

MECHANOCHEMICAL CONVERSION OF ACETYLENE IN QUARTZ – ULTRAFINE METAL POWDER SYSTEM

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Abstract

We have studied the effect of nano-sized metal powders (Zn, Ni), obtained by electric explosion of wires, on mechanochemical conversions of acetylene in the presence of quartz. In the process of acetylene mechanical treatment (MT) in the presence of quartz, benzene is formed. During the mechanical grinding of quartz in planetary-centrifugal mills, active radical sites are formed on quartz surface. It is possible to suppose that due to the influence of mechanical energy acetylene triple bond breaks to form ethyl radicals, which are subjected to chemisorption on active quartz sites with subsequent formation of benzene. The addition of ultrafine Zn powder decreased, while Ni powder considerably increased benzene yield. In the process of MT, particles of ultrafine Zn powder are agglomerated which results in the decrease of its catalytic activity. The increase in benzene yield at the use of ultrafine Ni powder as the additives is associated with catalytic conversion of acetylene into benzene on the newly formed nickel surface. The injection of ultrafine Zn and Ni powders in quartz-acetylene system caused no changes in quantitative composition of acetylene conversion products but affected the amounts of one or other component formation.

Introduction

Mechanical powdering of natural minerals in the environment of hydrocarbon gases is accompanied by chemical transformations of the gases [1,2]. In the long term, it is possible to consider this process as a way of processing hydrocarbon gases.

Mechanical activation (MA) of saturated gas hydrocarbon – solid substance system leads to chemical conversions of the initial hydrocarbons (HC). In all the cases, release of hydrogen was observed. The hydrogen content in products also increases with an increase in MA duration [3].

Natural quartz increases the degree of transformation of the initial components, i.e. natural gas and propane-butane mixture. It was determined, that in the course of MA of propane-butane fraction in the presence of quartz all initial hydrocarbon components destructed to methane, hydrogen and carbon [3]. Comparing preliminary thermodynamic calculations for the processes of classical thermal cracking of hydrocarbons with those based on the results of the experiment, we assumed an alternative channel of initiation of HC destruction processes in the reaction system,

that is, mechanical cracking of hydrocarbons is not only a thermal process.

A large volume of work on the study of the mechanism of light hydrocarbons conversion under the conditions of MA was carried out at the Institute of Petroleum Chemistry, SB RAS. It was shown, that mechanical destruction of hydrocarbons to lower-molecular homologs, hydrogen and carbon was the main direction of transformations. The further development of works in this area consists of the search of a possibility of conversion of light hydrocarbon gases into high-molecular hydrocarbons. It is possible to assume, that injection of a chemically active gas, for example acetylene, into a mixture of light hydrocarbons, will promote, with the participation of its radicals, the formation of longer hydrocarbon chains during mechanical treatment in the presence of a mineral additive (quartz) and ultrafine metal powders (UFMP).

Objects of Research

As the objects of the research, we used:

- Technical gaseous acetylene, State Standard 121004 - 85. The volume fraction of acetylene was not less than 98.5 %;
- Natural quartz (mineral SiO₂) with a grain size of 2 - 4 mm.;
- Gaseous argon (State Standard 10157-79);
- Ultrafine Zn and Ni powders with a particle size of 50-100 nm obtained by electric explosion of wires.

Experiment Technique

A gas was injected into the preliminary deaerated mechanochemical reactor, which was washed out by an inert gas. The internal volume of the reactor was 120 sm³. The reactor was filled with grinding balls 8 mm in diameter. The reactor and balls were made of hardened steel. Mineral additives were introduced by 10 g and ultrafine metal powders – by 1 g. Pressure in reactors after filling with a gas mixture made was 1.0 – 1.5 atm. MA was carried out on the installation AGO - 2M (hydraulically cooled activator, ISSCM SB RAS, Novosibirsk, Russia, ISSM, Novosibirsk, Russia). The process of MA of gases was carried out at room temperature.

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Results and Discussion

Mechanochemical Conversion of Acetylene in the Presence of Quartz

In the initial stage of research on mechanical activation, acetylene was mechanically treated without any mineral additives. The experiments were performed at reactor speed of 1290 rpm, where centrifugal acceleration of grinding bodies was 300 m/s^2 . The experiment showed that in 10 minutes of mechanical treatment acetylene began to destruct (Fig. 1). Hydrogen, methane and ethane traces were detected in the mixture obtained. At 20-minute treatment, the amounts of hydrogen, methane and ethane increase. After 30-minute mechanical treatment, more than 80% of acetylene remained in the mixture obtained. No other gases were detected in the studied durations of mechanical treatment.

