

## Effects of mineral loading methods on carbon solution reaction of coal-derived carbon material

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**Abstract:** 11 oxides (MgO, CaO, BaO, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, ZnO, PbO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>), often found in coal-derived carbon materials, were loaded into the coal-derived carbon material by two methods such as adsorbing oxides through solution onto the surface of coke and adding oxides into the coal before carbonization. The effects of oxides on carbon solution reaction of carbon material were investigated and compared. The results show that the effect trends are similar but the effect of oxides by adsorbing is remarkably greater than that of the oxides by adding oxides as BaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, CuO, ZnO, MnO<sub>2</sub>, PbO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. And the effect trends are similar. BaO, CaO and Fe<sub>2</sub>O<sub>3</sub> are the greatest affecting oxides. The saturation point of addition content is 3% and that of adsorption is 1%.

**Key words:** carbon materials; minerals; loading; adsorbing; adding; carbon solution reaction

### 1 Introduction

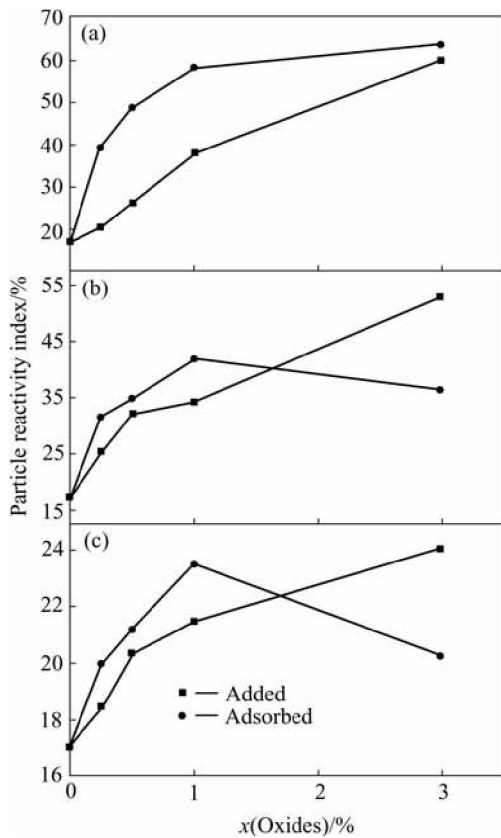
The addition of the same oxide into carbon material with different methods has been discussed in previous studies[1–6]. The results showed that different mineral loading method could lead to different effects on carbon solution reaction of carbon materials and even the opposite effects. In this study, the same oxides were added into carbon material derived from coking coal with two different methods. One is adsorbing oxides through solution onto the surface of carbon and the other is adding the oxides into the coal before carbonization. The effects on carbon solution reaction of carbon materials were compared. In addition, the factors leading to the effects were discussed.

### 2 Comparison between adding and adsorbing method

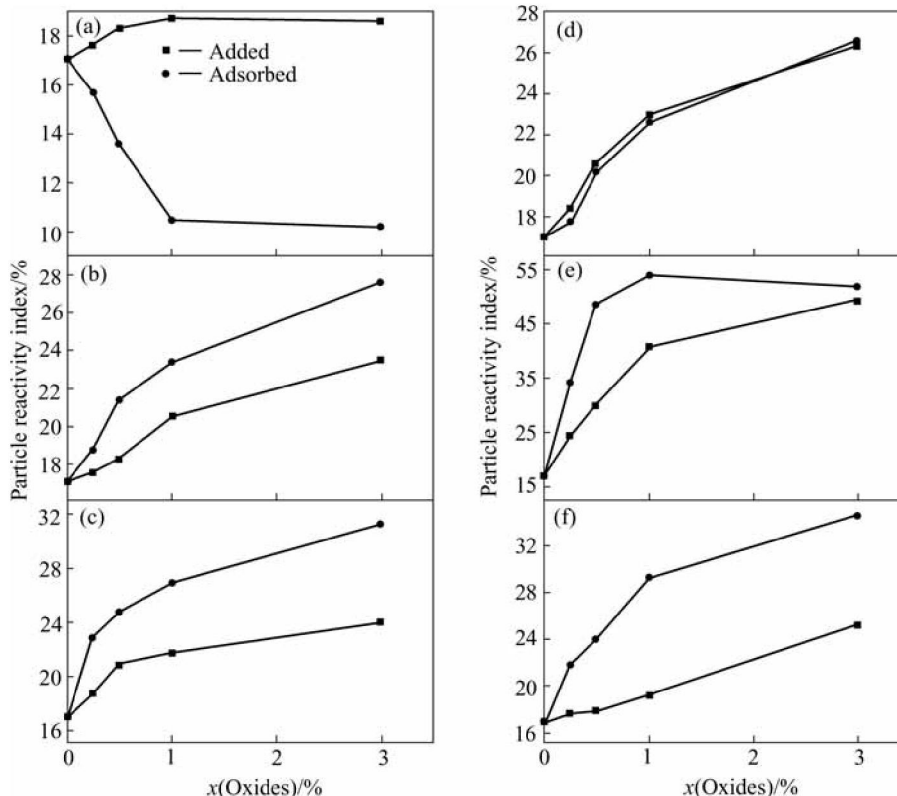
The effects of three alkali earth metal oxides (MgO, CaO and BaO) loaded on carbon material by adding and

