PRODUCTION OF HYDROGEN BY DIRECT DECOMPOSITION OF
NATURAL GAS, LPG AND METHANE

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Abstract

On γ-Al₂O₃ and SiO₂ oxide supports were formed the catalysts containing VI and/or VIII groups metals. This catalysts were tested in direct decomposition processes of natural gas, LPG and methane in temperature range: 500-700 °C. Hydrogen yield is maximum in catalysts containing VIII group of metals and lower in catalysts containing VI group of metals. Active catalyst support is γ-Al₂O₃. Oxidative regeneration number of more active catalysts was studied. Oxidation character and amount coke which formed in reaction condition were studied by DTA-TGA.

Keywords: Direct decomposition; Natural gas, LPG, methane; Catalyst; Coke formation and regeneration.

Introduction

The decrease in the resource of hydrocarbon fuels and particularly pollution of environment makes hydrogen an important energy source. For these reasons, production of hydrogen by effective methods, its reservation and wide application in fuel cells are important problems in the world.

In this work, hydrogen production from methane, natural gas and LPG by direct catalytic decomposition were studied. Production of hydrogen from hydrocarbon feed stocks by steam reforming/1-4/ and partial oxidation/5-10/ methods is well known. By the way, usage of hydrogen locally in fuel cells by direct decomposition from LPG and natural gas is important. By direct decomposition methods/11,12/, in spite of coke formation on the surface of catalysts, it's simple technology and this process does not sufficiently studied than other methods. Another aim of this work is to produce new active catalysts for low temperature decomposition. So, they were synthesised catalysts on the supports Al₂O₃ and SiO₂ containing elements from VI and/or VIII group metals and they were tested in hydrocarbon direct decomposition processes.

Results and Discussions

The direct decomposition processes of natural gas, LPG and pure methane were conducted in continuously fixed bed reactor pipe form by dimensions =2.2 cm, L=20 cm. The catalyst sample 5 or 2.5 gr. was used. The temperature in reactor was controlled by means of PID controller systems. The composition of natural gas, LPG and reaction products were analyzed by Agilent Technology 6890 N Network GC System. Generally experiments were provided in atmospheric pressure, 500-700 °C temperature range and 1500 hour⁻¹ gas velocity. The catalysts were prepared by adsorption of VI and/or VIII group of metal salts solutions on Al₂O₃ or SiO₂ supports.

The composition of natural gas, LPG and methane which were used in present work as row material are presented in table 1.
The results of H₂ formation on different synthesised catalysts by direct decomposition of natural gas are presented in fig.1. For the comparison in this picture, the results of the industrial Al-Co-Mo catalyst also are presented.

![Image of graph showing H₂ concentration (%) against temperature (°C) for different catalysts]

**Table.1**  The composition of natural gas, LPG and methane (mol, %)

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₃H₆ + C₃H₄</th>
<th>C₄ sotr.</th>
<th>C₄ unsotr.</th>
<th>C₅</th>
<th>N₂</th>
<th>O₂</th>
<th>CO</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>0,14</td>
<td>87,84</td>
<td>4,16</td>
<td>0,89</td>
<td>0,3</td>
<td>-</td>
<td>-</td>
<td>0,03</td>
<td>5,6</td>
<td>0,51</td>
<td>-</td>
<td>0,43</td>
</tr>
<tr>
<td>LPG</td>
<td>0,2</td>
<td>0,6</td>
<td>15,99</td>
<td>50,54</td>
<td>0,44</td>
<td>29,04</td>
<td>0,11</td>
<td>0,19</td>
<td>1,78</td>
<td>1,11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH₄</td>
<td>0,14</td>
<td>99,28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,37</td>
<td>0,19</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The results of H₂ formation on different synthesised catalysts by direct decomposition of natural gas are presented in fig.1. For the comparison in this picture, the results of the industrial Al-Co-Mo catalyst also are presented.

