_2 will be dissolved and the hydrate $SO_2 \cdot H_2O$ will be generated. A $SO_2 \cdot H_2O$ molecule is composed of one SO_3^{2-} and two H^+. The shape of SO_3^{2-} ^{2}is like a triangular cone and a pair of isolated electrons locate at the top of the cone.

SO_3^{2-} is a kind of strong reducing agent which can react with H_2O_2 to form SO_4^{2-} and H_2O. The shape of SO_4^{2-} is a regular tetrahedron which consist of four S-O σ bonds and four p-d π bonds without isolated electron.

Geometric configurations involved from above process are shown in Fig. 6.

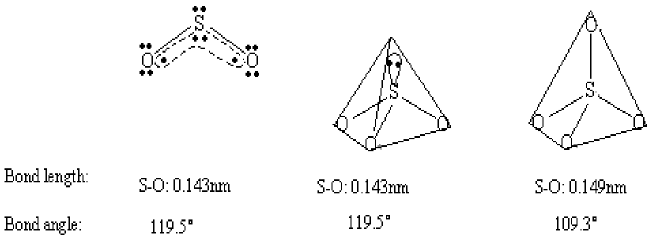


Figure 6. Geometric configurations of SO_2, SO_3^{2-} and SO_4^{2-}

Because the process of H_2O_2 oxidizing SO_3^{2-} is really the process of lone pair electrons of SO_3^{2-} bonding again, the fourth O atom must be provided from H_2O_2 molecule. In this process, O-H bond and O-O bond of H_2O_2 molecule must be broken successively.

When H_2O_2 is generated, it will be ionized into HO_2^- because of the acidity in water. An empty orbit appears in one of the O atom of HO_2^-.

$$H_2O_2 \Leftrightarrow H^+ + HO_2^- \ (K = 1.55\times 10^{-2}) \qquad (7)$$

It can nicely match the pair of isolated electrons and break the O-O bond of HO_2^-. An O atom is gained by SO_3^{2-} and SO_4^{2-} $^-$is generated. Synchronously, O-H bond coming from HO_2^- and H^+ already in the water combine together and H_2O is produced.

The form process of H_2SO_4 is shown as Fig.7.

Multi-molecules configuration of above reactions is shown as Fig. 8.

From Fig.8, it can be observed that the covalent bond in SO_3^{2-} and the fourth O atom can only be built when an O atom of the O-H bond in the H_2O_2 molecule is adjacent to the pair of isolated electrons of SO_3^{2-}. By estimating the critical dimension of above molecule configuration system, we can draw that the aperture width should be greater than 0.7 nm at least in order to produce effective reaction space.

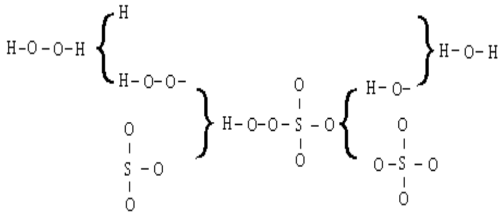


Figure 7. The form process of H_2SO_4

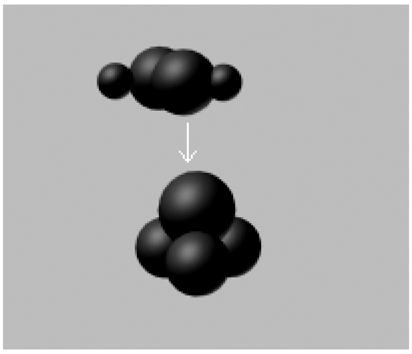


Figure 8. Molecule configuration system for producing H_2SO_4

Nevertheless, what we should know is that the existence form of H^+ in H_2O is not a single proton but a kind of hydrated ion such as $H_3O^+, H_5O_2^+$ and so on. With the decrease of the temperature, H_2O molecules hydrated with H proton will increase from which large-scale hydrated molecules can form. Critical dimensions of such large-scale hydrated molecules are greater than the aperture widths of many micropores, so these molecules can't enter these spaces.

On the condition of absolute physical adsorption, many micropores whose aperture widths are about 0.5nm to 0.7 nm become optimal pores. However, combined with above illustration, when chemical adsorption occurs, these pores can't be used absolutely. When water exists, aperture dimension of activated carbon required for desulfurazation technology should be larger than that of the only physical adsorption.

4) *Associated effect of multi- molecules configuration*

Molecules associated effect is an action combining some molecules altogether under van der Waals forth. By making time-division experiments about activated carbon desulfurizition process, Molina has an opinion that a small quantity of SO_2 molecules adsorbed firstly will produce greater van der Waals forth to make the adsorption of other

SO_2 gas molecules easy [11]. However, in flue gas desulfurization process, the partial pressure of SO_2 is too low to cause enough associated effect.

Nevertheless, when water exists, a lot of H_2O molecules go into aperture structures and force situations of such molecules are changed. The function of hydrogen bond must be considered.

