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Research of composite catalysts for the process of thermocatalytic hydrogenation processing of plastic waste

Abstract. Processing plastic waste in landfills is becoming unprofitable due to the increasing costs and poor biodegradability of commonly used polymers, as well as due to large public objections. Thus, the recycling of mechanical or chemical waste seems to be the only way to handle plastic waste in the direction of sustainable development. Polyolefins, mainly polyethylene (LDPE or HDPE) and polypropylene (PP) are the main type of thermoplastics used worldwide in a wide variety of applications. In the process of thermocatalytic hydrogenation during processing of polymer waste, hydrocarbon fractions similar to motor fuels will be obtained. In general, this will allow us to process secondary raw materials, add additional fuel materials to the market and have a positive impact on the environment. Studies of new catalysts based on natural zeolite from the Taizhuzgen deposit modified with tungsten and molybdenum salt were carried out in order to jointly study the processes of thermocatalytic hydrogenation of plastic waste and optimize the process. The purpose of the study is to study the characteristics and composition of catalysts based on natural zeolite, which contain active metals for the process of thermocatalytic hydrogenation using physical and chemical methods.

Key words: fuels, plastic, recycling, polymer, Taizhuzgen zeolite, composite catalyst.

Introduction

In recent years, due to the growing need for environmental problems, especially in developing countries, and a decrease in demand for heavy oils, there are high concentrations of macromolecules and the substances contained in them, which must comply with strict environmental norms and standards. Thus, the processes that turn high molecular weight oil solutions into clean and light products have attracted the attention of researchers [1–3]. Polymers have become common materials in our daily existence and many of their properties such as service life, universalism and light weight can be an essential factor in achieving significant elaboration. However, the use of polymeric materials also increases the amount of solid waste generated, as polymeric products are often only used once before being recycled. The problem of recycling is not only technical, but also has social, economic and even political dimensions. It is for this reason that several different methods have been investigated and applied to solve problems related to the management and disposal of polymer waste [4]. The key parameter is the use of plastic waste as a source of hydrocarbon fuel. The habit of discarding plastic waste has created many environmental problems and threats to water bodies. To solve this problem, various thermochemical recycling processes have been adopted, namely thermocatalytic, pyrolysis, incineration, gasification, pyrolysis-reforming strategies for converting plastic waste into fuel-class transport hydrocarbons.

Type of thermochemical process chosen for converting plastic waste into useful energy depends on the existence of feedstock and the conversion efficiency. All processes are multi-stage and require a special type of reactor to overcome the problems of toxic gas emissions into the atmosphere [5–9]. In this study, a method for using plastic waste for the synthesis of carbon-containing materials for energy production and the use of capacitors is proposed. Environmental problems caused by plastic waste are addressed properly [10].

Processing takes place thanks to hydrothermal liquefaction – waste melts at ultra-high temperatures and dissolves in supercritical water. After that, it turns

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into naphtha, which can be easily processed into fuel. The amount of fuel that can be obtained by recycling plastic will cover the need for gasoline by about 5%. Currently, it is considered as a method that develops the most the spectrum of environmental protection. Plastic waste can be processed into valuable gaseous and liquid fuels using chemical processing methods such as hydrogenation, chemical depolymerization, gasification, thermal cracking and catalytic transformations [10–12].

In addition, in order to ensure high conversion and selectivity for the target product, the catalysis is a great opportunity for converting polymer waste, since the catalysis provides low temperature and pressure, as well as high conversion and selectivity for the target product. Catalysts for energy recovery processes such as chemical processing and cracking, hydrocracking, and gasification have been studied. It is shown the effectiveness of zeolite for processing polymer waste by cracking and hydrocracking. In addition, zeolites are materials whose properties meet the requirements of the reaction, since in the liquid phase, the most important aspects are the restrictions taken into account by weight and thermal conductivity in the macromolecule of polymers of high viscosity and large size during the process of catalytic processing of the polymer in the liquid phase. Recently, the method of hydrogenation of polymer waste is used for processing various polymers, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terphthalate (PET) and its compounds. The reaction is carried out mainly under hydrogen at a pressure of 150 atmospheric, in some cases in an describet autoclave at a temperature of 400-450 °C in the presence of solvents. Scientists have described the process of diluting PE, PP, PET and their waste in the presence of hydrogen at a temperature of 420-450 °C (54 atmospheres of cold hydrogen) with the addition of oil and tetralin used as a solvent. The results of heat treatment are compared with the results of the latter process in the presence of ZSM-5 zeolite and a highly dispersed Fe catalyst (ferrihydrite, treated citric acid). One of the directions of using production wastes and polymers as secondary raw materials is thermal and thermocatalytic modification of hydrocarbon fractions used as high-quality motor fuels. In the process of thermocatalytic hydrogenation of polymer waste, hydrocarbon fractions similar to motor fuels will be obtained. In general, this will allow us to process secondary raw materials, add additional fuel materials to the market, and have a positive impact on the environment. New catalysts based on natural zeolite from the Taizhuzgen deposit modified with Mo (VI) salt were studied in order to jointly study the processes of thermocatalytic hydrogenation of plastic waste and optimize the process [13].