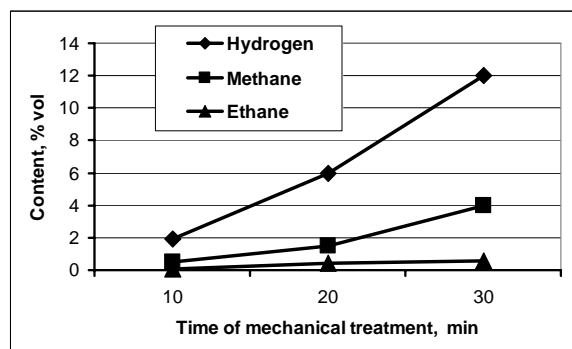
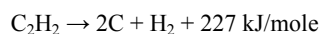
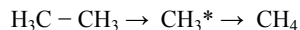
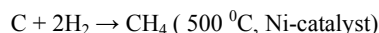


Figure 1. Dependence of generated gases content on the time of acetylene mechanical treatment

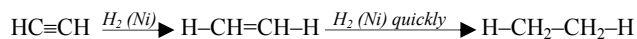
Since acetylene conversion is an endothermic reaction, hydrogen generation can occur both due to its direct thermal decomposition and as a result of heterogeneous catalytic reactions on the reactor walls. The reaction proceeds according to the equation:



Methane generation is feasible as a result of carbon hydrogenation or via methyl radical formation in the process of ethane destruction [4]:



Ethane formation proceeds according to the scheme:



The experiments on MA of acetylene in the presence of natural quartz have shown that intensive destruction of the gas occurred during the activation which increased with an increase in mechanical treatment time (Fig. 2). It is seen from Fig. 2 that the amount of released hydrogen substantially increased with prolongation of MA duration, while the amount of residual acetylene decreased. Though methane and ethane contents increased with prolonged MA duration, their contents remained practically similar to the level observed at mechanical treatment without quartz.

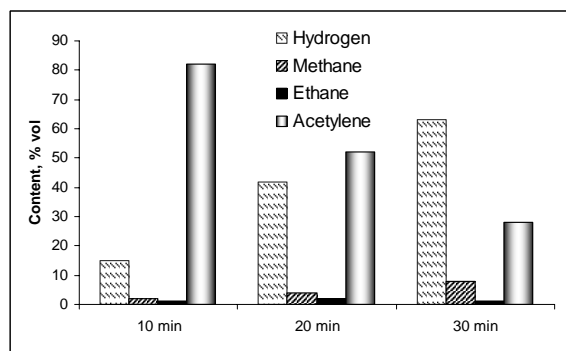


Figure 2. The effect of the time of acetylene mechanical treatment on the composition and content of generated gases

Similar results on the composition of light gases were obtained previously [3] during mechanical treatment of natural gas, which is connected with the active radical sites formed on a quartz surface. In the course of acetylene mechanical treatment benzene is formed. Figure 3 presents the dependence of benzene content on the time of mechanical treatment.

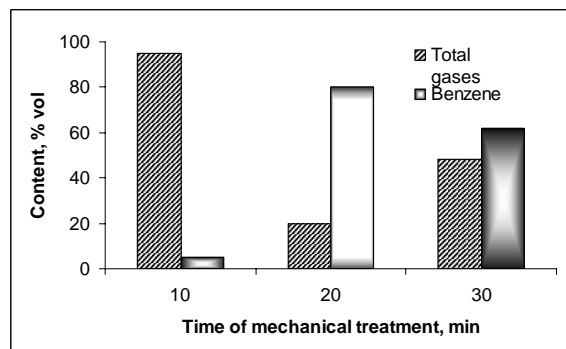
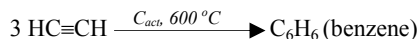


Figure 3. The effect of the time of acetylene mechanical treatment on benzene content in a gas phase

It is seen from Fig. 3 that after 10 minutes of mechanical treatment, insignificant amount of benzene was determined in the products of acetylene destruction. Its amount increased to 80 % after prolonged mechanical treatment upto 20 minutes. However, at an increase in time of mechanical treatment to 30 minutes, the amount of benzene decreased to 61 %. It is known from the literature [5] that the process of acetylene trimerization proceeds over the surface of activated coal heated to 600°C :



To check possible benzene formation in the presence of the activated coal, we mechanically treated acetylene in the presence of the activated coal of AP-3 type. The experiments showed that at mechanical treatment for 10, 20 and 30 minutes, only hydrogen, methane and CO_2 were determined in a gas phase.

