



Short communication

Deep catalytic desulphurization of heavy gas oil at mild operating conditions using self-functionalized nanoparticles as a novel catalyst



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HIGHLIGHTS

- Synthesis of novel cobalt nanoparticles by the electroless plating technique.
- Characterization of the prepared material using different tools.
- Investigating its efficiency in sulphur removal at different conditions.
- New advances are detected at the end of study.

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ABSTRACT

The desulphurization of diesel fuel fractions in order to obtain environmental friendly fuel has been extensively demanded worldwide. This in turn can positively minimize the harmful emissions; hence low potentiality for serious problems to take place. The utilization of effective chemical materials in order to attain this goal is always requested. In line with that trend, this research work is dedicated to the production of a low sulphur diesel fuel. The current study summarizes new advances in the desulphurization process based on some different perspectives. Firstly, nanoparticles of a novel cobalt structure are introduced as a selective material for the desulphurization, unlike the commonly known ones which are basically metals oxides. The production of a low sulphur diesel fuel accompanied with extremely low operating conditions is another advance, as revealed in this work. Approximately, 85% of the sulphur content in the starting feedstock was removed at the final diesel fuel at non-severe conditions.

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1. Introduction

Growing universal concerns regarding the environmental crises have emerged as a result of continuing the dependency on the fossil based diesel fuels as an energy source. These concerns are in a high relevance to the harmful emissions of diesel fuels owing to their sulphur contents [1,2]. Sulphur content of a diesel fuel has been cut down to ultra-low levels by the environmental regulation in many countries. This was aimed in order to reduce the diesel engine's harmful emissions and to improve the air quality [3]. In a prompt response to these claims, studies on the production of ultra-low sulphur diesel (ULSD) have been stimulated worldwide and grabbed an enormous interest in the scientific community

[4]. Developments in the deep catalytic desulphurization (DS) processes of the diesel fuel feedstock either on the scientific basis or via the introduction of new generation of catalysts industrially are raised lately [5]. Special attention has been paid to the progress in the alternative (non-hydrogenation) process concepts and technologies that are being developed for the ULSD production [6,7]. This attention has been extended to either the processes that are based on the utilization of developed catalysts or the non-catalytic based technologies. However, the processes in which the catalysts are inclusive for the DS of fossil fuel feedstock are suffering from a particularly difficult problem; namely the limitation of the catalyst life [8,9].

In line with the raised DS development issues, this study is directed toward the production of LSD via the catalytic route with a significant consideration for the operating costs. New type of catalyst for the desulphurization process is introduced throughout

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this research work which was prepared by the electroless deposition technique.

2. Experimental

2.1. Feedstock and materials

A heavy gas oil (HGO) fraction: as-received from the crude oil distillation and fractionation stage was used during this study. The HGO was conducted from Cairo oil refining company, Cairo-Egypt. The feedstock had obeyed several physical analyses. The main characteristics of the HGO are listed in Table 1.

For the preparation of the cobalt nanoparticles, cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$) salt as a metal precursor, hydrazine solution (35% in ethanol); as a reducing agent, were used. All the prior mentioned reagents were purchased from Sigma-Aldrich Ltd-UK and have got as high purity as 99.9%.

2.2. Synthesis of nanoparticles

The cobalt based material was prepared by a direct synthesis method using the electroless plating technique (ELP), as previously reported by El Naggar and his co-workers [10–12]. However, a slight modification to the preparation procedures was included. In the prior stated investigations, the utilization of complexing and pH maintaining agents during the preparation of the ELP solution was reported while in the current study such agents were not used. The preparation procedures in this work had based on the use of a metal source and reducing agents; as electrons provider, to obtain nanoparticles with a mixed structures at the end. In practical, 0.2 M solution of the cobalt chloride was prepared in 500 mL beaker. The solution was then heated up to 90 °C. Hydrazine solution was next added at once in order to produce the proposed catalyst. An amount equivalent to 0.1 M of the hydrazine solution was added to sufficiently reduce the content of Co in its solution. This molar ratio of the reducing agent was calculated on the basis of the electrons that could be donated by the reducing agent. Promptly after the addition of the reducing agents, the system was stirred vigorously at 600 rpm for about 30 min; to allow the metal reduction process to take place. At the end of the stirring time, the solution was left for approximately 60 min to get all the deposits segregated at the bottom of the reaction vessel. The obtained cobalt catalyst was then filtered and washed several times using double distilled water in order to remove any contaminants could be attached with its surfaces. After washing, the catalyst was left to dry over-night in a diskator contains silica gel.

