GASIFICATION OF THE KUZNETSK BASIN COAL CONCENTRATE USING OXIDE IRON-MAGNESIUM CATALYSTS

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Received 08 March 2018
Accepted 10 October 2018

ABSTRACT

The paper presents the results of a research on the catalytic properties of a contact substance obtained by integrated processing of high-magnesia sideritic ores of the Bakalskoye deposit (Chelyabinsk region, Russian Federation (RF), the reserves are of over 1 billion tones). The investigated material demonstrates catalytic activity in the process of carbon dioxide gasification of the bituminous coal of the Raspadskoye deposit, Kuznetsk coal basin, RF. The experimental results obtained show that the use of a contact substance based on the products of integrated processing of high-magnesia siderites results in an increase of the gasification rate by a factor of 2 - 4 as compared with the non-catalytic process.

Keywords: iron-magnesia oxide catalyst, integrated processing, high-magnesia siderites, catalytic coal gasification.

INTRODUCTION

Within the last few years the Department of Physical Chemistry and Chemical Engineering at Nosov Magnitogorsk State Technical University has carried out a research on integrated processing of the high-magnesia siderites of the Bakal deposit (Chelyabinsk Region, Russian Federation), whose total reserves are over 1 bn tons; however, they have a limited application in metallurgy due to their low content of Fe (28 % - 30 %) and high content of MgO (12 % and above). Besides they form highly viscous blast furnace slag [1]. The developed siderite ore processing technology contributes to the production of not only quality iron ore concentrate for metallurgy, but also of additional commercial products like highly pure and active magnesia [2 - 9]. The research reveals that the application of the patented high-magnesia siderite roasting method [10, 11] results in the formation of a porous oxide material with a developed surface and a defective crystal structure indicating that it could be used as an off-the-shelf catalyst.

Catalysts and catalytic technologies are the fundamental basis of the chemical industry. Thus, the expanded possibilities of the catalytic technologies and their increased efficiency, as well as the development and study of new catalysts are vital tasks. In view of the above, as part of a study on the integrated processing of the Bakal siderites, an investigation on the catalytic properties of the material produced as a product of such processing is carried out [12 - 14].

The use of such contact substances under conditions of a large-scale production, e.g. in the gasification of coal and carbonaceous materials looks promising as it provides to obtain a catalytically active, relatively inexpensive material on the ground of natural minerals.

The thorough analysis of the published scientific data demonstrates that most of the periodic table elements [15] could be used as catalysts for carbonaceous materials gasification.

The catalysts are used applied on the coal surface or mechanically mixed with the coal [16 - 18].

Inexpensive catalysts based on iron- and calcium-containing natural and technogenic raw materials are proposed in ref. [19] for use in coal steam gasification.

The combined catalysts for gasification are of a particular scientific interest. A recent research [20]
shows that the binary catalyst Na₂CO₃-FeCO₃ used in bituminous coal gasification causes a deeper catalytic effect in comparison with that in case of using each single component of the catalyst in its pure form.

Thus, an investigation of coal gasification features using catalysts based on various inexpensive natural raw materials and technogenic waste aimed at by the present research, remains an urgent task.

**EXPERIMENTAL**

**Obtaining a contact substance and its composition**

The Bakal sideritic ores were used as a key ore-forming mineral in obtaining a contact substance. It contained sideroplesite (≈ 80%), i.e. an isomorphous mixture of iron and magnesium carbonates. The iron and the magnesium, both present in the initial sideroplesite and in the products of its roasting, formed a common crystal lattice. The latter formed after the roasting carried out in accordance with the technology used by the Bakal Mining Administration (oxidative high-temperature (1000°C-1100°C) roasting with consequent dry magnetic separation) corresponded to chemically stable magnesioferrite spinel (MgFe₂O₄). We changed the heat treatment conditions and carried out the roasting at 550°C – 650°C in absence of atmospheric oxygen (the so-called “mild” roasting), thus preventing spinel (MgFe₂O₄) appearance. The main phases’ formation during sideroplesite “mild” roasting is described by the following equations [1-4].

The electron microscopic and X-ray diffraction studies (Diffractometer «D8 ADVANCE») revealed that the roasted sideritic concentrate (RSC) produced by “mild” roasting contained magnetite (Fe₃O₄), non-stoichiometric magnesiowustite [FeO]ₓ·[MgO]₁₋ₓ (1–x) and magnesioferrite [(MgO)ₓ·(FeO)₁₋ₓ]Fe₂O₃ (magnomagnetites) in addition to periclase (MgO), quartz, muscovite, calcite, dolomite, sideroplesite, ankerite, etc. A XRD pattern