adsorbing on particle reactivity index(PRI) of carbon material are shown in Fig.1. It shows that the oxides by adsorbing affects more greatly than by adding on carbon material PRI when their content is less than 1%. With increasing oxides content the content, the PRI of carbon material decreases when absorbed by MgO and CaO, while the PRI increases when absorbed by BaO. However, the effect of oxides added on PRI of carbon material is different. The PRI value still increases when the addition content oxides is up to 3%. According to Figs.1(a) and (b), the effect by adding is greater than that by adsorbing with the exception of BaO.

Fig 2 shows the changes of PRI of carbon material after addition and adsorption of transition element oxides (TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO and ZnO). The effects of addition and adsorption of TiO<sub>2</sub> on the effects of addition and adsorption of TiO<sub>2</sub> on carbon material PRI are absolutely reverse (Fig.2(a)). The adsorption of TiO<sub>2</sub> shows apparent negative effect and makes PRI decrease, whereas the addition of TiO<sub>2</sub> exhibits slightly positive effect. Both the addition and the adsorption of V<sub>2</sub>O<sub>5</sub> make positive effect (Fig.2(d)) although the effect of



**Fig.1** Comparison of effects of oxides added or adsorbed on carbon materials PRI: (a) BaO; (b) CaO; (c) MgO



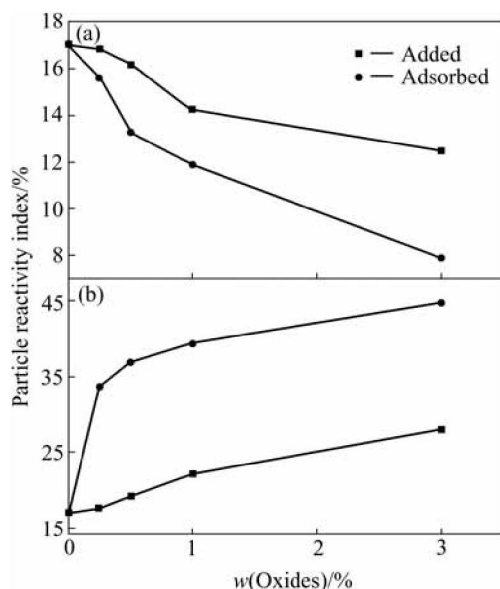
**Fig.2** Comparison of oxides added or adsorbed on carbon materials PRI: (a) TiO<sub>2</sub>; (b) MnO<sub>2</sub>; (c) CuO; (d) V<sub>2</sub>O<sub>5</sub>; (e) Fe<sub>2</sub>O<sub>3</sub>; (f) ZnO

addition greater than that of adsorption. Moreover, the difference between them decreases with the increasing of V<sub>2</sub>O<sub>5</sub> content in carbon material. Their PRIs are nearly the same at the content of 3%. The effects of MnO<sub>2</sub>, CuO and ZnO by two methods on PRI of carbon material are almost uniform, that is the effect of adsorption is greater than that of addition (Figs.2(b), (c) and (f)). The effect of Fe<sub>2</sub>O<sub>3</sub> shows similar trend. The PRI of carbon material starts to decrease at the absorbed content of Fe<sub>2</sub>O<sub>3</sub> up to 1% (saturation point). However, the PRI of carbon material goes up with the increasing content of Fe<sub>2</sub>O<sub>3</sub> added. When Fe<sub>2</sub>O<sub>3</sub> content is up to 3%, addition or adsorption of Fe<sub>2</sub>O<sub>3</sub> make PRI value of carbon material up to 51.85 % and 49.2% from 17.05%, respectively. Their effects are almost the same at this point. This result is consistent with the previous study on the effect of Fe<sub>2</sub>O<sub>3</sub>[2, 3, 7].

Fig.3 shows the effects of the addition and adsorption of PbO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> on PRI value of carbon material. PbO<sub>2</sub> exhibits positive effect (Fig.3(b)) while B<sub>2</sub>O<sub>3</sub> shows negative effect (Fig.3(a)). For both PbO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>, the effect of adsorption is greater than that of addition. Moreover, there is no saturation point at oxides content of 3%.

