Enhancement in the oxidative stability of commercial gasoline fuel by the goethite nanoparticles

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Abstract

It is well-established that traces of the transition metals strongly accelerate the gasoline oxidation significantly decreasing the gasoline storage time. This paper explores the opposite effect of the goethite nanoparticles on the oxidative stability of the commercial gasoline. The goethite nanoparticles were obtained in a colloidal solution by a simple thermal decomposition of iron(II) oleate. The size and the structure of the nanoparticles are confirmed by TEM, Mössbauer spectroscopy, and elemental analysis. Model study of the benzyl alcohol oxidation shows that the goethite nanoparticles significantly inhibit the oxidation process. Study of the effect of the goethite nanoparticles on the induction period of the commercial gasoline reveals a significant elongation of the induction period. It highlights that the goethite nanoparticles are capable to enhance the storage time of a gasoline. The effect may be associated with a quenching of free radicals by the goethite nanoparticles.

Keywords: Goethite nanoparticles, Oxidative Stability, Induction period

1. Introduction

Automotive gasoline is a motor fuel extensively used in spark-ignition engines. Compounds presented in a gasoline fuel are susceptible to oxidation by oxygen under the effect of high temperature and light. The compounds are mainly hydrocarbons, which react with oxygen to form peroxides, peroxyacids, carboxylic acids, etc. The formation of these compounds increases the viscosity of the gasoline, its color, and reduces its octane number. The process of gasoline oxidation is characterized by the appearance of hydroperoxides, which, with time, decompose into aldehydes, ketones, and acids. These processes result in the formation of impurities, such as aromatic aldehydes and ketones, which are undesirable for engine operation. In addition, oxygen can react with the double bonds of unsaturated hydrocarbons to form peroxides and hydroperoxides, resulting in the formation of gums, varnish, and sludge in the fuel system. This can lead to clogging of filters, carburetors, and other components of the fuel system, reducing the efficiency and performance of the engine.

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by the atmospheric oxygen forming undesirable oxidation products between
the production and final use of a gasoline \[1,2\]. The formation of the oxida-
tion products results in a degradation in properties of a gasoline. Additives
are frequently added to gasoline to address oxidative stability and other
issues \[3\]. Among various additives, the phenolic antioxidants are of spe-
cial interest because they are able to directly seize peroxyl radicals formed
during the oxidation, thus breaking the auto-oxidation chain reaction. The
two different types of antioxidants used in gasoline are phenylenediamines
and various phenols \[3,4\].

It is well-established that traces of the transition metals strongly acceler-
atate the gasoline oxidation, catalyzing the decomposition of hydroperoxides
into radical species, in particular, those suffering a transfer of one electron,
such as copper, iron, cobalt, and manganese ions, which are the most ef-
efective \[5-8\]. The presence of the metallic species in automotive fuels is
generally undesirable because it is associated with corrosion, metal depo-
sition on engine parts, and poor fuel performance as a result of oxidative
decomposition reactions \[6,9\].

On the other hand, the metal oxide nanoparticles of the sizes in the
range of 1-20 nm are widely used in various fields of science and technol-
ogy because they show unique properties \[10-13\]. The metal-containing
nanoparticles have already shown a capability to inhibit chemical reactions
\[14-16\]. Group VIII metal nanoparticles, e.g., platinum and palladium,
accelerate the rate of the radical chain reactions \[17,18\]. Among vari-
ous metal-containing nanoparticles, the iron-containing nanoparticles have
found wide applications as catalysts, drug delivery system, high-density
memory devices, and others \[19\]. Based on the literature data, there is a
reason to believe that the iron-containing nanoparticles can also change the
rate of the radical chain oxidation processes.

This study shows the effect of the goethite nanoparticles on the rate of
the radical chain oxidation of benzyl alcohol with atmospheric oxygen. The
goethite nanoparticles with average size of 7.1 nm are found to inhibit the
benzyl alcohol oxidation. These model studies allowed us to reveal that
the goethite nanoparticles effectively enhance the oxidative stability of the
commercial gasoline.

2. Materials and methods

The preparation of the FeOOH nanoparticles colloidal solution was per-
formed according to a modification of the procedure described earlier \[20\].
The procedure is based on the iron(II) oleate thermal decomposition. The average nanoparticles size was determined by a transmission electron spectroscopy (TEM). The structural characteristics of the nanoparticles were found by the Mössbauer and Fourier transform infrared spectroscopies. The total iron content was measured by a photochemical method and the oxygen pulse titration method.

