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Transformations of Acetylene during Mechanochemical Treatment in the Presence of Quartz

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Abstract

Transformations of acetylene during mechanical activation in the presence of quartz were investigated. The destruction of quartz is accompanied by the formation of radicals on the surface; they initiate gas-phase transformations of acetylene. It was demonstrated that, in addition to acetylene destruction proceeding with the formation of hydrogen, methane and ethane, acetylene polymerization with the formation of benzene takes place. It was established that the yield of the products of chemical transformations of acetylene depends on the time of mechanical action.

Key words: mechanochemistry, acetylene, quartz, chemical transformations

INTRODUCTION

For the last decades, non-thermal (radiation, mechanical, microbiological) processing of hydrocarbon raw material is actively used. Chemical transformations were revealed in the course of mechanical operation with heterophase systems containing hydrocarbons and various solid phases.

The mechanical grinding of naturally occurring minerals in the environment of hydrocarbon gases is accompanied by chemical conversion of the latter [1, 2]. In the long term, one could consider this process as a method for the processing of hydrocarbon gases.

The main direction of chemical transformations consists in the destruction of initial hydrocarbons (HC). In the experiments, both with natural gas, and with propane -butane mixture, changing is observed in the componential composition of the initial gas mixture due to the destruction of C_2–C_3 hydrocarbons (in the case of natural gas) and C_2–C_4 hydrocarbons (in the case of propane/butane mixture). In all the experiments, hydrogen evolutions observed. With the increase in the duration of mechanical processing (MP) the content of hydrogen in products grows [3]. It is known, that chemically reactive radical centres are formed on the surface under the destruction of crystalline quartz [4]. The use of naturally occurring quartz in the composition heterophase systems results in an increase in the conversion level of the initial components of natural gas and propane/butane mixture. It was established that in the course of MP of propane-butane fraction in the presence of quartz, all the initial hydrocarbon components convert into methane, hydrogen and carbon [3]. Basing on the comparison of preliminary thermodynamic calculations for processes of classical thermal HC cracking with the calculations according to the results of mechanochemical experiments, a hypothesis was put forward concerning the initiation of HC destruction processes in the re-

action system due to the formation of radicals in the course of solid phase destruction.

Studies on mechanochemical reactions in the unsaturated HC–solid phase system are of interest. The chemical reactivity of alkenes is higher as compared to alkanes due to the presence of double bonds in the molecules [5]. Olefins are formed in significant amounts at the early stage of the thermal cracking of oil raw material, and their transformations determine the composition of the reaction end-products [6].

One of the stages mechanochemical transformations of unsaturated HC includes the formation of a saturated HC such as propane [3]. A process of the initial alkene hydrogenation by hydrogen, the product of destruction propylene is observed. Under the mechanical activation of ethylene in a steel reactor without quartz added, the formation of small amounts (up to 0.4 mol. %) of propane is observed, which indicates occurring radical reactions in the system [3].

One could assume that the introduction of light chemically reactive hydrocarbons, for example acetylene, into the mixture would promote the formation of longer hydrocarbon molecules under the conditions of mechanical impact. Earlier the chemical transformations of acetylene under the conditions of mechanical activation were not studied.

The aim of this work consisted in experimental studies concerning mechanochemical transformations products of acetylene in the system containing such solid phase as quartz.

EXPERIMENTAL

In this work, were used technical gaseous acetylene (the State Standard GOST 121004–85) with the volume fraction of acetylene higher than 98.5 % and naturally occurring quartz (mineral SiO_2) with the grain size 2–4 mm.

Gas was introduced into a mechanochemical reactor that was preliminary evacuated and washed by an inert gas. The internal volume of the reactor amounted to 135 cm^3. The reactor was filled with milling balls (60 pieces), 8 mm in diameter. The reactor and milling balls were made of stainless steel. As much as 10 g of quartz was placed into the reactor. The pressure in the reactor after filling with acetylene amounted to 1.0–1.5 atm. The mechanical activation was carried out using AGO-2M installation (hydraulically cooled activator, the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk). Experiments were carried out at the reactor rotation frequency equal to 1290 min^{-1}, the centrifugal acceleration of milling bodies amounting to 300 m/s^2. The process of the mechanical activation of gases was carried out at the cooling water temperature (~15 °C).