### 3 Results and discussion

Effects of the adsorption and addition of the same oxide on PRI of carbon material can be classified as

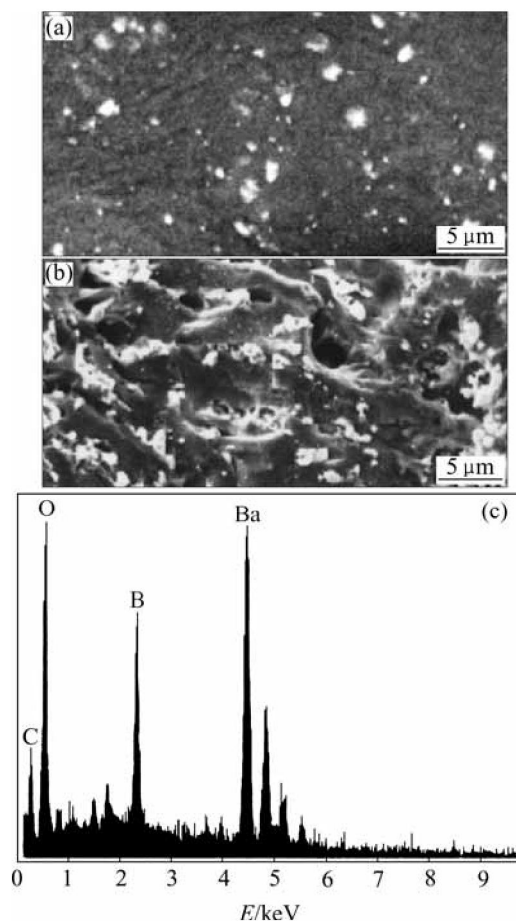


**Fig.3** Comparison of B<sub>2</sub>O<sub>3</sub>, PbO<sub>2</sub> added or adsorbed on carbon material PRI: (a) B<sub>2</sub>O<sub>3</sub>; (b) PbO<sub>2</sub>

follows. 1) Effect trends are similar whereas the effect of adsorption is apparently greater than that of addition. Oxides having the effect include BaO, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, CuO, ZnO, MnO<sub>2</sub>, PbO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. 2) Effect trends are similar whereas the effect of addition is greater than that of adsorption. The typical oxide is V<sub>2</sub>O<sub>5</sub>. 3) Effect trends of oxide adsorption and addition are obviously different, e.g. TiO<sub>2</sub>. 4) BaO, CaO and Fe<sub>2</sub>O<sub>3</sub> are the most effective oxides on PRI of carbon material. Addition and adsorption saturation content are 3% and 1%, respectively.

The different affecting mechanisms may come from the different oxides added or adsorbed. The oxides in carbon material show catalysis on carbon solution reaction of carbon material. The principle of carbon solution reaction is gas-solid reaction between carbon and CO<sub>2</sub>. The catalysis of different oxides is related to carbon structure as well as catalytic activity of the oxide. The catalytic mechanism of different oxides has been investigated by the authors in the previous study[3]. If catalysis is the only factor considered, the effect of addition and adsorption of same oxide should be similar. However, effects of the addition and adsorption of the same oxide vary greatly. Therefore, the other factors must be considered.

In order to investigate the factors leading to different effects, oxide-loaded carbon material by different methods were observed and analyzed under SEM and EDS. Figs.4–6 show the SEM images and EDS spectra of carbon material containing BaO, Fe<sub>2</sub>O<sub>3</sub> and CaO. The EDS of carbon material (Figs.4(c), 5(c), 6(c)) indicates clearly that the minerals existing in form of their oxides in carbon material. It is also indicated that

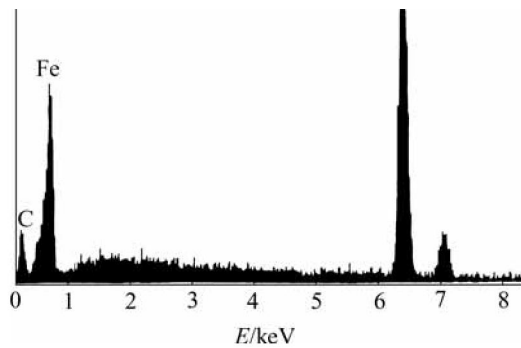


**Fig.4** SEM images and EDS analysis of carbon material loaded with BaO: (a) 1% BaO by adding; (b) 1% BaO by absorbing; (c) EDS spectrum of containing BaO

oxide loaded by adding or absorbing exists in the same form. This is due to high temperature treatment of carbon material and the physicochemical actions between oxides and carbon material matrix are uniform.

