STUDYING THE INFLUENCE OF THE CATALYTIC EFFECT OF TRANSITION METALS AND THEIR OXIDES ON THE PROCESS OF STEAM GASIFICATION OF STONE COAL

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1. Introduction. In the modern chemical industry a number of processes are widely used, which are based on gas-phase catalytic synthesis with using synthesis gas. Synthesis gas is the basic product for the production of many chemicals [1]. So, for example, synthesis gas is used in the Fischer-Tropsch process, used for the synthesis of methanol, required in obtaining esters, as well as in the processes of oxosynthesis (hydroformylation) [2].

At present, the most promising way to get synthesis gas, based on modern trends of world chemical industry development, is steam gasification of stone coal.

The application of aerosol nanocatalysis technology will greatly improve the technical and economic parameters of the process of steam gasification of stone coal [3]. The principles of aerosol nanocatalysis technology are described in the paper [4].

2. The aim of the study. The aim of this work is to study the influence of the catalytic effect of transition metals Ni and Co and transition metal oxides ZnO, Cr₂O₃ and V₂O₅ on the process of steam gasification of stone coal in the conditions of aerosol nanocatalysis technology in a rotating reactor. To accomplish the aim, the following tasks have been set:

   – Explore the influence of catalysts Ni, Co, ZnO, Cr₂O₃ and V₂O₅ on the process of steam gasification of stone coal in the conditions of aerosol nanocatalysis technology in a rotating reactor. To accomplish the aim, the following tasks have been set:

   – Conduct an analysis experimental data and investigate the change in the composition of the resulting synthesis gas from replacing catalysts one by one.

3. Research methodology. Before starting the experiment, the catalytic system and the explored mass of coal were placed into the reactor. The volume of the reactor was 160 cm³. The mass of placed coal was 23.82 g. (which is equal in volume ≈ 37.6 cm³). The volume of the catalytic system – 40 cm³. The catalytic system consists of dispersing material (metal balls with a diam-
eter 1.6–1.8 mm) and a catalyst. The material of the
balls – stainless steel, ferrite class, mark AISI 430. As
catalysts studied were taken some transition metals –
Ni, Co, as well as transition metal oxides – ZnO, Cr₂O₃
and V₂O₅ in a powdered state. The following catalysts
were chosen for research, because on the basis of the
analysis of literary data on the subject, these catalysts
are widely used in the processes of steam gasification of
coal.

In the course of this work we investigated stone
coal (mine named D. Melnikova, Lugansk region) with
such characteristics: mark of coal – G (gas), analytical
(hygroscopic) moisture $W^*_a = 5.17\%$, ash content of
dry coal $A_d = 10.21\%$. Before placing, the coal was
crushed to the fraction with particle size not more than
1.2 mm.

The research was carried out in the temperature in-
terval from 873 to 1173 K. After reaching the tempera-
ture being studied, water began to enter the reactor. Wa-
ter supply was carried out using a syringe dispenser.
The rate of water flow – 3.43 ml/min (0.2058 l/h). This
rate of flow provided a ratio organic part of coal:water =
1:1.3. The duration of the experiment was equal 440 s.

The mechanochemical activation (MCA) was
worked out with frequency $\nu = 3$ Hz. According to
previous research results, activation with this frequency
is the best. MCA was implemented by means of rotation
of the reactor in a vertical plane and characterized by
the speed of rotation. The rotation of the reactor
promotes the creation and activation of aerosol catalyst
nanoparticles.

Scheme of laboratory installation with a rotating
reactor described in detail in the article [5]. Since air is
an undesirable component for steam gasification of coal
– before the experiment, the reactor was purged with
nitrogen.

Analytical control was performed using a
chromatograph «LHM-8» (made in the USSR).
Sensitivity of the thermal conductivity detector (TCD)
is $1 \cdot 10^{-3}$.

4. Results of the research and their discussion.

Figure 1 shows how replacing one catalyst with another
catalyst influences the change of hydrogen content in
gas at the output of the reactor.

During the study, it was found, that all used
catalysts have a similar effect on the change of
hydrogen content (figure 1) and carbon monoxide
content (figure 2). At least in the studied temperature
interval. So change of the content $H_2$ and $CO$ in
conditions of use of the studied catalysts when the
temperature increases has a clearly expressed character
– is growing.

In this case, catalysts differ in their effectiveness.
The powder of nickel was the best, if we talk about the
yield of target substances (figures 1 and 2).

So, for example, at temperature 1173 K and with
nickel catalyst the hydrogen content was 62.2 % vol.,
the content of CO – 29.3 % vol. In this case the hydrogen content more by 0.7 percentage point (p.p.) or
by 1.14 % (in comparison with the use of cobalt). When
using other catalysts under study the content of $H_2$ was
(at temperature 1173 K): 56.9 % vol. – when using
V₂O₅, 55.6 % vol. – when using Cr₂O₃, 54.0 % vol. –
when using ZnO (figure 1). That is, when using nickel
at temperature 1173 K the hydrogen content was more
by 5.3 p.p. (or by 9.31 %), more by 6.6 p.p. (or by 11.87
%) and more by 8.2 p.p. (or by 15.19 %) in comparison
with the use of catalysts V₂O₅, Cr₂O₃ and ZnO
respectively.