2.3. Characterization of the prepared nanoparticles

The essential structural and surface characteristics of the as-synthesized catalyst were determined by several tools of analysis:

Table 1
Physical characteristics and chemical contents of the heavy gas oil fraction.

Physicochemical Characteristics	Gas Oil fraction
Boiling range, °C	180–340
Pour point, °C	–10
Kinematic viscosity, $(\text{mm})^2/\text{s}$ (cSt)	3.98
Density, 25 °C, g/cm^3	0.8560
Color (ASTM-D 1500)	3.5
Sulfur content, ppm	10,000
Total ash, wt%	Ash-less
Water content, wt%	Nil
Carbon content, wt%	0.16
Inorganic Acidity	Nil

X-ray powder diffraction (XRD): model Bruker AXS-D8 Advance (Germany) supplied with nickel-filtered copper radiation ($\lambda = 1.5405 \text{ \AA}$) at 60 kv and 25 mA with a scanning speed of 8° in 20 min^{-1} .

BET Surface area analyzer: model Quanta-chrome Nova 3200 instrument (USA). N_2 adsorption–desorption isotherms was carried out at -196°C . The sample degassing conditions was 200°C and 3 h under a reduced pressure in order to pull out any contaminants that might be included within the sample structure. Specific surface areas (S_{BET}) were calculated from multi-point isotherm at relative pressure (P/P_0) ranging from 0.05 to 0.30. Pore size distribution was obtained from Barrett, Joyner and Halenda (BJH) method using the adsorption points of the isotherm.

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC): model SDT-Q600 V20.5 Pouild 15, USA. The sample analyses were carried out under N_2 atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$.

Transmission electron microscope (TEM): the morphology of the prepared catalyst was studied by the aid of Transmission electron microscope; model Jeol TEM-1230 microscope, Japan. This instrument cab provides as high power as 200 keV and magnification up to 600,000 times.

2.4. Procedures of the desulphurization process

The production of an environmental friendly diesel fuel via the removal of the sulphur compounds of the HGO fraction was carried out using a flow system. Before introducing the cobalt nanoparticles into the processing system, it was diluted via using glass beads in order to get them well dispersed along the reactor of the flow system. The dilution step was also necessary in order to get a good temperature distribution profile along the whole catalyst surface during the process. Afterward, the diluted catalyst was introduced into the reactor and the flow system was fully set up and heated for the desired temperature. Then the desulphurization process had promptly started via introducing the HGO feedstock into the reactor of the flow system. Different temperatures and liquid hour spaced velocities (LHSV) were applied during the execution of the sulphur removal process. In particular, temperatures of $100\text{--}400^\circ\text{C}$ were used with an interval increase of 100°C at each experiment, while using a constant LHSV of 2.5. As soon as the best sulphur removal percentage was detected, the corresponding temperature was selected for testing the influence of LHSV change on the sulphur removal process. Different LHSV were utilized; namely 1, 1.5, 2 and 2.5. After both the optimum temperature and LHSV were determined, a flow of hydrogen gas was introduced into the reactor in order to assess the efficiency of the hydrodesulphurization (HDS) on the quality of the produced diesel fuel. The HDS step was carried out at feed to hydrogen ratios of 1:100, 1:200 and 1: 300 (V/V). At the end of each run, the collected product out of the reactor was forwarded for analysis to identify the efficiency of the sulphur removal processes. X-ray fluorescence spectrophotometer device was used to determine the sulphur content (by weight%) in he acquired diesel fuels.

3. Result and discussion

3.1. X-ray analysis

The detailed XRD analysis of the as-prepared Co material is presented through Fig. 1.

The XRD pattern has confirmed the formation of a self-functionalized cobalt catalyst based on the detection of mixed structures in various phases. The catalyst had shown crystalline structure in terms of the observed sharp intense peaks through

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