\[
\begin{align*}
[(\text{FeCO}_3)\times\cdot \text{(MgCO}_3)\text{(1-x)}]_\text{(s)} & \rightarrow [(\text{FeO})\times\cdot \text{(MgO)}\text{(1-x)}]_\text{(s)} + \text{CO}_2\text{(g)}, \\
3[(\text{FeO})\times\cdot \text{(MgO)}\text{(1-x)}]_\text{(s)} + x\text{CO}_2\text{(g)} & \rightarrow x\text{Fe}_3\text{O}_4\text{(s)} + 3(1-x)\text{MgO}_\text{(s)} + x\text{CO}_\text{(g)}, \\
(\text{FeO})\text{Fe}_2\text{O}_3\text{(s)} + x\text{MgO}_\text{(s)} & \rightarrow x\text{FeO}_\text{(s)} + [(\text{MgO})\times\cdot \text{(FeO)}\text{(1-x)}]\text{Fe}_2\text{O}_3\text{(s)} \\
2\text{CO}_2\text{(g)} & \rightarrow \text{C}_\text{(s)} + \text{CO}_2\text{(g)}
\end{align*}
\]

Fig. 1. A XRD pattern of RSC obtained by “mild” roasting.
of RSC obtained by “mild” roasting is given in Fig. 1.

The chemical and the electron microscopic studies (CAMEBAX–MICROBEAM analyzer; Tescan Vega 3sbu scanning electron microscope with Oxford Instruments X-act energy-dispersive detector) proved that RSC produced by “mild” roasting contained carbon within the range of 0.1 % - 1.1 %. It was obtained in the course of the Bell-Boudouard reaction (4) catalyzed by the roasted material surface. Reaction (4) hardly occurs in absence of a catalyst. The considerable amount of soot in RSC indicated the catalytic properties of the produced material. Moreover, the reactions taking place under “mild” roasting conditions brought about the formation of a porous material with a defective crystal structure and non-stoichiometric composition of some of the phases, which favored its catalytic activity. The conducted X-ray microanalysis showed that at a crystal structure level both iron and magnesium carbonates in the initial ore, as well as iron and magnesium oxides in RSC acting as catalyst components are distributed uniformly (Fig. 2).

The catalytic activity of the produced material was also determined by its specific area. It amounted to 5 m²/g - 18 m²/g depending on the specific conditions of the material treatment. These results were obtained by the low-temperature nitrogen adsorption method (BET method).

The contact substance was produced by roasting of high-magnesia sideritic ore (+5 mm - 20 mm fraction) at 600°C in absence of atmospheric oxygen within 3 h in a laboratory electric muffle furnace. Then the roasted material was activated according to the following techniques. The sample was initially heated, then slowly cooled and then roasted in the furnace with consequent isothermal (500°C) passing of steam through it within 1 h. This step was followed by dry magnetic separation. The magnetic part of ore was crushed and rated to a grade of +0.5 mm - 2 mm. The chemical composition of the initial ore and the product of its treatment (an iron-magnesium oxide catalyst (IMOC)) is given in Table 1.

**The coal-catalyst contact formation**

A robust contact between the catalyst and solid raw materials is required to ensure a high catalyst activity in the reactions of carbon direct conversion to gaseous products. That is why the solid material crushed. However, the tendency of agglomeration increased, while the gas permeability of the charge decreased when the coal grains were too fine. A relatively coarse coal fraction

<table>
<thead>
<tr>
<th>Materials</th>
<th>Content, mass percentage (%)</th>
<th>Loss on ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe (total)</td>
<td>FeO</td>
</tr>
<tr>
<td>Original siderite ore</td>
<td>27.4</td>
<td>34.0</td>
</tr>
<tr>
<td>Catalyst (IMOC)</td>
<td>51.6</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Table 1. A chemical composition of the materials investigated.
(+1 mm -2 mm) was used in the experiments to avoid these effects.

The coal and the catalyst were contacted according to two different techniques: I – the catalyst of a fine fraction (-0.2 mm) in the amount of 10 % (w) was mixed with the coal and pyrolized at 800°C for 2 h; II – the coal was pyrolized in absence of the catalyst; the pyrolysis product was cooled and mixed with a finely ground catalyst of the -0.2 mm fraction. The material prepared was placed in a tube furnace and subjected to subsequent CO₂ gasification.

Three tests were carried out in several iterations:

Test No 1 - the coal and the catalyst were contacted by technique I (the catalyst was applied on the coal);

Test No 2 - the coal and the catalyst were contacted by technique II (mechanical mixing of the catalyst and the medium-temperature coke made from the coal);

Test No 3 – a “blank” experiment (coal gasification without any catalyst).

The mass content of the catalyst referred to 10 %. This value was chosen based on the preliminary experiments aiming to provide the closest possible contact with the catalyst. It was indirectly assessed by the gasification products CO content. The CO content in the gas phase stopped in case of using higher amounts of the catalyst (20 % and 50 %). This demonstrated a dependence on the amount of the catalyst used. Hence, the additional amounts of the catalyst were obviously excessive. Probably, this was determined by the fact that the amount of the plastic mass of coal being formed during the heating was not enough to provide a close contact between the catalyst particles and the coal, as well as the efficient use of their surface. In case of using lower amounts of the catalyst (5 % and lower) the lack of a contact substance was observed as the CO content started to decrease.