With regard to the carbon monoxide content – in
case the situation is similar. The catalyst ZnO has
shown the lowest efficiency, namely 25.6 % vol. at
temperature 1173 K (figure 2).
When using Ni the carbon monoxide content was by 3.7 p.p. or by 14.45 % higher than when using zinc oxide (in conditions of constant temperature). When using nickel the content of CO was by 0.4 p.p. or by 1.38 % higher than when using cobalt, by 2.5 p.p. (or by 9.33 %) higher than when using V\(_2\)O\(_5\) and by 3.1 p.p. (or by 11.83 %) higher than when using Cr\(_2\)O\(_3\) at temperature 1173 K.

The results of the study showed, that at other temperatures (in the interval from 873 to 1123 K) by efficiency catalysts are arranged in the same order, in which and at temperature 1173 K.

So in the row of efficiency reduction the catalysts can be arranged in the following order: Ni > Co > V\(_2\)O\(_5\) > Cr\(_2\)O\(_3\) > ZnO. Where the powder of nickel is most effective for getting hydrogen and CO, and zinc oxide – is the least efficient in the process of steam gasification of stone coal. And since hydrogen and carbon monoxide are the target products in the investigated process – it is possible to make appropriate conclusions regarding the choice of catalyst.

It was also investigated how the use of different catalysts influences on change the content of carbon dioxide (figure 3).

The use of the catalyst ZnO has promoted the highest content of carbon dioxide. At that, in conditions of different temperatures impact on the content of CO\(_2\), from catalyst change, has a different value.

So at temperature 973 K the reduction of the carbon dioxide content was 48.07 % – from 18.1 to 9.4 % vol. (when using nickel in comparison with the catalyst ZnO). At temperature 1023 K the carbon dioxide content decreased by 62.58 % or by 9.7 p.p. At temperature 1073 K, when using ZnO – content decreased by 76.52 % or by 10.1 p.p. At temperature 1123 K the reduction of the content of CO\(_2\) was 91.34 %. And most of all, at temperature 1173 K – the carbon dioxide content decreased by 95.04 % or by 11.5 p.p. (from 12.1 to 0.6 % vol.).

In accordance with the technological features of the process, in accordance with the methods of further use of synthesis gas – carbon dioxide is a side product of gasification of stone coal. And the increase of the carbon dioxide content in the resulting gas is a negative phenomenon.

So, for example, the reduction of the content of CO\(_2\) can lead to an increase of the functional \(f\), the increased value of which, definitely needed for obtain certain chemical products. For the production of methanol from synthesis gas the value \(f\) should be from 2.05 to 2.20. Based on this, experiment methodology and catalyst selection were motivated by the desire to reduce the carbon dioxide content.

Cobalt powder and, to a greater extent, nickel powder are the optimal catalysts in the process of steam gasification of stone coal. Because, when using these catalysts the content of CO\(_2\) in the resulting synthesis gas was the lowest. In accordance with the results of experiments, in the conditions of use of the nickel catalyst, at temperature 1173 K the value of the functional \(f\) of the resulting synthesis gas is equal 2.06.

The results of the study showed, that the nickel catalyst promotes to the formation of methane stronger than other used catalysts (figure 4). Next, in order of decreasing abilities to form methane are located: vanadium(V) oxide, chromium(III) oxide, zinc oxide. When using cobalt powder the methane content in the gas sample was the smallest.
Low content of methane in the gas at the outlet of the reactor, when using a cobalt catalyst, can be explained by, that this catalyst promotes the formation of other chemical compounds.

Use of nickel catalyst to a large extent promoted to the methanation process – the process of methane formation. So when used as a catalyst the powder of nickel at temperature 873 K the content of methane was 30.1 % vol. what is in 3.17 times more (or by 20.6 p.p.) than in the case of the use of cobalt (figure 4). At temperatures 1073 K and 1123 K the increase of the content of CH$_4$ happened in 3.13 and 3.17 times respectively (or by 213 and 217 %). The biggest difference of the change of the methane content when using a nickel catalyst marked at temperature 1173 K and it was 4 times (in comparison with cobalt).

After some research it became clear, that the cobalt catalyst promotes to the formation of saturated and unsaturated hydrocarbons – the formation of ethylene (figure 5) and the formation of ethane (figure 6). In comparison with other catalysts, that have been used in the study, in the case of using cobalt the content of these substances in the gas at the outlet of the reactor was the biggest.

As results of data processing have shown, when using catalysts ZnO, Cr$_2$O$_3$ and V$_2$O$_5$ there was an increase of the ethylene content (in comparison with the use of nickel). Moreover, according to efficiency of theirs influence on the change of the content of C$_2$H$_4$ these transition metal oxides almost do not differ from each other (figure 5).

