Original Research

Metal Salts as Homogeneous Catalysts for Effective Combustion of Liquid Fuels

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Abstract

Findings of research on the manufacture of metallic catalysts based on iron salts and iron-and-cerium salts of fatty acids dissolved in fuel oil are presented. Fatty acid metal salts are characterized by good solubility in fuel oil and the resulting catalyst solutions show low viscosities. The obtained metallic catalysts were used in mazout combustion tests in which reduced emissions of NO_x and additional heat recovery were obtained as the result of complete fuel combustion.

Keywords: metallic catalysts, air pollution, emission of pollutants

Introduction

Emissions to the atmosphere of various gaseous pollutants resulting from technological processes or technical operations, as well as the permissible levels of air pollution, are regulated by laws. Now that Poland is a member of the European Union, the permissible levels of certain pollutants in the atmosphere ought to be reduced (e.g. from 40mg/m^3 to 20 mg/m^3 for SO_2, and from 40 mg/m3 to 30 mg/m^3 for NO_2) [1, 2].

Afterburners, or catalysts for the afterburning of harmful components of industrial offgases, are known in the art. This group of catalysts include platinum or palladium catalysts supported on Al_2O_3 and used in the afterburning of industrial offgases as well as honeycomb catalysts used in the afterburning of automobile exhaust gases. However, such catalysts may not be used in the combustion of liquid fuels owing to the fact that the metal is washed out of the surface of the solid support. The development of a new group of metallic catalysts dissolved in an organic solvent will allow their introduction to the liquid fuel, thus enabling significant reduction of the emission of pollutants from local sources [3].

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The catalyst contains compounds of Group VIII metals and lanthanides. They are mainly organometallic salts of rare-earth metals, usually Ce, Pr, Nd, dissolved in aromatic organic solvents. Such salts are obtained in the reaction of a water-soluble metal salt or a metal hydroxide with carboxy acids containing 7-8 carbon atoms in a molecule. Attempts to replace parts of the costly rare-earth metals with less expensive ones, such as Mg, Fe, Ca etc., without significantly losing the advantages of the catalysts were reported in the literature [5]. The catalysts are added to liquid fuel in amounts from 10 to 100 ppm, in terms of the metal. During the combustion of, for instance, fuel oil containing large amounts of asphalthenes, the catalyst is absorbed on its surface, thus enabling complete combustion of the fuel oil [4].

High concentrations of the metal in organic solvents were achieved by forming metal soaps which enabled further emulsification of metals existing in the form of their hydroxides. Research shows that in order to obtain high metal concentrations in the organic solvent (170 g Fe/dm^3 and 60 g Ce/dm^3), approximately 25% of the metal must be in the form of a metal soap while the rest of the metal in the form of a hydroxide must be suspended in the solvent in a colloidal form [5].

Experimental

Materials and Auxiliaries

The following materials were used: iron(III) sulfate nonahydrate, pure, POCh Gliwice; cerium(III) nitrate hexahydrate, pure, Metal Rare Earth Limited China; thall oil, acid number 187 mgKOH/g, Imperial-Oil-Import Germany; NH_3 (25%) solution, POCh Gliwice S.A.; fuel oil. Mazout was used to assess the influence of the catalyst on the effect of burning the catalyst according to PN-76/C-96024.

Synthesis of Metallic Catalysts

The synthesis of an iron-based catalyst proceeds in two steps according to the reaction:

$$Fe_2(SO_4)_3 + 6NH_3 + H_2O \rightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4 \quad (1)$$

$$Fe(OH)_3 + 3R\text{-}COOH \rightarrow (R\text{-}COO)_3Fe + 3H_2O \quad (2)$$

Iron(III) hydroxide obtained in step I was filtered and reacted with thall oil dissolved in fuel oil.

A schematic diagram of the process to obtain the iron based catalyst is shown in Fig. 1.

Waste water from the step of separation of the organic and water phases is mainly composed of ammonium sulfate, which may be recovered by water evaporation. A reaction with CaO and ammonium sulfate processing into a

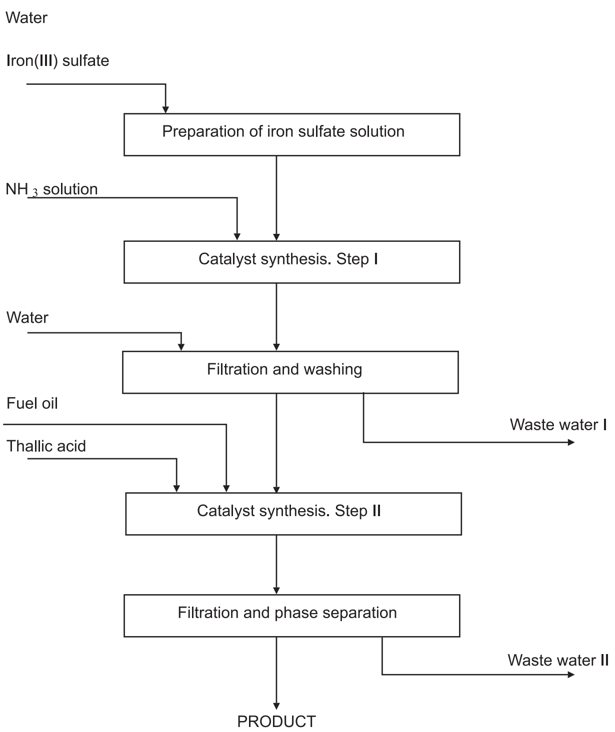

Fig. 1. The process to obtain the iron based catalyst – schematic diagram.

sodium sulfate dihydrate, or gypsum, is another potential method for waste water neutralization.