In the course of mechanical powdering of quartz temperature locally rises at the points of grinding bodies impacts. However, it does not lead to the total rise in temperature in the reactor volume owing to high heat conductivity of metal and intensive external cooling. It is possible to assume that mechanical energy causes

rupture of acetylene triple bond to form radicals containing a double bond, which are chemisorbed on the active sites of quartz followed by benzene formation.

At MA of solid substances, inevitable, destruction of crystal structure occurred. The specific surface of quartz increased from 0.1 m²/g before MA to 12.7 m²/g after MA (time mechanical treatment was 20 minutes). Value of specific surface of a crystal substance is directly connected with concentration of the active sites. The increase in specific surface in the process of mechanical treatment practically always increases the number of active sites on the surfaces of solid substance, being ready to chemical reactions.

In the course of quartz powdering in the environment of various gases, their tribosorption occurs on quartz surface. Tribosorbed gases are localized in an amorphous phase of silicon dioxide and partially react with it. The amount of tribosorbate, as the amount of chemically transformed share of gas, increases with increase in treatment duration and therefore with the increased share of an amorphous phase [6]. Various solid-phase free radicals are formed at quartz mechanical treatment in the presence or absence of some gases. E¹- sites arising at the rupture of Si - O bonds, i.e. silicon radicals are the most representative paramagnetic sites in quartz [6]. At treatment in hydrogen atmosphere only a part of E¹- sites reacts with tribosorbed hydrogen, while E¹- sites are not formed at the treatment in acetylene atmosphere. It indicates that hydrocarbons react with E¹- sites.

Chemical conversions at mechanical treatment of the systems containing solid phases may be both of thermal and non-thermal character. As it was shown in work [7], the temperature reaches 800 K at points impact of grinding bodies. If we assume, that in our case destruction of hydrocarbons (acetylene) proceeds due to heating between the balls during their collision, it would be logical to apply a mechanism of acetylene thermal cracking to our system. But at acetylene thermal cracking along with hydrogen and methane unsaturated hydrocarbons should be formed. However, chromatographic analysis of the products of mechanically treated acetylene proved the absence of unsaturated hydrocarbons. Hence, it is impossible to assert definitely that acetylene cracking at mechanical treatment is a thermal process.

We consider that destruction mechanism is complex. Initiation of a radical process occurs probably during mechanical destruction of quartz crystals. The ruptured or deformed silicon - oxygen bonds can become chemisorption sites [8]. The molecules of initial gas can be sorbed on these paramagnetic sites followed by bond splitting in a hydrocarbon molecule and, as a consequence, by the formation of low-molecular radical products initiating chain conversion in a gas phase.

The Effect of Ultrafine Metal Powders on Acetylene Conversion at Mechanical Treatment in the Presence of Quartz

Ultra-sized metal powders arouse interest due to their high activity in various physical and chemical processes including mechanical activation of gases. It is possible to assume, that introduction of ultrafine metal powders along with quartz in the composition of a solid phase will change a direction of acetylene conversions at mechanical treatment.

The experiments on MA of acetylene in the presence of quartz and ultrafine Zn powder as additive at ratio of 10:1 demonstrated that at gas activation its intensive destruction occurred, which increased with the time of mechanical treatment (Fig. 4).