The initiated oxidation of benzyl alcohol was studied volumetrically according to the procedure described elsewhere [21, 22]. The benzyl alcohol, chlorobenzene, and azobisisobutyronitrile used in the oxidation reaction were purified by the standard procedure [23]. The conditions of the reaction were chosen as follows: the temperature was kept at 50°C, the oxygen pressure was $P(O_2) = 0.1$ MPa, the concentration of benzyl alcohol was 4.82 mol/L, and the rate of the initiation reaction was $W_i = 2.98 \cdot 10^{-8}$ mol/(L·s).

The rate of the oxidation was evaluated from the amount of oxygen consumed, which was measured volumetrically. The rate of the oxidation was determined by the procedure described elsewhere [24].

The fresh gasoline used in this study was provided by a local refinery and fulfilled specified quality requirements. The physical and chemical properties of the gasoline are presented in Table 1.

The oxidative stability of gasoline was measured by the induction period test according to the standard procedure [25]. The test method covers the determination of the stability of gasoline in finished form only, under accelerated oxidation conditions. According to the standard procedure, the 50 mL of gasoline is oxidized in a pressure vessel with the oxygen pressure at 700 kPa and heated at a temperature of 100°C. The pressure was recorded continuously until the breakpoint is reached. The time required for the sample to reach this point is the observed induction period. The induction period was determined as an elapsed time between starting the test and the breaking point, which is defined as a pressure drop of 10 % below the maximum pressure as detected in the pressure versus time curve. We tested two samples of gasoline. One sample is a fresh gasoline, whereas the second sample is the gasoline containing 0.007 % of the goethite nanoparticles.

3. Results and discussion

Fig. 1(a) shows a TEM image of the FeOOH nanoparticles prepared by the thermal decomposition of the iron(II) oleate. The average size of the FeOOH nanoparticles is found to be 7.1 nm. The corresponding size distribution of the nanoparticles shows that the size distribution is almost
normal. The sample is characterized by a narrow width of the particle
size distribution with the standard deviations less than 15 %. Fig. 1(b)
presents Mössbauer spectrum of the FeOOH nanoparticles giving the isomer
shift of 0.37 mm·s$^{-1}$ and the quadrupole splitting of -0.26 mm·s$^{-1}$. These
values correspond to the goethite ($\alpha$-FeOOH) [26]. Based on the elemental
analysis and pulse O$_2$ titration methods, it was found that the iron content
in nanoparticles is 63.0 %.

Fig. 2 gives the dependence of the rate of the benzyl alcohol oxidation on
the goethite concentration and on the bulk Fe$_2$O$_3$ concentration. The rate of
the oxidation without iron-containing compounds was found $W_0 = 2.0 \cdot 10^{-6}$
mol/(L·s). The bulk iron oxide does not change the oxidation rate of the
benzyl alcohol for the studied concentrations. Contrary, the oxidation rate
falls almost monotonically down with increasing the goethite nanoparticles
concentration. The oxidation of the benzyl alcohol is fully suppressed by the
goethite nanoparticles at the concentration $C_{FeOOH} = 0.35$ g/L. As a matter
of fact, the goethite nanoparticles used in the oxidation are the $\alpha$-FeOOH
nanoparticles stabilized by oleic acid and hexane in a colloidal solution.
Effect of the oleic acid and hexane on the oxidation rate of the benzyl
alcohol was separately tested under the same conditions. Neither oleic acid
nor hexane does not change the rate of the oxidation and its value remains
constant $W_0 = 2.0 \cdot 10^{-6}$ mol/(L·s).

Our studies show that a presence of the goethite nanoparticles with the
size of 7.1 nm results in an inhibiting the chain oxidation of the benzyl
alcohol. The liquid-phase oxidation of benzyl alcohol by molecular oxy-
gen is the radical process that occurs via a formation of the intermediate
free benzyl radicals (Bn$^\cdot$) and benzyl peroxyl radicals (BnOO$^\cdot$) [27, 28]. It
includes reactions of the chain initiation, the chain generation, the chain
propagation, the chain branching, and the chain termination. The inhibi-
tion of the oxidation process by nanoparticles may occur as a result of the
appearance of the additional reaction that involves interaction between the
goethite nanoparticles and the Bn$^\cdot$ or BnOO$^\cdot$ radicals. Therefore, based on
the obtained results, we assume that the goethite nanoparticles are capable
to react with Bn$^\cdot$ or BnOO$^\cdot$ radicals. It opens up the possibility to inhibit
by the goethite nanoparticles the oxidation of various organic compounds
and the complex hydrocarbon mixtures, e.g., the automotive gasoline.

