Low-Temperature Oxidation of Methylene Bridge Bond in Coal by Model Compound

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In order to find out characteristics of active structures in coal at early phase of oxidation, diphenylmethane was adopted as the model compound to study the oxidation properties of bridge bond (methylene) in coal with low-temperature experimental condition (293 K-423 K), according to structure of molecular coal. Mean while, the generated oxidation products under different reaction conditions were analyzed qualitatively *via* FTIR spectrometer and GC-MS. The results show that the new structures which involve C-O, C=O, Ar-O and Ar-OH are constantly generated with temperature rise in the process of low-temperature oxidation of diphenylmethane, especially after the 393 K. Besides, the phenols, benzaldehyde, diphenylmethanone, phenyl benzoate, 2-benzyl phenols and 2-phenolic-diphenylmethanone were detected in oxidation products, which demonstrated this oxidation is a multi-step reaction. Meantime, the substitution between O and H is more easily occurs in -CH_2- than in benzene ring. The temperature and time are major factors which affecting low-temperature oxidation of diphenylmethane. In conclusion, this study provides reference for explaining and controlling the low-temperature oxidation of coal from chemical perspective.

Keywords: Low-temperature oxidation, Methylene, Diphenylmethane, Model compound, Spontaneous combustion.

INTRODUCTION

The spontaneous combustion of coal is a worldwide disaster[1], which often occurs in the coal-related industries. Coal fire raised by self-heating of coal also responsible for the environmental problems such as surface subsidence, toxic gas emissions and water pollution[2-3]. Since the 17th century, numerous reasons[4-7] were considered to be inducing factors which effect on spon-combustion of coal. Although many scholars attempted to reveal variations of various coal molecular structure in the process of self-ignite with multiple testing means[8-11], its mechanism is still unknown. At present, making use of model compound to study complicated chemical system is a effective research approach which widely applied in processes such as coal liquefaction[12-13], coal desulfuration[14] and petroleum refining[15].

In line with molecular structure of coal, the main construction units of coal are aromatic rings which interrelated *via* bridged bond (aliphatic hydrocarbons bond, thioether bond and ether bond *etc*.) and active group[16]. Besides, chemical characteristics of aromatic ring are relatively stable. Bridged bonds and active groups in coal molecular structure are firstly oxidized[17-18]. In other words, the oxidation of such structures as bridged bonds and active groups play an important role in inducing spontaneous combustion of coal. As a result, well targeted study of oxidation properties of bridged bond and active group in coal in the process of low-temperature oxidation has become the top priority of study concerning spontaneous combustion of coal.

The low-temperature oxidation of coal is the most important initial part[19-21] for the whole process on self-ignite. Methylene is typical bond in coal molecule[21,22]. Therefore, studying low-temperature oxidation properties of methylene is of certain guiding significance to reveal spontaneous combustion of coal. Thus, model compound comprised by methylene and its coupled aromatic ring was adopted as experimental subject in this paper.

EXPERIMENTAL

Experimental set-up: The schematic diagram of experimental apparatus was shown in Fig. 1. In experimental system, dry air uniformly passes through pipeline. The temperature control system assures that the sample can enables to be conducted by temperature programming and stabilized at the setting temperature.

Experimental procedure: The diphenylmenthane (50 g) was placed into glass bottle and the air (2 L/m) passed into it
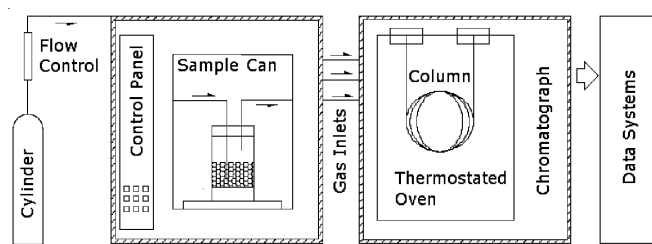
Fig. 1. Experimental set-up

continuously for oxidation. Keep oxidizing 24 h. under different setting temperatures (333 K-393 K) and collect the sample of 1 mL at intervals of 4 h. Afterwards, products constituents were qualitatively analyzed through GC-MS (split ratio of 30:1). The concentration variation of its oxidation products under different reaction conditions was analyzed quantitatively *via* gas chromatograph. Meanwhile, the variation features of its functional group under different reaction conditions were tested by FTIR.