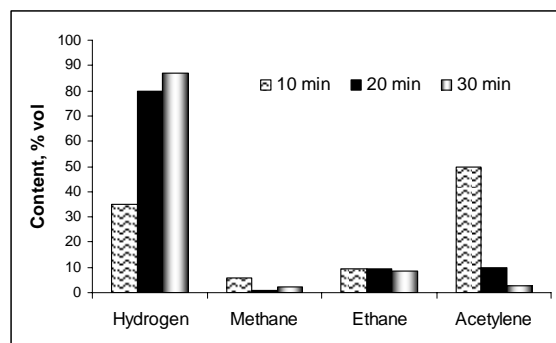


Figure 4. The effect of the time of mechanical treatment of acetylene - quartz system, in the presence of ultrafine Zn powder as additive, on the composition and content of generated gases

It is seen from the figure that hydrogen was the main product of the destruction. Its content constantly increased with increase in the time of mechanical treatment; reaching the maximum value - 78 % at 30-minute treatment, when acetylene was practically completely destroyed (1 %). Considerable hydrogen content is explained by its weak sorption on Zn surface and also with particle agglomeration, which decreased Zn catalytic activity. The increase in the time of mechanical activation (10, 20 and 30 minutes) increased methane content (10 %, 10 %, and 13 %, respectively). The formation of ethane did not depend on the time of mechanical treatment and reached the maximum value in 10 minutes of mechanical treatment (10 %).

Figure 5 presents the effect of the time of mechanical treatment of acetylene - quartz system in the presence of ultrafine Zn powder as additive on butane and benzene contents in a gas phase. It is seen from Fig. 5 that butane and benzene are formed but they are formed in insignificant amounts and their formation slightly depends on the time of mechanical treatment. Thus, MA of acetylene - quartz system in the presence of ultrafine Zn powder as additive can be used to obtain hydrogen and is not suitable to obtain C₂ and higher hydrocarbons.

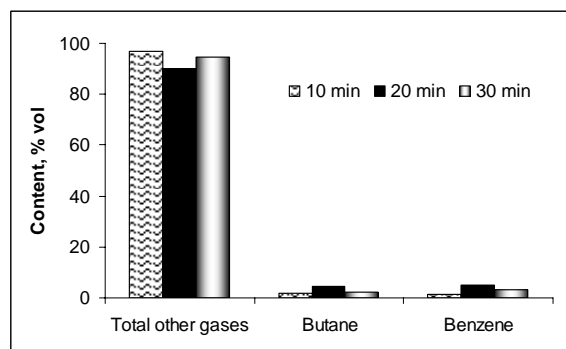


Figure 5. The effect of the time of mechanical treatment of acetylene - quartz system, in the presence of ultrafine Zn powder as additive, on butane and benzene contents in a gas phase

Figures 6 and 7 present the results of the experiment on MA of acetylene - quartz system in the presence of ultrafine Ni powder as additive.

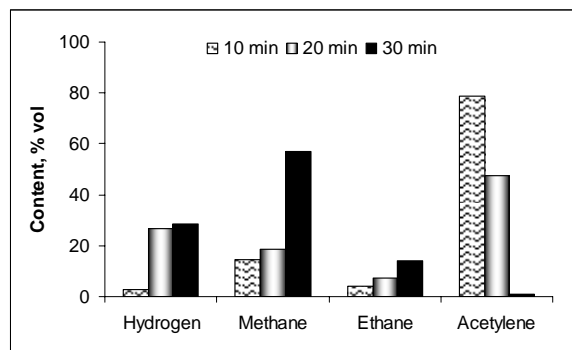


Figure 6. The effect of the time mechanical treatment of acetylene - quartz system in the presence of ultrafine Ni powder as additive the composition and content of the generated gases

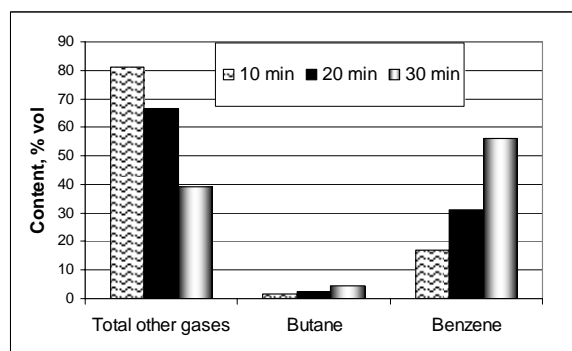


Figure 7. The effect of the time of mechanical treatment of acetylene - quartz system in the presence of ultrafine Ni powder as additive on butane and benzene contents in a gas phase

It is seen from Figure 6 that the yield of methane is considerably intensified as compared with the data obtained for ultrafine Zn powder used as additive. The methane content constantly increased with the increase in the time of mechanical treatment (5 % at 10-minute and 49 % at 30-minute activation of the initial gas). The ethane content increased in the same manner The hydrogen content also increased with the increase in the time of mechanical treatment (12 % at 10-minute and 41 % at 30-minute mechanical treatment).