**Fig.1.** Influence of catalyst type and reaction temperature to the H₂ formation from direct decomposition of natural gas (Where: K-3,K-7,K-9,K-10,K-11 catalysts containing VIII group metals, K-V/17 –containing VI group metals , K-5A, K-6A ,K-15 containing VI+VIII groups metals . K-12 industrial catalyst - Al-Co-Mo).
As shown in fig. 1, for all catalysts independently the raw material types, at temperature 500 °C conversion yield of methane is low. Increasing of temperature from 500 °C to 700 °C independently of the nature of catalysts conversion yield of hydrogen is increased.

Experimental results are shown, that in the same experimental condition and the same supports high H₂ yield, independently the raw material were observed on the catalysts containing only VIII group metals (K-9 and K-11). The catalysts containing VI group metals were lowest activity (K-V/17). The catalysts containing VI+VIII group of metals (K-5A, K-6A, K-12, K-15), were middle activity, than the catalysts containing VI or VIII group metals separately. It was also shown, that the catalysts supported on γ-Al₂O₃(K-9), more active than the catalysts supported on SiO₂ (K-11). Maximum value of H₂ concentration observed at 700 °C on surfaces of K-9 (91.2 %). H₂ concentration for both catalysts- Al-Co-Mo and Al-Ni-Mo was about % 19 at 700 °C.

Influence of temperature to the H₂ formation on different catalysts in direct decomposition of LPG is presented in fig. 2.

![Fig.2. Influence of catalyst type and reaction temperature to the H₂ formation from direct decomposition of LPG.](image)

For comparison, influence of reaction temperature of the H₂ formation on some catalysts in direct decomposition for pure methane is presented in fig. 3.
Fig. 3. Influence of catalyst type and temperature of the H₂ formation by direct decomposition of pure methane.

Comparison of the experimental results from figures 2 and 3 with fig.1 confirmed that, explaining of experimental results for the activity of catalysts for natural gas is the same for LPG and methane.

The analysis of gas products by direct decomposition of LPG confirmed that H₂ is formed by decomposition of CH₄, which formed subsequent transformation of C₂-C₄ hydrocarbons. This fact generally does not depend on the activity, type of catalysts and temperature range. Some observations dependence of temperature presented in fig.4/A, B.
Fig 4. Influence of reaction temperature to the formation of H₂ and C₁-C₄ hydrocarbons by LPG direct decomposition on K-9 (A) and K-5A (B) catalysts.
Behaviour of most active catalyst was studied in direct decomposition condition of natural gas in durability time. It was observed that during working time 2-2.5 hours the hydrogen yield increased 1.8-2 times at temperature 650°C. This fact may be explained by the reduction of metal oxides to metals by means of hydrogen which is formed by the decomposition of hydrocarbons. Metal form in the composition of catalysts is more active in decomposition processes. During next 5 hours the catalyst did not change its activity. After this time catalysts were regenerated in reactor multiple times after coke formation.

Influence of number of oxidative regeneration to the activity of K-9 catalyst is presented in fig.5. The oxidative regeneration of catalysts was realised in reactor at 650°C and in air velocity 2000 hour⁻¹.

![Fig.5 Influence of number of oxidative regeneration to the activity of K-9 catalyst in direct decomposition process of natural gas.](image)

In this matter H₂ concentration in gas products increased from 86% to 92%. The character of coke which formed in reaction conditions were investigated by DTA-DTG method. The results confirmed that, by direct decomposition of LPG and natural gas on the surfaces of K-9 catalysts was formed 38%-39%. The same conditions on the surfaces of K-5A and K-6A were formed 21.8 and 15.2% of coke respectively. The results of DTA analysis for some catalysts are presented in fig.6.
Conclusion

Direct decomposition process of natural gas, LPG and methane for hydrogen production were studied. It was shown that the catalysts containing VIII group of metals, sufficiently active, than catalysts containing VI or VI +VIII metals. As a support material Al_2O_3 is more effective than SiO_2. For all prepared catalysts were established that, increasing of temperature from 500 to 700 °C, H2 yield has significantly increased. After numerous oxidative regenerations with air, the surfaces of catalysts has not change compared to its first level of activity. Mass of coke which was formed on the surface of catalysts mainly depends on the activity of catalysts and their working time.

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