RESULTS AND DISCUSSION

Infrared spectroscopy is a kind of test method which could effectively reflect the changes of functional groups in organics[23]. As shown in Fig. 2, the main characteristic peaks of infrared spectrogram of diphenylene include absorption peak at 3023 cm^{-1} representing C-H stretching vibration on aromatic ring, at 2907 cm^{-1} and 2843 cm^{-1} representing C-H
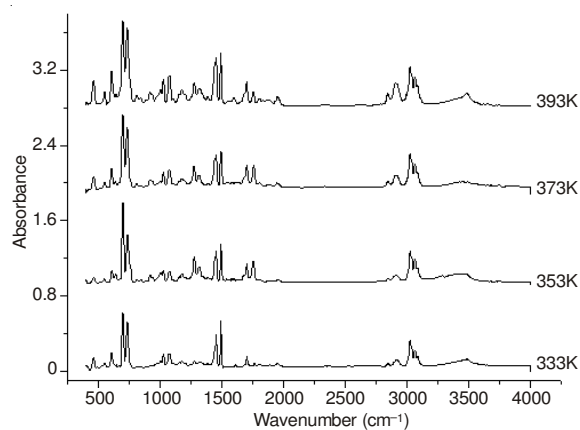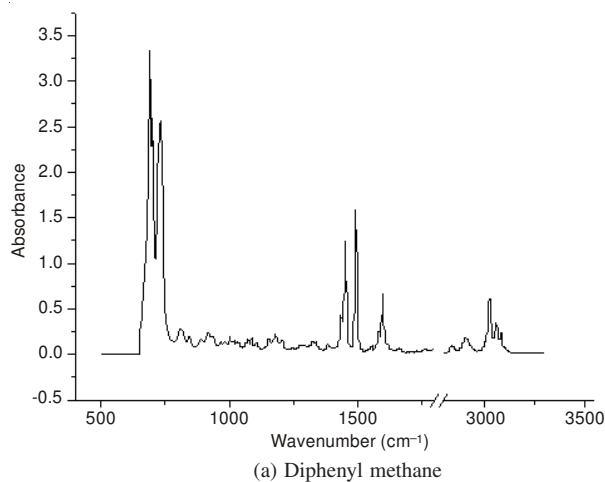
(a) Diphenyl methane

(b) Diphenyl methane after oxidized 24 h

Fig. 2. Infrared spectrum of diphenyl methane and its oxidation

stretching vibration in alkane, at 1601 cm^{-1} representing C=C skeletal vibration on aromatic ring, at 1492 and 1444 cm^{-1} representing C-H flexural vibration in alkane, at 729 and 681 cm^{-1} representing C-H out-of-plane deformation vibration of aromatic hydrocarbon where H was replaced.

The activity structure in dipenylmethane was oxidized continuously with the ceaseless temperature increase. After oxidation, there lies in larger variation of activity structure in dipenylmethane. To be specific, when the reaction temperature was 333 K, absorption peak representing C-O stretching vibration occurred at 1072 and 1034 cm^{-1} after low-temperature oxidation for 48 h, which indicated that C-O bond was gradually generated. Meanwhile, a small adsorption peak representing C=O (ketone) also emerged at 1076 cm^{-1}. And there were fewer changes among other adsorption peaks. When reaction temperature rose to 353 K, the adsorption peak representing ether bond gradually appeared at 1319 and 1277 cm^{-1}, which showed that stretching vibration of aliphatic ether structure and aromatic ether structure started to appear along with temperature rise. Besides, at 1706 and 1746 cm^{-1} signified that adsorption peak of C=O gradually enhanced. When the temperature reached 373 K, at 2907 and 2843 cm^{-1} representing CH$_2$ antisymmetric stretching vibration in naphthene or aliphatic series involved slight enhancement aside from adsorption peaks represented by previously generated structures.

Finally, when reaction temperature reached 393 K, the adsorption peak of Ar-OH was relatively obvious showing at 3487 cm^{-1}. Yet, this adsorption peak under reaction temperature of 333 K exhibited in the spectrogram. Its intensity gradually increased along with temperature rise, which indicated that phenolic compounds were generated in low-temperature oxidation process of diphenylmethane.
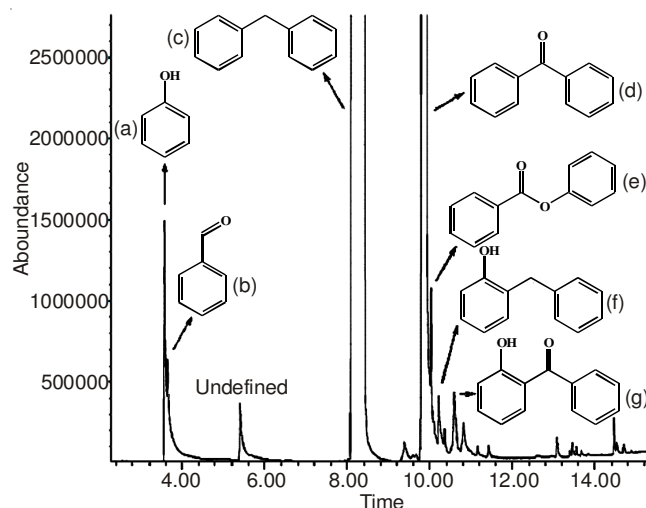