The uniformity of the catalyst distribution on the coal surface was indirectly controlled by convergence of the results of the parallel catalytic experiments.

**Experimental conditions**

Carbon dioxide coal gasification is based on the reaction:

\[ C + CO_2 = 2 CO \Delta H = +161.5 \text{ kJ/mol} \]  

(5)

Carbon monoxide, which is formed as one of gasification products, is a valuable industrial raw material for obtaining various chemical products.

As the investigated process was endothermic, an increase of the temperature of the produced gas caused an increase in the concentration of the product (CO) and a decrease of the content of the initial substance (CO₂). For example, Equilibrium (5) was almost completely shifted to the right within the range of 950 °C - 1000°C, but it was shifted to the left at 400 °C - 450°C.

The experiments were carried out at a temperature corresponding to the lower limit of the temperature range for medium-temperature gasification – 800°C. A gas-fat coal concentrate from the Raspadskoe deposit of the Kuznetsk Basin was gasified. This coal concentrate had a high volatile yield amounting to 37.7 %. It tended to go into a plastic state and sinter when heated. The results of the screen and technical analyses of the initial coal concentrate are given in Table 2.

The experiments were conducted in a flow reactor representing a horizontal electric resistance tube furnace. The material being gasified was placed inside this unit (20 g). The operating gasification temperature was 800°C, the carbon dioxide throughput rate was 200 ml/min, while the process duration was 1 h.

A number of “blank” experiments on coal gasification were conducted within a volumetric flow rate range of 30 ml/min - 200 ml/min for determining CO₂ throughput rate. Thus a rate value of 200 ml/min was chosen, as in this case the system was far from the equilibrium state (the equilibrium content of CO in the gas phase of the reaction products at the temperature of

<table>
<thead>
<tr>
<th>Grade / parameter</th>
<th>W (humidity)</th>
<th>A (ash), %</th>
<th>V (volatile yield), %</th>
<th>S (sulfur), %</th>
<th>R (vitrinite reflectance), %</th>
<th>V (vitrinized components), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas fat coal concentrate</td>
<td>9.0</td>
<td>8.8</td>
<td>37.7</td>
<td>0.94</td>
<td>0.875</td>
<td>87</td>
</tr>
</tbody>
</table>

Table 2. Technical analysis of the coal concentrate of the Raspadskoye deposit, Chelyabinsk region.
the experiments amounted to 88%, but at the selected rate - only 6%). The gasification was conducted within 1 h or less. It provided the minimization of the effects connected with rate decrease due to reduction of the surface of the gasified material.

The gaseous reaction products were analyzed by gas-adsorption chromatography (Chromatec Crystal 5000 gas chromatograph). The chromatograms were processed using the Chromatec Analytic software. The calibration for quantitative analysis was conducted by certified calibration gas mixtures.

RESULTS AND DISCUSSION

CO content in the gaseous phase of the reaction products observed in experiments No 1 - 3 plotted versus the experiment duration is shown in Fig. 3.

The catalyst fraction of -0.2 mm in test No 1, dispersed over the surface of relatively coarse coal grains of +1 - 2 mm fraction (technique I), sinks rather deeply, as it seems, into the upper layer of the material while the heated coal is in a plastic state. That is why the catalytic effect in this case is greater than that in test No 2, where a mechanical mixture of pre-carbonized coal particles of the same size fraction with finely dispersed IMOC (technique II) is used.

The comparison of experiments 1 and 2 with the “blank” experiment 3 reveals that in both cases the use of IMOC causes a significant increase of carbon monoxide content in the gas mixture of the reaction products. The observed time decrease of the catalyst activity can be attributed to unavoidable loss of its contact with the coal surface.

When the process is over, IMOC is easily separated from the solid ash residue by dry magnetic separation because of magnetic properties. It can be reused or sent to a sinter plant for further use as a component of a blast furnace charge.

CONCLUSIONS

The study reveals that:

- the product of the “mild” roasting of natural high-magnesia siderite demonstrates catalytic activity in the process of carbon dioxide gasification of coal;
- the contact between the catalyst and the coal while the latter is in a plastic state during the heating provides higher activity of the catalyst as compared with that of the mechanical mixture of the catalyst and the carbonized coal;
- the use of the contact substance based on the products of the integrated processing of high-magnesia siderites results in an increase by a factor 2-4 of the coal gasification rate as compared to that of the non-catalytic process;
- the spent catalyst can be sent to a sinter plant for further use as a component of the blast furnace charge or for regeneration following dry magnetic separation.
REFERENCES