The purpose of the work was to develop resource-saving technologies for the preparation and joint processing of industrial and household waste based on carbon-containing raw materials and solid fuels into fuel materials; and to establish the mechanism and regularities of chemical transformations of hydrocarbons on composite catalysts made of natural zeolites modified with active metals, as well as to develop and pilot test the technology of joint thermocatalytic hydrogenation processing of coal, shale, rubber and plastic waste in motor fuels on the developed catalysts. Improving the technology of the process and the use of appropriate catalysts can minimize losses and produce high-quality fuel distillates from spent carbon and hydrogen-containing raw materials.

Materials and methods

The experimental work in this paper differs from previous studies [13] in that the process was first studied in a continuous catalytic reactor operating under pressure in a cyclo-mixing mode with catalysis and hydrogenation of raw materials by direct distillation of liquid distillate and removal of gases. The process was carried out without the stage of draining the liquid product and its further distillation. Liquid products of thermocatalytic hydrogenation processing of polymer waste in the presence of a new composite catalyst were divided into fractions with boiling points: up to 180 °C, 180-250 °C and 250-320 °C. At the end of the process, the product is divided into fractions at a boiling point of 0-180 °C, 180-250 °C and 250-320 °C as described in the article [13].

The raw material used was a mixture of polymer waste-fuel oil with particle sizes of 2.0-6.0 mm and catalysts based on natural zeolites from the Taizhuzgen field (Kazakhstan). Natural zeolite of the Taizhuzgen deposit was activated with a solution of NH_4Cl without 1 M acid and with 1.0% Mo and 1.0 % W by the method of absorption with activated zeolite. The catalyst obtained during application is 2.0% of the total mass. The process was carried out in a continuous mixing mode at a pressure of 0.5-0.6 MPa at a temperature of 450 °C. The duration of the experience is 15 minutes [13]. To determine the crystal nature of the materials, a powder X-ray diffraction analysis was performed using a RigakuUltima IV diffractometer equipped with a Cu Kα radiation source (λ=0.15406 Nm). XPS analysis was made on the technical characteristics of the 300 device. The

XPS analysis data was adjusted for charge bias using the standard C1s 284.5 eV binding energy.

Results and discussion

The results of the study of the process of processing polymer waste showed that the nature of the catalysts affected the yield of liquid products and the optimal catalyst was 1Mo1W@Taizhuzgen; and the yield of liquid products in the thermocatalytic processing of waste polymers with heavy oil residue was high.

According to the TGA results the thermal decomposition of catalysts does not affect the processing of polymer waste, since the process takes place at a temperature of 800ºC. The results of samples of TGA composite catalysts are shown in Figure 1.

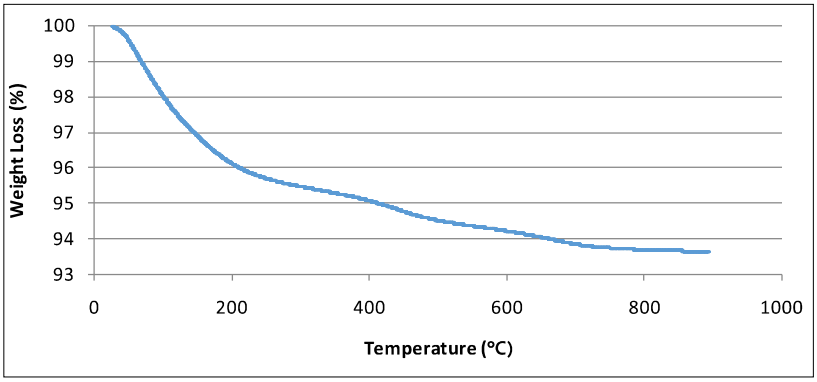

Figure 1 – TGA samples of a composite catalyst based on natural zeolite of Taizhuzgen: 1Mo1W@Taizhuzgen

The XRD pattern of the composite catalysts is shown in Figure 2. The study of the effect of the introduction of various transition metals-active components of catalysts on the heat resistance of zeolites was carried out at the next stage [14]. Figure 2 shows X-ray spectra of the Taizhuzgen zeolite and the composite catalyst 1Mo1W@Taizhuzgen, as well as catalysts based on them after heating in air at 500 °C for 1 hour. It was found that the introduction of transition metals contributes to the modification of the crystal structure of aluminosilicates, especially after high-temperature calcination [15]. The introduction of cations of group VIII elements of molybdenum and tungsten contributes to the preservation of the zeolite framework (Figure 2). It was found that the amount of MoO_3 and WO_3 oxides varies depending on the method and supporting procedure.

Thus, X-ray data indicate that significant changes in the structure of the catalyst, leading to the formation of amorphous aluminosilicate. All the regularities are valid both for natural zeolites and for 1Mo1W@Taizhuzgen.