Fig. 3. Chromatograms for composition of oxidation products from diphenylmethane at 393 K

The liquid oxidation products of diphenylmethane were qualitatively analyzed *via* GC-MS. It can be clearly shown from Fig. 3 that (d) diphenylketone was generated by diphenylmethane oxidation. Meanwhile, such substances as (a) phenol, (b) benzaldehyde, (d) diphenylketone, (e) phenyl benzoate, (f) 2-benzylphenol, (e) 2-phenolic -diphenylketone were tested. As we all know, the active group included in

diphenylmethane is methylene on which αC atom and bilateral benzene rings involve δ-π hyperconjugation. As a result, the electron cloud between αC atom and αH atom and conjugated system of aromatic ring could be integrated into one. In this way, electron delocalization extent enlarged where free radical can be easily formed. And, bridged bond among benzene rings was easier than benzene ring itself to make adsorption with oxygen. Combined with oxidation products detected by experiment, it can be inferred that the reaction course of diphenylmethane and O_2 is as follows (Fig. 4):
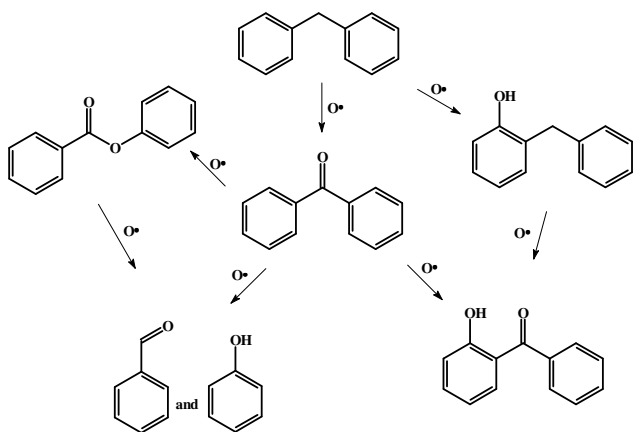

Fig. 4. Simple oxidation reaction pathway of diphenyl methane

This pathway suggested that the supplant primarily happened between oxygen atom and hydrogen atom on bridge bond of methylene during the oxidation of diphenylmethane. Meantime, some oxygen atoms replaced the hydrogen atom on the benzene ring. In the process of reaction, the generation of carbon monoxide and carbon dioxide along with the breaking of bonds.

In the experiment the production rate of diphenyketone was the highest among diverse oxidation products. Thus, it was deemed as the vital product to make qualitative analysis. As shown in Fig. 5, at 333 K, phenol concentration generated in reaction increased slightly as time increased. But, it still remained at lower level (0.33 %). As the temperature constantly escalated, phenol concentration generated in reaction increased continuously. When reaction temperature was 353 K, phenol concentration slightly increased compared with that under the temperature of 333 K. But when reaction temperature was 373 K, the generated phenol concentration clearly rose through oxidation for 24 h. (0.82 %). Especially, when reaction temperature was 393 K, the generated phenol concentration sharply rose. And phenol concentration reached 0.95 % after reacting for 12 h. However, the phenol output had no substantial increase along with constant increase of reaction time. It just rose slowly over time. The phenol concentration reached 1.25 % after reacting for 24 h. By contrast, the concentration of the other major product, diphenyl-ketone in reaction rose stably as temperature and reaction time increased. However, the rising rate of product concentration was higher. Based on the above, it can be found that reaction time is one influential factor. Besides, it also proves the significant influence of temperature on this reaction.