Acetylene and reaction products were analyzed using the method of gas-liquid chromatography. C_1–C_4 hydrocarbons and non-hydrocarbon components (hydrogen, nitrogen, oxygen, carbon dioxide) was determined by means of a Chromatron chromatograph. Hydrocarbons containing more than four carbon atoms of in the molecule were determined using a Crystal-2000M gas-liquid chromatograph with a flame ionization detector. IR spectra of solids were registered using a Nicolet 5700 Fourier transform IR spectrometer within the range of 4000–400 cm^{-1}. The XRD phase analysis was carried out with the use DRON-3 X-ray diffractometer (CuK_α radiation.) The specific surface area of powders was determined using the method of argon thermal desorption by means of a Sorbtometer M specific surface analyzer.

RESULTS AND DISCUSSION

At the initial stage of the works, we conducted the experiments concerning the MP of acetylene with no adding any solid phase. It

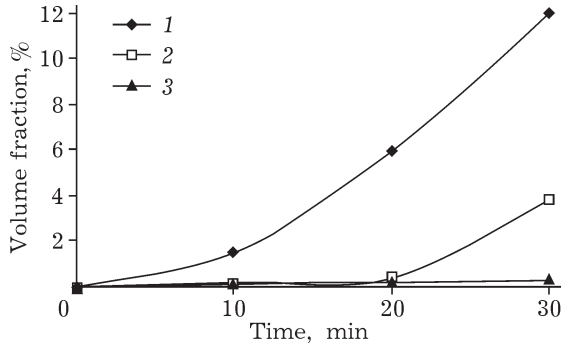


Fig. 1. Content of gases formed depending on the duration of acetylene mechanical treatment: *1* – hydrogen, *2* – ethane, *3* – methane .

was established that acetylene begins to decompose after 10 min of starting the MP procedure (Fig. 1).

The mixture of gaseous products obtained was revealed to contain hydrogen, acetylene and the traces of methane. After the processing during 20 min the amount of hydrogen, methane and ethane increases. After 30 min of the MP procedure, one can observe a 20 % conversion level of acetylene. No other gases were revealed within the MP duration range under investigation. The formation of hydrogen could occur both due to the direct thermal decomposition of acetylene, and as the result of heterogeneous catalytic reactions on the reactor walls:

$C_2H_2 \rightarrow 2C + H_2 + 227$ kJ/mol

The formation of methane is possible either as the result of carbon hydrogenation, or through the stage of methyl radical formation in the process of ethane destruction [5]:

$C + 2H_2 \rightarrow CH_4$ (500 °C, Ni catalyst)

$H_3C{-}CH_3 \rightarrow CH_3^{\bullet} \rightarrow CH_4$

The formation of ethane proceeds according to the reaction scheme

$$H{-}C{\equiv}C{-}H \xrightarrow{H_2(Ni)} H{-}CH{=}CH{-}H$$

$$\xrightarrow[\text{quick}]{H_2(Ni)} H{-}CH_2{-}CH_2{-}H$$

The experiments on the mechanical activation of acetylene with a specially introduced additive of naturally occurring quartz demonstrated that an intense destruction of acetylene occurs under these conditions whose conversion level grows with the increase in the duration of MP procedure (Fig. 2). One can see that with the MP duration the amount of hydrogen evolved increases to a considerable extent, whereas the residual amount acetylene decreases. In this case the content of methane and ethane is almost comparable to those corresponding to MP without quartz.

Similar results concerning the composition of light gases were obtained earlier [3] for the MP of heterophase systems containing natural gas. The authors of [3] connected this with the formation of active radical centres on the surface of quartz.

The MP procedure with heterophase systems containing acetylene results in the formation of benzene. Figure 3 demonstrates the amount of benzene formed depending on MP duration time. One can see, that after 10 min of MP procedure the products of acetylene destruction contain insignificant amount of benzene increasing up to 80 % with the increase in MP duration up to 20 min. However, with the increase in MP duration up to 30 min the amount of benzene decreases down to 61 %.