The cobalt catalyst showed the greatest selectivity which is aimed at the formation of C$_2$H$_4$. Particular growth of the ethylene content, when replacing nickel powder on cobalt powder, occurs at temperatures 1073–1173 K. So, for example, at temperature 1073 K an increase of the content of this olefin was recorded by 3.17 times or by 2.6 percentage point. At temperature 1173 K – an increase was recorded by 3.83 times or by 283.33 % (from 0.6 to 2.3 % vol.).

Next, let's take a closer look the aforementioned change of the ethane content (figure 6).

The content of the second member of the homologous series of alkanes at temperature 1023 K is increased, in comparison with the use of nickel, by 50 % when using ZnO, by 53.57 % when using Cr$_2$O$_3$ and by 57.14 % when using V$_2$O$_5$. And this content is equal 4.2 % vol., 4.3 % vol. and 4.4 % vol. respectively. At temperature 1123 K the content of C$_2$H$_6$ is equal 2.9 % vol. when using zinc oxide (an increase by 52.63 %) and is equal 3 % vol. when using chromium(III) oxide – an increase by 57.89 %. At temperature 1173 K the ethane content has increased by 56.25 % when using catalyst ZnO and by 62.50 % when using chromium(III) oxide or vanadium(V) oxide.

![Fig. 5. Dependence of ethylene content on temperature when using different catalysts.](image)

![Fig. 6. Dependence of ethane content on temperature when using different catalysts.](image)

The cobalt catalyst promotes to the increase the content of C$_2$H$_6$ by 2.68 times or by 6.7 p.p. at temperature 973 K (in this case the ethane content was 10.7 % vol.). At temperature 1023 K the increase of the ethane content happened in 2.71 times – to 7.6 % vol. Also, a significant increase of the ethane content was recorded at temperature 1173 K – the increase of the content happened by 2.63 times or by 162.50 % (from 1.6 to 4.2 % vol. when using a nickel catalyst).

**Conclusions.** Summing up the results, we can say, that each of the catalysts, which were used in the study, differently accelerate various chemical reactions, which occur in the process of steam gasification of stone coal. And since, the steam gasification – a process that occurs...
with a lot of reactions, some of which are target reactions, and some of which are side reactions, that from the choice of catalyst will depend the composition of the resulting gas and the process efficiency.

Laboratory studies have shown, that the use of such catalysts as V$_2$O$_5$, Cr$_2$O$_3$, and especially ZnO leads to obtaining gas with a relatively high content of carbon dioxide (figure 3), which is undesirable. The cobalt catalyst promotes the formation of saturated and unsaturated hydrocarbons, namely such substances as C$_3$H$_6$ and C$_2$H$_4$ (figures 5 and 6). The use of nickel powder as a catalyst promotes to the formation of methane (when using cobalt, the content of CH$_4$ was the smallest). This is visible from the figure 4. Moreover, the nickel powder was the most effective regarding the obtain of target products – regarding hydrogen and carbon monoxide (figures 1 and 2). Also, when using nickel, it is possible to obtain a synthesis gas with the functional $f$, the value of which is favorable for the production of methanol. And at that no need to apply any additional technological operations regarding the change in the composition of the resulting synthesis gas.

References


Literature


Lutovskaya A. I., Glizik M. A., Kudryavtsev C. O., Glizik I. M. Doslidzhennia vplivu katalitichnogo efekta perехідних металів i їх оксидів на процес парової газифікації кам'яного вугілля

Продовжується дослідження процесу парової газифікації кам’яного вугілля в умовах технології аерозольного нанокатализу (AnC). Особливістю даного процесу є втвorenня і активація наночастинок катализатора, що реалізується за допомогою обертання реактора. Досліджено вплив найбільш широко використовуваних катализаторів газифікації вугілля на склад синтез-газу в умовах технології AnC. Наведено обґрунтування вибору катализатора для одержання синтез-газу того чи іншого складу. Розглянуто можливість отримання синтез-газу, склад якого сприятливий для виробництва метанолу.

Ключові слова: аерозольний нанокатализ, парова газифікація, синтез-газ, кам’яне вугілля.

Lutovskaya A. I., Glizik M. A., Kudryavtsev C. A., Glizik I. M. Izuchenie vlyaniya kataliticheskogo effekta perehodnykh metallov i ikh oksidov na process parovoi gasifikatsii kamennykh uglov

Продолжается исследование процесса паровой газификации каменного угля. Процесс исследовался в условиях технологии аэрозольного нанокатализата (AnC). Особенностью изучаемого процесса является образование и активация наночастиц катализатора, что реализуется в результате вращения реактора. Исследовано влияние катализаторов на состав синтез-газа в условиях технологии AnC. Для этого были взяты катализаторы, которые наиболее широко используются в процессах газификации угля. Приведено обоснование выбора катализатора для получения синтез-газа требуемого состава. Рассмотрена возможность получения синтез-газа, состав которого соответствует требованиям для производства метанола.

Ключевые слова: аэrozольный нанокатализ, паровая газификация, синтез-газ, каменный уголь.

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Стаття подана 10.05.2019.