Figure 7 evidences acetylene conversions to form butane and benzene. The contents of these gases increased with the increase in time of mechanical treatment. The yield of benzene reached more than 50 % from the total other gases at 30-minute mechanical treatment.

It is possible to assume that at MA of acetylene together with quartz and ultrafine Ni powder as additive catalytic acetylene conversions proceed on fresh formed nickel surface at simultaneous proceeding of radical reactions on active quartz sites formed in process of MA, that leads to the considerable yields of

gaseous products in the mixture obtained (except ethane and butane).

All examples under study can be associated with the change in specific surfaces of solid phase elements during mechanical activation. The data are presented in Table 1.

Table 1. Change in specific surfaces of solid phase elements during acetylene mechanical activation

| Solid phase element | Specific surface, m ² /g |
|---|-------------------------------------|
| Initial quartz | 0.1 |
| Initial Zn UFP | 3.4 |
| Initial Ni UFP | 5.7 |
| Mechanically activated quartz | 12.7 |
| Mechanically activated Zn UFP | 0.1 |
| Mechanically activated Ni UFP | 5.1 |
| Mechanically activated quartz with added Zn UFP | 12.1 |
| Mechanically activated quartz with added Ni UFP | 8.5 |

It is seen from Table 1 that during mechanical treatment specific surface of Zn UFP decreased. The decrease in specific surface indicates agglomeration of zinc particles. The effect of just this factor on acetylene chemical conversions can be appreciable only at the initial time of mechanical treatment, when metal structure is still chemically active. At the final stages of MA when mechanical treatment runs for half an hour, the sizes of Zn particles reach several millimetres and as a result their catalytic activity decreases. The specific surface of the quartz sample in this experiment increased from 0.1 m²/g (before MA) to 12.7 m²/g - after MA. The value of a specific surface of crystal substance directly depends on the concentration of active sites. The increase in specific surface during mechanical treatment practically always involves the increase in the content of reactive sites on the surface of a solid substance, which are ready for chemical reactions.

However, specific surface at MA of the solid substance is known to change nonuniformly during the treatment. It was previously described [9], that at the beginning of mechanical treatment of crystal quartz one observed the increase of specific surface to a certain maximum and then it decreased to a certain constant equilibrium value. In case of quartz - Zn UFP system activation, the specific surface approximates to the value obtained on pure quartz. It indicates that acetylene chemical conversions proceeds on quartz active sites only, excluding the effect of ultrafine metal powders at the final stage of mechanical treatment. For Ni UFP one observed insignificant decrease in specific surface value during mechanical treatment (5.7 m²/g for the initial Ni UFP and 5.1 m²/g for the mechanically activated Ni UFP), i.e. there was insignificant increase in the sizes of metal particles. However using quartz - Ni UFP system as a solid phase one observed obvious increase in quartz specific surface but it did not exceed the value obtained on pure quartz. It is difficult to judge about the change of the given parameter for nickel in the given system. In

literature [10], it was shown, that a degree of metal UFP agglomeration during mechanical treatment is defined by their melting heat, i.e. among mechanically activated Zn UFP - Ni UFP metal particles aggregation decreased with increase in melting heat of metals (7.2 kJ/mole for Zn; 17.5 kJ/mole for Ni, that corresponds to melting temperatures: 419.6 °C, 1455 °C respectively).

Nevertheless, it is possible to assume, that all considered cases of MA are the consequence of mutual influence of freshly formed metal surface and active sites (radicals) formed on the quartz surface during MA, i.e. catalytic and radical reactions proceeding on the surface.

Conclusions

- It was shown, that at mechanical treatment of acetylene it partially destructs to yield hydrogen, methane, ethane, butane and benzene.
- Optimum conditions for acetylene destruction on hydrogen, methane and benzene were specified.
- It was determined that depending on the nature of catalytic additive and conditions of mechanical treatment it is possible to do the process of MA selectively.
- It was shown, that the intensity of destruction of MA products is considerably intensified in the presence of quartz and ultrafine metal powders and is determined by duration and intensity of mechanical treatment.

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