It is of common knowledge [7] that the process of acetylene trimerization occurs over the surface of activated coal heated up to 600 °C according to the following reaction

$$3HC{\equiv}CH \xrightarrow{C_{act},\ 600\ ^\circ C} C_6H_6 \text{ (benzene)}$$

In order to examine the possibility of benzene formation in the presence of activated coal we conducted experiments concerning the MP of acetylene together with AR-3 activated coal.

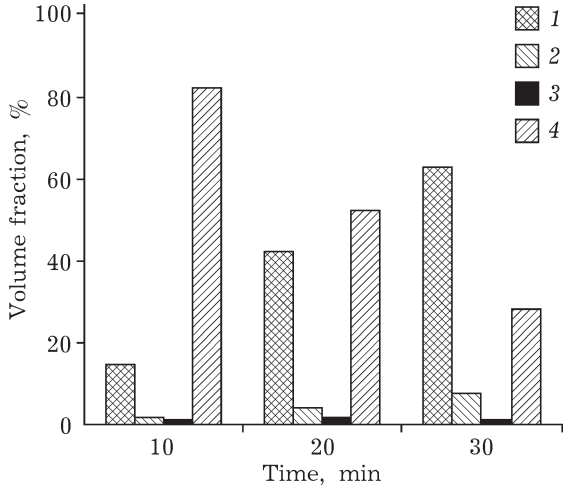


Fig. 2. Influence of acetylene mechanical treatment duration in the presence of quartz upon the composition and content of gases formed: *1* – hydrogen, *2* – methane, *3* – ethane, *4* – acetylene.

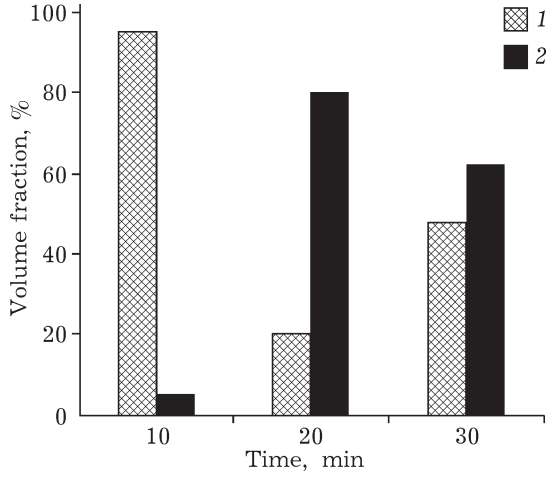


Fig. 3. Influence of acetylene processing duration upon the formation of benzene: *1* – sum of other gases, *2* – benzene.

After the MP duration time amounting to 10, 20 and 30 min, we revealed only hydrogen, methane and CO_2 in the gas phase.

One could assume that the triple bond of acetylene is broken as the result of mechanical energy impact to form radicals containing double bond those are chemisorbed onto the active centres of quartz with the subsequent formation of benzene.

The grinding of solid matter results in an increase in the surface area and, correspondingly, the contact area between reagents. As a consequence, the rate and level of heterogeneous chemical conversion increases. Besides, under mechanical impact on the solid one could observed a decrease of crystallinity level and formation of the new solid substances influencing the course of chemical reactions.

The data of elemental analysis for quartz MP demonstrated that the content of carbon after the MP during 20 min increased from 0.35 mass % (MP in the environment of argon) to 2.58 mass % (MP in the environment of acetylene). The results obtained indicate the destruction of acetylene to produce free hydrogen and carbon.

Figure 4 demonstrates IR spectra of natural and mechanically activated quartz. One can see that quartz MP with HC results in a decrease of the relative intensity of narrow absorption bands at 799–780, 695, 515, 467 cm^{-1}; the absorption band at 1092 cm^{-1} is displaced to 1094 cm^{-1}. Splitting between the band at 467 cm^{-1} (general phase) and the band at 515 cm^{-1} of mechanically activated sample indicates an increase in the amorphization level in the MP process.