In the strict sense, hydrogen bond is not a kind of chemical bond, but its bond enthalpy is much larger than van der Waals forth. Enthalpy of the hydrogen bond among H_2O molecules is 18.8kJ/mol while van der Waals forth among them is only 6.2kJ/mol. A stronger force arises among H_2O molecules because of the existence of the hydrogen bond and some molecules associated each other shown as Fig.9.

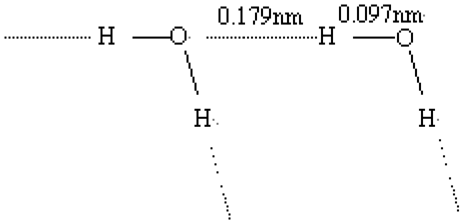


Figure 9. Associated effect between H_2O molecules

H_2O molecule can enter tiny micropore because its critical dimension is only 0.27nm. However, the critical dimension of $(H_2O)_2$ is 0.45nm. Associated effect occurs not only between two molecules, but also among many molecules. When associated coefficient x increase, the critical dimension of $(H_2O)_x$ must be larger and can't be accepted by some small pores. These H_2O molecules in $(H_2O)_x$ can't reach the adsorption sites at the edge of the six-membered rings and the sites can't obtain the reactant H_2O molecules required by the oxidizing reaction, so that the oxidizing reaction process of SO_2 is hampered to some extent.

From Fig.3 we can see, there are two pairs of isolated electrons around each O atom inside H_2O_2 molecule so as to produce hydrogen bonds. Because there are four pairs of isolated electrons inside H_2O_2 molecule and four hydrogen bonds formed at most, the association degree of H_2O_2 molecules must be much higher than that of the H_2O molecules (see fig.10).

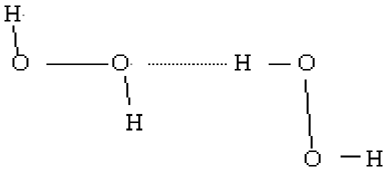


Figure10. Associated effect between H_2O_2 molecules

Furthermore, associated effect will also occur between H_2O_2 molecule and H_2O molecule because of the similarity of their structures (see fig.11).

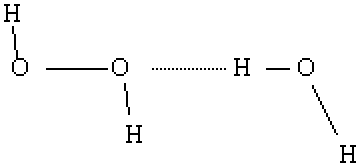


Figure11. Associated effect between H_2O_2 molecule and H_2O molecule

The associated effect of H_2O molecules and H_2O_2 molecules caused by hydrogen bonds leads to the further increase of the critical dimension of the multi-molecules configuration. Associated coefficient is a crucial parameter in estimating the critical dimension of the whole configuration. It will decrease when the liquid temperature increases

When water vapor is at its saturation temperature, 3.5% bimolecular polymers exist. With the decrease of the temperature, associated effect is being enhanced to make more H_2O or H_2O_2 molecules combining. In H_2O or H_2O_2 molecule groups, the range of the average associated coefficient are 2~3 under normal conditions.

At the time SO_2 exists, H_2O_2 will react with SO_2 hydrate. If H_2O_2 exists in the form of molecular group, the space volume occupied by the whole reaction system will contain this molecular group and will be sure to be larger. This leads to further increase of the aperture width lower limit and more micropores won't be utilized inevitably.

D. Adsorption performance analysis among different materials

From above illustration we can realize, there is a lower limit in the pores of the activated carbon. Reaction space can only be produced at the sites whose width exceeds this lower limit. But on the other hand, not all of the pores whose width exceeds the lower limit can be regard as reaction space. As activated site of six-membered ring is located on the surface of the pore, H_2O_2 molecule is certain to be produced near the aperture wall at first. The quantity of the activated sites is limited, so the quantity of H_2O_2 molecules is confined. For some large pores, these H_2O_2 molecules are surely to center near the aperture wall and few H_2O_2 molecules can diffuse to the pore space. The larger of the pore volume is, the smaller of the proportion of the space that can become reaction space.

Furthermore, when the aperture width is too large, the adsorbing potential energy field is weakened. This also becomes a hindrance to make large pores becoming adsorption sites. Therefore, most of the space can't be regarded as reaction space for all macropores and some mesopores having larger aperture width.

Seen from Table I, the aperture peak values of MHY10 and MHY40 are less than 1.0nm and no more than one reaction configuration can exist inside most of their aperture structure. Moreover, many micropores whose aperture widths are less than 0.7nm are not available for adsorption at all. At the same time, the aperture peak values of MHY30, MHY60 and MHY100 are more than 1.0nm. Few tiny pore structures exist inside these kinds of mesopore-type activated carbon. Reaction configurations required for adsorption process will be realized inside a majority of their pores. H_2O molecules inside these pores can participate in SO_2 oxidizing process adequately so as to convert SO_2 to H_2SO_4.