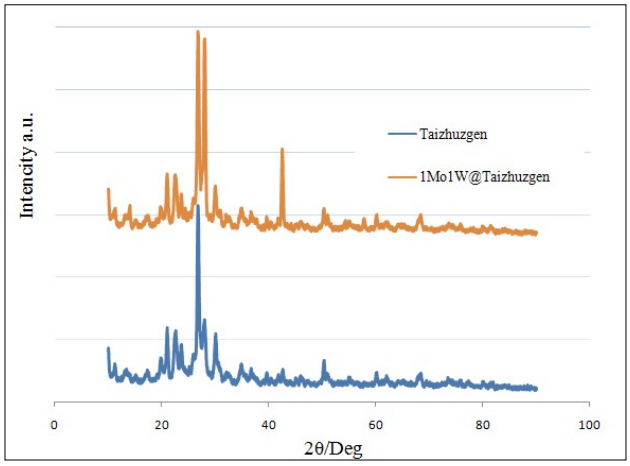

Figure 2 – XRD pattern of the catalyst 1Mo1W@Taizhuzgen

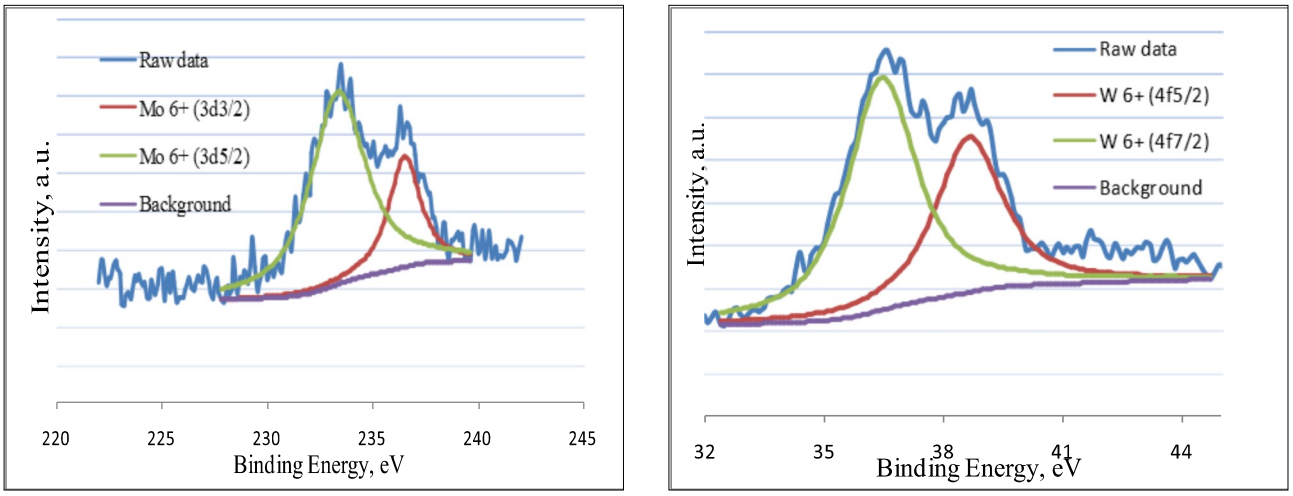

Figure 3 – XPS spectra of the catalyst 1Mo1W@Taizhuzgen

To determine the nature of the compounds, X-ray structural analysis of the catalyst was performed and the full spectra of molybdenum and tungsten were collected (Figure 3). The results of the XPS analysis determined the oxide forms of Mo and W metals in the structure of the catalysts. In the XPS 1Mo1W@ Taizhuzgen spectra, two peaks refer to the Mo^{6+} oxidation of molybdenum and two peaks to the W^{6+} oxidation of tungsten. These peaks are for MoO_3 (3d3/2 and 3d5/2) and WO_3 (4f5/2 and 4f7/2).

Conclusion

To date, the most effective processes for processing rubber and polymer waste is the process of thermocatalytic hydrogenation. This is, for the purpose of searching for alternative sources of hydrocarbons for oil and natural gases, secondly, allows these processes to be carried out with the participation of cheap and effective catalysts and in soft conditions. For the resource-saving technology of thermocatalized hydrogenation of polymer waste on liquid motor fuel, a catalyst was developed with the method of impregnation of 1.0% molybdenum ion and 1.0% tungsten ion on non-acid activated Taizhuzgen zeolite, and demonstrated the activity of a new composite catalyst. In addition, it was shown that modification in combination with zeolite salts of molybdenum and tungsten salts has different effects on the catalyst morphology and on the yield of the hydrogenation process of thermocatalytic treatment of hydrocarbons and the chemical composition of liquid fractions. On the basis of physical and chemical studies of the products of the process of hydrogenation of plastic waste in the presence of a new composite catalyst, the possibility of implementing a resource-saving technology for the process of recycling waste into synthetic motor fuels is shown.

Conflict of interest

All authors have read and are familiar with the content of the article and have no conflict of interest.

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