The Investigation of Reducing PAHs Emission from Coal Pyrolysis by Gaseous Catalytic Cracking

Yulong Wang, Ruifang Zhao, Chun Zhang, Guanlong Li, Jing Zhang, and Fan Li

State Key Laboratory Breeding Base of Coal Science and Technology Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China

Correspondence should be addressed to Fan Li; lifan66@hotmail.com

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The catalytic cracking method of PAHs for the pyrolysis gaseous products is proposed to control their pollution to the environment. In this study, the Py-GC-MS is used to investigate in situ the catalytic effect of CaO and Fe$_2$O$_3$ on the 16 PAHs from Pingshuo coal pyrolysis under different catalytic temperatures and catalyst particle sizes. The results demonstrate that Fe$_2$O$_3$ is effective than that of CaO for catalytic cracking of 16 PAHs and that their catalytic temperature corresponding to the maximum PAHs cracking rates is different. The PAHs cracking rate is up to 60.59% for Fe$_2$O$_3$ at 600°C and is 52.88% at 700°C for CaO. The catalytic temperature and particle size of the catalysts have a significant effect on PAHs cracking rate and CaO will lose the capability of decreasing 16 PAHs when the temperature is higher than 900°C. The possible cracking process of 16 PAHs is deduced by elaborately analyzing the cracking effect of the two catalysts on 16 different species of PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hazardous organic pollutants widely existing in the environment. Many of them have the carcinogenic, teratogenic, and mutagenic effects which mainly come from incomplete combustion of fossil fuels and hydrocarbons or from the pyrolysis in their reducing process [1]. Although the amount of PAHs in environment is trace, it has become a great menace to human health because it distributes widely in the air, soil, water, and vegetation through continuous generation, transformation, migration, and degradation and will enter the human body through the respiratory tract, skin, and digestive tract. Consequently, the sources of PAHs have received considerable attention from people.

The coal pyrolysis is the most important step of coal conversion process, and the thermal processing of coal is considered as the main source of PAHs in the environments [2]. The generation and emission control of PAHs in the coal transforming processing were focused on by many researchers. In recent years, many researchers have investigated the influence of metal oxide catalysts on PAHs yields during coal combustion and organic matter decomposition [3–7]. A prominent catalytic effect on cracking biomass oil by using olivine or dolomite was found [8–11]. Using the characteristic online coal pyrolysis and products catalytic cracking analysis technology, this paper probed into the cracking effects of CaO or Fe$_2$O$_3$ which were the main effective compositions of olivine or dolomite on the 16 PAHs of the coal pyrolysis products on the Environmental Protection Agency (EPA) Priority Pollutant List. The applicable catalysts and catalytic conditions reducing the PAHs emission during coal pyrolysis were selected. The results also provided a theoretical foundation for the industrial application.

2. Materials and Methods

2.1. Materials

2.1.1. Coal Sample. PS coal (from Pingshuo coal mine, China) that can generate more PAHs during coal pyrolysis was chosen as the sample in the study. The particle size was between 100 and 120 mesh. The proximate and ultimate analysis of PS coal was shown in Table 1.
2.3. Quantitative Analysis of PAHs. For the convenience of investigating the catalytic effects of metallic oxidant on PAHs with different ring number, the 16 PAHs were divided into LMW-PAHs (2-3 rings PAHs): naphthalene (2 rings), acenaphthylene (3 rings), acenaphthene (3 rings), fluorene (3 rings), phenanthrene (3 rings), anthracene (3 rings), MMW-PAHs (4 rings PAHs): fluoranthene (4 rings), pyrene (4 rings), benzo[a]anthracene (4 rings), chrysene (4 rings), HMW-PAHs (5-6 rings PAHs): benzo[b]fluoranthene (5 rings), benzo[k]fluoranthene (5 rings), indeno[123-c,d]pyrene (6 rings), dibenzo[a,h]anthracene (6 rings), and benzo[g,h,i]perylene (6 rings) [13].

The cracking rate of 16 PAHs was defined as

$$ X = \frac{C_1 - C_2}{C_1} \times 100\% $$

where $C_1$ is the concentration of 16 PAHs in pyrolysis gas and $C_2$ is the concentration of 16 PAHs after catalytic cracking.