Efforts to obtain the Fe/Ce dimetallic catalyst were made in a comparable manner except that iron(III) sulfate was replaced by a mixture of iron(III) sulfate and cerium(III) nitrate.

The metallic catalysts were obtained from water-soluble salts of Fe^{3+} and Ce^{3+}. In step I, ammonia water was added to a solution obtained by dissolving in water either iron(III) sulfate monahydrate or a mixture of iron(III) sulfate monahydrate and cerium(III) nitrate hexahydrate. A solution obtained by dissolving thal oil in fuel oil was added to the resulting solution. The mixture was heated at about 80^0C for 5 hrs while stirring vigorously. When the reaction was complete, the organic phase was separated from the aqueous one by centrifuge. The organic phase is the catalyst.

The efficiency of the catalysts was assessed in combustion tests using a metering system for fuel calorimetry.

The test assembly is composed of a Junkers-type flow calorimeter and a metering system for the flow of liquid fuels and exhaust gas. The system used enables determination of the heat balance of fuel combustion in the presence or absence of a catalyst, and the mass balance of the combustion process.

The exerted caloric value was calculated as an average from two separate measurements different by less than 3%.

Analysis of the exhaust gas from the combustion process was carried out using the IMR Ultramat 6 exhaust analyzer.

Dermination of Fe and Ce content in catalyst made by Atmomic Absorption Spectrometry.

Fuels without a catalyst and with a monometallic (Fe) or dimetallic (Fe/Ce) catalyst were used in the fuel combustion tests. The metal concentration in the combustion fuel was 60 ppm.

Results

The catalysts Fe and Fe/Ce are characterized by low viscosity and high stability in time. The monometallic catalyst contained 200g Fe/dm^3, and the dimetallic one did 150g Fe and 50g Ce in 1 dm^3 of the solution. The catalyst solutions are readily soluble in the test fuel and phase separation does not occur.

The obtained catalyst was used in laboratory tests consisting in mazout combustion with the use of a plant comprising a Junkers combustion furnace, a system for the accurate metering of fuel and air, and a system for sampling exhaust gases for analysis.

The conditions of the mazout combustion tests are shown in Table 1. The use of metallic catalysts in mazout combustion processes enables a more efficient combustion of the fuel, as evidenced by improved heat recovery per mass unit of the fuel.

Table 1. Parameters for mazout combustion tests.

Parameter	Test 1	Test 2	Test 3
Catalyst	–	Fe	Fe/Ce
Catalyst concentration in mazout, ppm	–	60	60
Mazout flow rate, dm^3/h	1200	1200	1200
Excess air factor	2	2	2

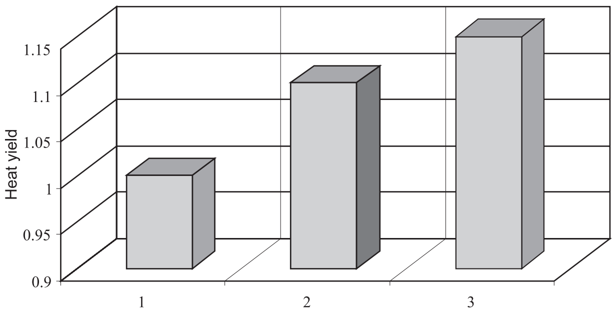

Fig. 2. Heat yield from mazout combustion process (1 – no catalyst, 2 – Fe catalyst, 3 – Fe/Ce catalyst).

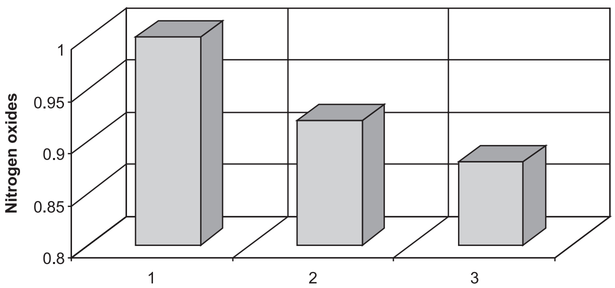

Fig. 3. Content of nitrogen oxides in flue gases from mazout combustion proces (1 – no catalyst, 2 – Fe catalyst, 3 – Fe/Ce catalyst).

Fig. 2 shows a comparison of heat recovery in the process of mazout combustion without a catalyst and with Fe and Fe/Ce catalyst.

The heat recovery per mass unit of mazout is assumed to be 1. The use of the monometallic Fe catalyst leads to improved recovery of heat by about 8%. The dimetallic Fe/Ce catalyst shows higher activity in the reaction of oxidation of heavy organic residues contained in the fuel. In this case, additional recovery of heat is about 14%.

Fig. 3 shows comparison of NO_x emission in the process of mazout combustion without the catalyst and with the use of the mono- and dimetallic catalysts.

The monometallic catalyst (60 ppm Fe) in the process of mazout combustion improved NO_x emission in the exhaust gas by about 9%. In the case of the dimetallic catalyst (45 ppm Fe and 15 ppm Ce) the emission of NO_x in the exhaust gas was reduced by about 13%.

Conclusions

A catalyst based on Fe and Fe/Ce, with the metal content of 200 g in 1 dm^3 of fuel oil, was obtained by the formation of metal soaps which enable emulsification of further amounts of metal in the form of their hydroxides. In the mazout combustion tests, carried out with the use of the obtained catalysts, heat recovery was improved by 8% (Fe catalyst) and 14% (Fe/Ce catalyst); while NO_x emission was reduced by 9 and 13%, respectively, in the tests carried out with the mono- and dimetallic catalysts.

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