When the external surface areas differ not so much, the adsorption performances of different aperture distributed activated carbons behave quite different. For example, the external surface areas of MHY30 and MHY40 are both about 0.003~0.004 m^2/g, but the adsorption performances of them are 4.8 to 1. These results prove that a lot of micropores whose aperture width is less than 1.0nm can’t become effective reaction sites.

From experimental results, conclusion can be drawn that the most effective adsorbing reaction space can be generated when aperture width is nearly 1.0nm.

From another point of view, it can also be seen from Table I, when the aperture distributions are approximate, the adsorption performances are affected very much by the external surface area. The aperture peak values of MHY30, MHY60 and MHY100 are all more than 1.0nm,but the adsorption performances of them are different too. The activated carbon MHY30 having large external surface area is apparently superior in its adsorption performance.

IV. CONCLUSIONS

Under the condition of desorbing by water, the mechanism of activated carbon desulfurization is complicated. When water exists, the oxidation of SO_2 to H_2SO_4 must depend on a certain reaction space, effective adsorption sites can only be generated at the adsorbent surface where can form appropriate distances and configurations between reactant molecules. Adsorption capacities of activated carbons are restricted by the multi-molecules configuration critical effect and some micropores can’t be utilized. Consequently, the aperture distribution of adsorbent is a crucial factor in the adsorption process and a type of good adsorbent MHY30 whose peak value of aperture is over 1.0nm and granule size is about 3mm is put forward.

ACKNOWLEDGMENT

The article is funded by the natural science foundation of ministry of education of Jiangsu Province (07KJD610252).

REFERENCES

[1] S.M.Molina, M.A.Munecas, R.F. Rodriguez,“Adsorption of CO2and SO2 on activated carbons with a wide range of micropore size distribution”,Carbon,vol.33,1995,pp.1777-1782.

[2] K Nilgün，O Ilkün，Y Reha，et al · “Sulfur dioxide adsorption by activated carbons having different textural and chemical properties,” Fuel，vol 26, 2008，pp:1-9.

[3] B Grzyb，A Albiniak，E Broniek，et al · “SO2 adsorptive properties of activated carbons prepared from polyacrylonitrile and its blends with coal-tar pitch,” Microporous and Mesoporous Materials，vol 118, 2009,pp:163-168.

[4] L Jianjun ，K Noriyuki，H Yongqi, · “The activated coke preparation for SO2 adsorption by using flue gas from coal power plant,” Chemical Engineering and Processing，vol 47, 2008, pp.118-127 ·

[5] I. Mochida，Y. Korai， M. Shirahama， “Removal of SOx and NOx over activated carbon fibres,” Carbon，vol. 38, 2000，pp. 227-239..

[6] A. A. Lizzio, J. A. DeBarr, “.Mechanism of SO2 removal by carbon,” .Energy and Fuels，vol. 11, 1997，pp.284-291..

[7] B. Rubio, M. T. Izquierdo, “Low cost adsorbents for low temperature cleaning of flue gases,” Fuel，vol. 77, 1998，pp. 631-637.

[8] J. Zawadzki · “Infrared studies of SO2 on carbon- Ⅰ.Interaction of SO2 with carbon films,” Carbon，vol. 25, 1987, pp. 431-436.

[9] J. Zawadzki, “Infrared studies of SO2 on carbon-Ⅱ.The SO2 species adsorbed on carbon films,” Carbon，vol. 25, 1987, pp. 495-502.

[10] J Zawadzki ，M Wisniewski · “An infrared study of the behavior of SO2 and NOx over carbon and carbon-supported catalysts,” Catalysis today，vol.117, 2006:pp.213－218.

[11] Y. Liu, Z. G. Zhang，Q. Tang, “Application of ACF in desulfurization process from flue gas,” .Plasma Science and Technology，vol. 6, 2004, pp. 2419-2422.

[12] K. Nilgün， O. Ilkün， Y. Reha, “Sulfur dioxide adsorption by activated carbons having different textural and chemical properties,” Fuel， vol. 26, 2008, pp. 1-9.

[13] G. Vivekanand, A. Ritesh, V. Nishith, “Removal of SO2 by activated carbon fibers in the presence of O2 and H2O,” Carbon, vol. 44, 2006， pp. 46-60.

[14] P. Davini, “Flue gas desulphurization by activated carbon fibers obtained from polyacrylonitrile by-product,” Carbon, vol. 41, 2003， pp. 277-284.

[15] H. Fortier，C. Zelenietz，T. R. Dahn, “SO2 adsorption capacity of K2CO3-impregnated activated carbon as a function of K2CO3 content loaded by soaking and incipient wetness,” Applied Surface Science, vol. 253, 2007, pp. 3201-3207.

Yi Liu received his PhD degree in power engineering and engineering thermodynamics in 2004 from Xi’an Jiaotong University. Currently his main efforts are taken to the mechanism of activated carbon desulfurization process as well as to exploit its potential application for industry.