The IR spectrum did not exhibit any bands within the range of 2950–2850, 1465–1380 cm^{-1} indicating the presence of methylene and methyl groups [8], as well as absorption bands corresponding to aromatic cycles ((C–H) – 3070–3030 cm^{-1}; (C=C) – 1580–1600 cm^{-1}), triple bond (C=C) – 1450–1500 cm^{-1}). The absence of benzene absorption bands, to all appearance, could be connected with its low concentration on the surface of quartz.

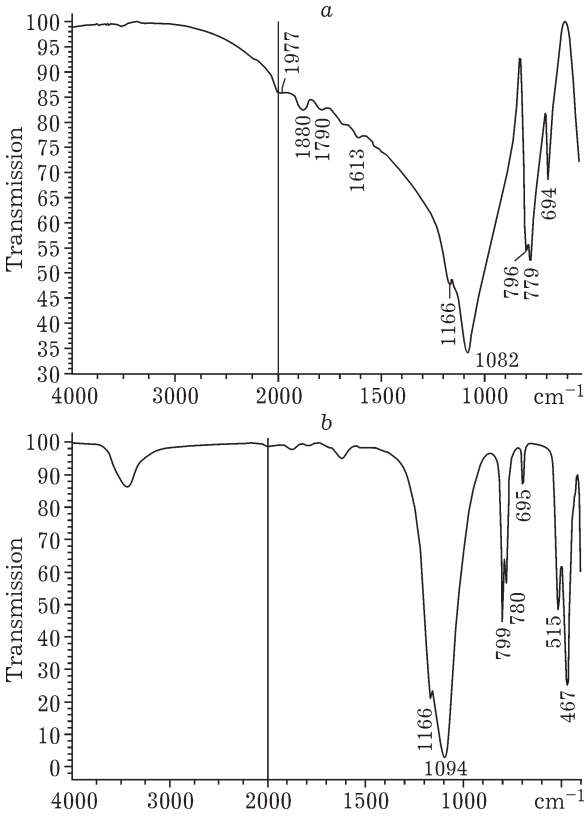


Fig. 4. IR spectra of quartz: *a* – initial, *b* – after MP with acetylene within 20 min.

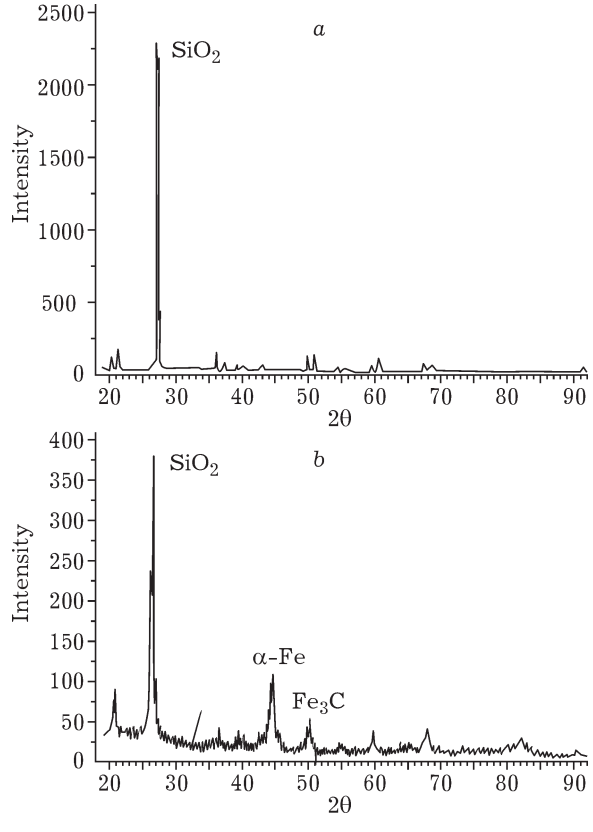


Fig. 5. X-ray XRD profiles of quartz: *a* – initial, *b* – after MP with acetylene within 20 min.