However, SEM pictures prove that distribution of oxides (bright spots in picture) loaded in different ways is quite unlike. The adsorbed oxides uniformly disperse on the surface of carbon material in the form of molecule cluster (Figs.4(b), 5(b) and 6(b)), which provides many catalytic active sites for solution reaction. While oxides added into carbon material before coking are particles in big size and sometimes surrounded by matrix of carbon material pore wall (Figs.4(a), 5(a) and 6(a)). Consequently, for the same amount of oxides in carbon material, the oxides added provide lesser catalytic active sites than absorbed ones. With carbon solution reaction going on, matrix-surrounded oxides will be exposed and participate in the reaction. Therefore, catalysis of absorbed oxides is apparently greater than that of added ones at the beginning of carbon solution reaction.

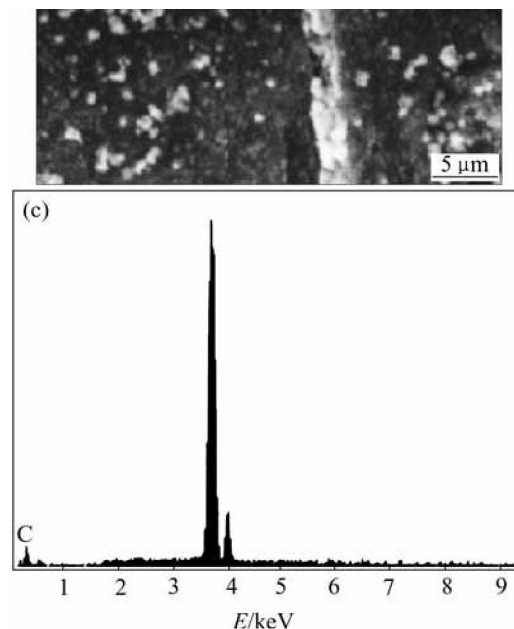
However, the difference diminishes with ongoing reaction. Owing to the difference, the saturation points



**Fig.5** SEM images and EDS analysis of coke loaded with  $\text{Fe}_2\text{O}_3$ : (a) 1%  $\text{Fe}_2\text{O}_3$  by adding; (b) 1%  $\text{Fe}_2\text{O}_3$  by absorbing; (c) EDS spectrum of containing  $\text{Fe}_2\text{O}_3$

Different distribution of oxides in different loading ways in carbon material is one of the main reasons for the different effects on carbon solution reaction. The reserve effects of added oxides and absorbed oxides are due to their different ways in affecting carbon material microstructure[8,9]. The absorbed oxides have little effect on carbon material microstructure, whereas oxides loaded by addition into the coal bring disorder to microcrystals of the carbon material and increase carbon solution reactivity.

Therefore, the oxides that have a negative catalysis on carbon solution reaction when loaded by absorption will destroy the arrangement order of microcrystals in carbon material during coking after added into the coal[10,11]. The effect of the destruction on structure will exceed the one caused by negative catalysis of the oxide itself. That's why solution reaction increases when oxides ( $\text{TiO}_2$  typically) are loaded by addition. It can be



**Fig.6** SEM images and EDS analysis of carbon material loaded with  $\text{CaO}$ : (a) 1%  $\text{CaO}$  by adding; (b) 1%  $\text{CaO}$  by absorbing; (c) EDS spectrum of containing  $\text{CaO}$

Exceptionally, the adding effect of  $\text{V}_2\text{O}_5$  is greater than its adsorption effect. This is due to a relatively weak positive catalysis of  $\text{V}_2\text{O}_5$  on the carbon solution reaction. Thus the destruction of carbon material microstructure makes the increase of carbon solution reactivity more greatly.

## 4 Conclusions

1) The effect trends are similar but effect of oxides

by absorbing is remarkably greater than those of oxides added by BaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, CuO, ZnO, MnO<sub>2</sub>, PbO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>.

2) The effect trends are similar but effect of added oxides is greater than that of absorbed oxides, V<sub>2</sub>O<sub>5</sub>.

3) The effect trends are noticeably different, e.g. TiO<sub>2</sub>, BaO, CaO and Fe<sub>2</sub>O<sub>3</sub> are among the greatest affecting oxides. When loaded by addition, the saturation point of addition content is 3%. The saturation point is 1% for oxides by absorption. The following factors lead to different effects of oxides loaded into cokes by two methods: different catalyzing ability of different oxides on the same carbon material; different distribution of same oxides loaded into carbon material by different methods and different effects of different oxides on microstructure of same carbon material.

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