The quantitative analysis of 16 PAHs was performed by the external standard method. The standard curve of 16 PAHs was generated by the GC-MS using five PAHs standard solutions with different PAHs concentrations (0.2 µg/mL, 0.4 µg/mL, 0.8 µg/mL, 1.0 µg/mL, and 1.2 µg/mL). The correlation coefficient ($r^2$) of each standard curve was greater than or equal to 0.991. In order to research the effect of metallic oxide on PAHs, the quantitative analysis of 16 PAHs was performed by mass spectrometer in SIM mode which had high selectivity and sensibility for the PAHs. Meanwhile, the qualitative analysis of pyrolysis production was performed by mass spectrometer in full scan mode to study the change of some important compounds in the pyrolysis process. All the experiments were replicated at least three times to make sure that the results were reproducible. Quality control of PAHs analysis was the same as the previous study [12].

3. Results and Discussion

3.1. The Effects of Temperature on Catalytic Cracking of PAHs. The influences of temperature were discussed on the emission of 16 PAHs cracked by CaO and Fe$_2$O$_3$ during coal pyrolysis, and the amount and the particle size of CaO and Fe$_2$O$_3$ were 0.4 mg and 140–160 mesh, respectively. Figure 1 showed that CaO and Fe$_2$O$_3$ can reduce the total PAHs (represented the total amount of 16 PAHs). The maximum cracking rate for Fe$_2$O$_3$ is 55.64% at 600°C and it is better than that of CaO which is 44.29% at 700°C.

It can be inferred that there were many active centers on the CaO surface. These active centers could deform p-electron cloud of the condensed aromatic compounds generated from the coal pyrolysis [14]. That is to say, the stability of PAHs was weakened and the activation energy of catalytic cracking PAHs was lowered. It illustrated that CaO was advantageous in cracking PAHs.

When the temperature is higher than 900°C, total account of PAHs from catalytic cracking coal pyrolysis products was higher than that generated from the raw coal pyrolysis. As
is shown by Figures 1 and 2, the PAHs cracking rate increased with the increase of temperature, especially that of the HMW-PAHs. At a high temperature (900–1000 °C), CaO played a major role in PAHs dehydrogenization which led to a polycondensation of PAHs [15], generating more PAHs from the catalytic coal pyrolysis products.

So the conclusion was that CaO had different catalytic roles at different temperatures for PAHs. At the high temperatures, CaO would lose the capability of decreasing 16 PAHs. At the low temperatures (600–800 °C), CaO played a major role in catalytic cracking of PAHs.

Compared with CaO, Fe$_2$O$_3$ was observed to have the cracking effect on PAHs at different temperatures (600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C), but the cracking rate for total PAHs did not reveal a principle tendency with the increase of the temperature. At 800 °C, the total PAHs cracking rate was the minimum for Fe$_2$O$_3$. Some possible reasons are that the coal pyrolysis process released CO and H$_2$ reacting with Fe$_2$O$_3$ and the products Fe$_3$O$_4$, FeO, and Fe or other materials were generated and had an effect on catalytic cracking of PAHs [16].

By comparing Figures 2 and 3, it can be found that the cracking capacity of Fe$_2$O$_3$ on LMW-PAHs and MMW-PAHs was better than that of CaO at a temperature in the range of 600 °C–700 °C. CaO exposed a better cracking capacity on LMW-PAHs at 800 °C than Fe$_2$O$_3$, and the corresponding cracking capacity on MMW-PAHs for the two catalysts was similar. When the temperature was higher than 900 °C, Fe$_2$O$_3$ exposed cracking effect on LMW-PAHs and MMW-PAHs while CaO had the catalytic forming effect on all the PAHs. Besides, a more remarkable catalytic forming effect on HMW-PAHs was found at 1000 °C by CaO.

3.2 Effects of Particle Size during Catalytic Cracking of PAHs. In order to reveal the influence of particle sizes on the catalytic cracking effect, different particle sizes (60–80 mesh, 100–120 mesh, 140–160 mesh, and 180–200 mesh) were selected for a fixed amount of catalyst. Temperatures of 700 °C and 600 °C were chosen which were the highest cracking rate for CaO and Fe$_2$O$_3$, respectively. The amount of catalyst was set to 0.4 mg.