In the course of the experiment, we observed changes in the solid phase: the XRD profile of mechanically activated quartz exhibited a considerable reduction of signal intensity inherent in SiO_2 within the range of $2\theta = 27-28$ degrees as compared to the initial data (Fig. 5). This fact indicates grinding of particles and amorphization of the solid, which really occurs in the course of quartz MP [9].

The XRD profile exhibits a peak within the range of $2\theta = 45$ degrees which can be attributed to α-iron, since the system contains metal resulting from the walls of the reactor and milling bodies. In the course of the treatment, inevitable introducing a material into grinded solid substance is observed to occur. According to the results of elemental analysis, the mechanically activated quartz contains up to 24 mass % of iron.

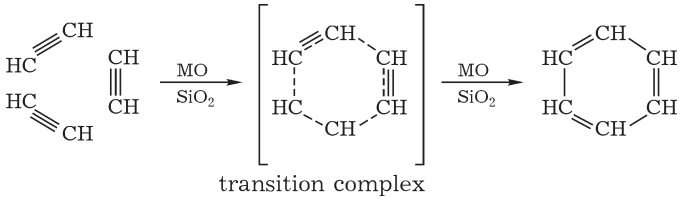
Besides α-iron, the solid products of the reaction could contain iron carbide Fe_3C (cementite) since the XRD profile demonstrates a widened reflex at $2\theta = 50$ degrees. The formation of this product could be connected with a process similar to the reaction of gas cementation.

The specific surface area of quartz in the mentioned experiment increased from 0.1 m^2/g for the initial sample to 12.7 m^2/g for a sample after 20 min of MP duration. The value of the specific surface of crystalline substance is directly connected with the concentration of active centres, and its increase in the process of MP results in an increase in the content of active centres in the system.

In the course of quartz grinding in the environment of various gases, a tribosorption of the latter on the surface of quartz occurs. The gases tribosorbed are located in the amorphous phase of silicon dioxide and partly react with it. The amount of tribosorbate, as well as the amount of chemically converted gas fraction grows with the increase in the duration of the processing and, hence, with the increase in the fraction of the amorphous phase [1]. Various free radicals are formed under the MP of quartz both in the presence, and in the absence of some gases. The most representative paramagnetic centres in quartz are E′ centres arising due to breaking Si–O bonds, *i.e.* silicon radicals [1]. Under the processing in hydrogen atmosphere, only a part of E′ centres react with tribosorbed hydrogen, whereas under the processing in the atmosphere of acetylene E′ centres are not formed. The latter indicates the reaction between HC and E′ centres to occur.

Chemical transformations under MP of the systems containing solid phases could be either of thermal or non-thermal nature. It is known [10] that the temperature value in the impact zones of milling bodies can amount up to 800 K. When assumed that in our case the destruction of HC (acetylene) occurs due to local heating between the balls in the course of their collision it is reasonable to propose for the system under consideration a mechanism of thermal acetylene cracking. The thermal cracking of acetylene, alongside with the formation of hydrogen and methane, should result in the formation of unsaturated HC. However, the chromatographic analysis of acetylene MP products revealed no presence of them in the mixture. Hence, the process of acetylene cracking under MP differs from thermal one, first of all, in the composition of products.

We consider that the destruction occurs according to a combined mechanism. The initiation of the radical process occurs, to all appearance, in the course of the mechanical destruction of quartz crystals. The centres of chemisorption could be represented by broken or deformed silicon-oxygen bonds [4]. On these paramagnetic centres, molecules of initial gas can be sorbed with the subsequent breaking bonds in molecule HC and, as a consequence,



Scheme 1.

the formation of low-molecular radical products those initiate chain reactions in the gas phase. The polymerization of acetylene in the presence of quartz proceeds according to Scheme 1.

CONCLUSION

1. Under the mechanical activation of the acetylene–quartz heterophase system one can observe mainly a partial destruction of acetylene with the formation of hydrogen, methane and ethane.

2. For the first time it was demonstrated that under the conditions of a longer MP procedure there is acetylene polymerization observed to give benzene.

3. It was established that the duration of mechanical impact exerts a considerable effect on a level and direction of acetylene chemical conversion in acetylene–quartz heterophase system.

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