(a) Phenol
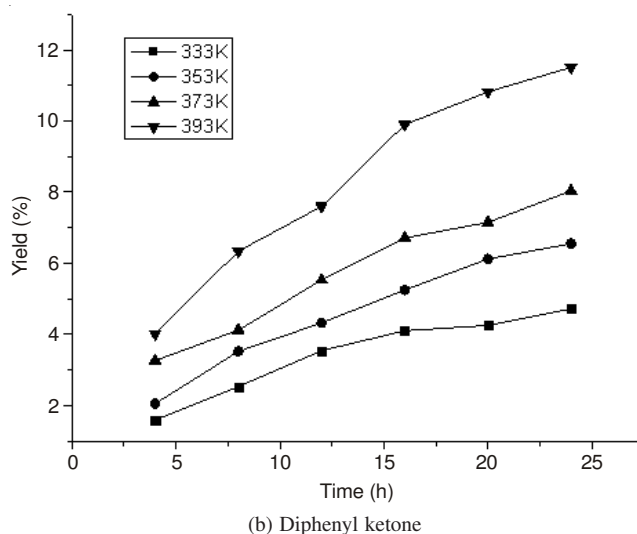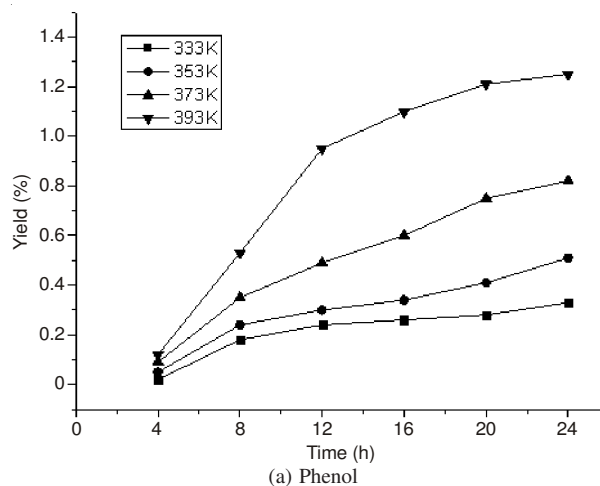

(b) Diphenyl ketone

Fig. 5. Effect of temperature and time on the oxidation of diphenyl methane

Air flow also exerts evident impact on oxidation of diphenylmethane. To be specific, the larger the air flow is, the higher the contact efficiency of diphenylmethane and oxygen in air is.
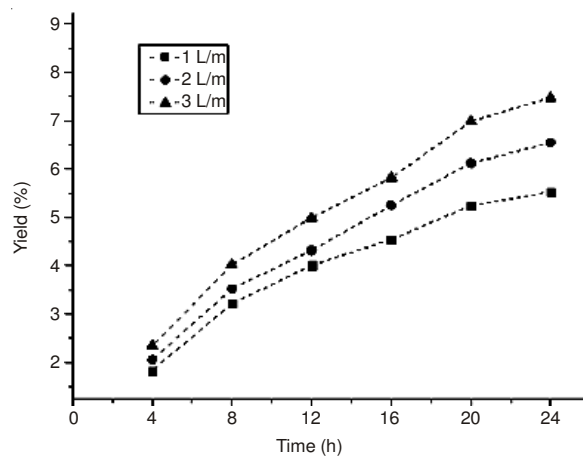

Fig. 6. Yield of diphenyl methanone from oxidation of the diphenylmethane under different airflow at 353 K

As show in Fig. 6, oxidation rate of diphenylmethane increased constantly along with air flow increase. Under the same reaction time, the proportion of diphenylketone generated in

reaction was increased with the growth of air mass flow. When air flow increased from 1 to 3 L/min, the proportion of generated diphenylketone rose from 5.53 to 7.48 % after reacting for 24 h. In the early stage of reaction, the impact of increasing ventilation mass flow on diphenylmethane was hardly obvious. However, as time passed by, the impact of increasing ventilation mass flow on productivity of diphenyl-ketone was more and more obvious. The concentration difference of diphenylketone generated in reaction was larger and larger, which indicates air flow is one of factors affecting low temperature oxidation of diphenylmethane.

Conclusions

The oxidation process of diphenylmethane is complicated multistep reaction ranging from the initial chemisorptions, final multistep decomposition reaction to eventual generation of various products.

• It can be deduced that methylene in diphenylmethane can make composite oxidation with oxygen under normal temperature. Even its oxidative activity is weaker under normal temperature, it would constantly improve along with temperature rise.

• The substitution is easily happens between O and -CH₂-connected two benzene rings and then two benzene rings will lose connection through a further multi-step oxidation. Only small part of the oxygen will directly substitute the H on the benzene ring. No matter what kind of reaction happened, various intermediate products such as aldehydes, phenols and ketones were generated in this oxidation, which demonstrated the transfer of O free radicals is very active in this reaction.

• Furthermore, reaction time exerts the certain impact on activity structure oxidation in diphenylmethane. But the impact of reaction temperature is much larger. More absorption peaks (C-O, C=O, Ar-O and Ar-OH) were increasely appeared as long as the temperature reached 393 K, which meant this reaction efficiency would rise greatly after 393 K.

• Besides, air flow involved in reaction is also another factor that affects reaction efficiency. In the early stage of reaction, the influence of air flow on reaction is not apparent. However, as reaction time grows continuously, this influence of air flow on reaction efficiency is increasingly obvious.

These studies demonstrate that the oxidation of methylene bridge bond is prone to occur at low temperature conditions and also an important part of the radical chain reaction caused self-heating of coal. More importantly, the detail information on oxidation properties and reaction pathway of methylene bridge bond supply a foundation for selecting inhibitors used in hindering self-ignite of coal, while the targeted retardant usually has better inhibiting effect.

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