Figures 4 and 5 demonstrated that the total PAHs cracking rate decreased with the decrease of catalyst particle size. The maximum cracking rate of PAHs was 52.88% and 60.59%, respectively, for CaO and Fe$_2$O$_3$ with 60–80 mesh. Figures 6 and 7 showed that the cracking rate of LMW-PAHs and MMW-PAHs declined with the increase of particle size through CaO or Fe$_2$O$_3$, while the HMW-PAHs cracking rate had a contrary tendency. The reason for these phenomena could be that the cracking activity of two catalysts increased with the increase of particle size. The organic macromolecular
3.3. Catalytic Cracking Mechanism. To deeply understand the catalytic cracking effect on coal pyrolysis products and find out possible process formed or cracked the PAHs, the distribution of catalytic cracking products was analyzed in the GC-MS on full scan mode. This experiment used CaO and Fe$_2$O$_3$ as catalysts with 0.4 mg and 140–160 mesh, respectively. CaO performed a catalytic cracking effect on 16 PAHs at 700°C and a forming effect at 900°C. But Fe$_2$O$_3$ only showed a catalytic cracking effect on 16 PAHs. So, 700°C was selected for the contrast.

The LMW-PAHs, MMW-PAHs and their isomers was shown in Figure 8, and they were catalyzed by CaO at 700°C as mentioned above. In addition, the PAHs and their derivatives were decreased synchronously. It was illustrated that CaO had an effect on breaking both the aromatic rings of PAHs, aromatic hydrocarbons with branches and aliphatic hydrocarbons. With the amount of naphthalene decreased by CaO, the alkyl-substituent benzene also decreased. It was known that naphthalene is more favorable to transforming into the gas, small molecular alkanes and alkenes, alkylene-substituent benzene, or their isomers.

In the case of methyl-naphthalene, Figure 9 showed the probable path to forming and cracking of PAHs with CaO. The compound on the left represents the aromatic ring with...
branches, the naphthalene in the middle is aromatic ring, and the ethenylbenzene is the aromatic ring with alkenyl.

At 900°C, CaO played a major role in PAHs dehydrogenation and catalyzed the coal pyrolysis products to polymerize. Taking methylbenzene as an example, when the temperature was higher, the methylbenzene should lose a hydrogen atom, then become the free radical; the free radical reacted with other lower weight molecules and formed naphthalene. On the contrary, the naphthalene and the methylbenzene increased. It was illuminated that the amount of naphthalene that came from free radical reaction was lower than that from other macromolecules cracked during the catalytic cracking process; the catalytic effect of CaO did not facilitate the naphthalene formation reaction shown in Figure 10. Also referring to Figure 2, CaO had a more significant forming effect on HMW-PAHs at 900°C, but less on medium-low-ring. It shows that CaO was possessed of selectivity on the polycondensation of PAHs.

Results of the experiment showed that the aromatic ring with aliphatic group could be transformed by Fe$_2$O$_3$, and some phenols such as phenol and cresol were formed after the catalytic cracking of 16 PAHs by Fe$_2$O$_3$. The likely reason was that many reactive oxygen species (O$_2^-$, O$_3^-$, O$_2^2-$) existed on the surface of metallic oxide [17]; these reactive oxygen species would crack the 16 priority controlled PAHs to some phenols.

4. Conclusions

Fe$_2$O$_3$ plays an obvious catalytic role than CaO in reducing PAHs emission during coal pyrolysis. Their catalytic temperature at which the splitting rate reaches its maximum is different, that is, 60.59% at 600°C for Fe$_2$O$_3$ and 52.88% at 700°C for CaO, respectively.

Fe$_2$O$_3$ only shows a cracking effect on 16 PAHs and has better catalytic cracking effect for medium-low-ring PAHs than that of CaO in the temperature range of 600°C to 1000°C. The cracking effect on PAHs of CaO is predominant at medium-low temperature. At higher temperature that effect is converted to promote the forming of 16 PAHs, which may be caused by more macromolecular PAHs split.

The cracking rate of 16 PAHs increases with the increase of the particle size of CaO and Fe$_2$O$_3$. This increase in the cracking rates mainly contributes to the medium-low-ring PAHs and the cracking rate of higher-ring PAHs tends to decrease.

The possible cracking process of PAHs from coal pyrolysis products is proposed by analyzing elaborately the cracking effect of the two catalysts on the 16 different PAHs species and comparing the composition difference of the pyrolysis products before and after the catalytic cracking. Some phenols may form after the catalytic cracking of 16 PAHs by Fe$_2$O$_3$.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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