The oxidative stability is one of the most important characteristics of
the automotive gasoline. The stability of the gasoline to oxidation with the
goethite nanoparticles was tested by the standard method. The results are
presented in Fig. 3. The induction period goes up to 405 min in the presence of the goethite nanoparticles in the gasoline. Therefore, the goethite nanoparticles in the concentration of 0.007 % enhance the gasoline stability. It is unexpected that the iron-containing nanoparticles presenting in the gasoline behave as an antioxidant preventing the gasoline oxidation. Fig. 4 shows the dependence of the induction period on the goethite concentration. The results demonstrate increasing the induction period for the gasoline exposed to increasing concentrations of the goethite nanoparticles. Therefore, increasing the concentration of the goethite nanoparticles increases the storage time for the automotive gasoline.

The main antioxidants used in the industry that prevent automotive gasoline from oxidation are the aromatic compounds, particularly, hindered phenols, aromatic amines, and diamines, or mixtures of aromatic diamines (e.g., phenylenediamines) and alkyl phenols. They are able to directly seize peroxyl radicals formed during oxidative degradation, thus breaking the auto-oxidation chain reaction. A mechanism is based on interrupting this chain of reactions (removing free radical intermediates), preventing the formation of hydroperoxides, peroxides, soluble gums, or insoluble particulates. Our findings show that the iron-containing nanoparticles, contrary to the bulk iron-containing solids, exhibit a similar effect on the gasoline oxidation by the air oxygen.

It is well-known than the traces of transition metals, particularly, iron, strongly accelerate the gasoline oxidation, catalyzing a decomposition of hydroperoxides into radical species \[ \text{phenols} + \text{H}_2\text{O}_2 \rightarrow \text{phenoxyl radicals} \]. As a result, a presence of the various metals in the automotive gasoline is undesirable. Our study shows that, contrary to this opinion, the iron-containing nanoparticles are capable to effectively inhibit the oxidation of organic compounds. The inhibition may occur as a result of the appearance of the additional reactions in the termination step of the oxidation mechanism. Probably, for the benzyl alcohol oxidation, there is an interaction between the goethite nanoparticles and reactive \( \text{BnOO}^* \) radicals. Moreover, it allows us to assume that the goethite nanoparticles inhibit the oxidation processes in gasoline according to the similar mechanism. The goethite nanoparticles interact with peroxyl radicals preventing a formation of hydroperoxides and peroxides. As a result, the goethite nanoparticles significantly enhance the oxidative stability of the automotive gasoline.
4. Conclusion

The goethite nanoparticles material was prepared using the thermal decomposition method. The size and structure of the prepared material were confirmed by TEM, Mössbauer spectroscopy, and elemental analysis. The goethite nanoparticles exhibit a significant inhibition activity in the radical chain oxidation reaction which has been shown by our studies for the benzyl alcohol oxidation. Based on these studies, we reveal that the use of the goethite nanoparticles was shown to improve the oxidative stability of the commercial gasoline. Increasing the goethite concentration up to 0.06 g/L increases the gasoline induction period up to 600 min., i.e. almost two times. Therefore, using the goethite nanoparticles as an antioxidant additive may significantly enhance the gasoline storage period. It is worth noting that goethite is the main component of a rust. Therefore, our results show that not only the goethite nanoparticles but also the nano-rust have a capability to enhance the oxidative stability of gasoline. That opens a new avenue for a design of new generation of antioxidants. A new advance in the fuel storage may be also provided by a technique for a preparation of the storage containers covered by the nano-rust.

5. Acknowledgment

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References


Fig. 1. (a) TEM image of the colloidal solution of the goethite nanoparticles. Inset - size distribution of the nanoparticles. (b) Mössbauer spectrum of the goethite nanoparticles.
Fig. 2. Dependence of the oxidation rate of the benzyl alcohol on the concentration of the goethite nanoparticles.
Fig. 3. The time dependencies of the $O_2$ pressure for the fresh gasoline (line) and mixture gasoline and goethite nanoparticles (dotted). The goethite nanoparticles content in gasoline are 0.007 %
Fig. 4. The dependence of the induction period ($T_{\text{ind}}$) on the concentration of the goethite nanoparticles.
Table 1. Properties of the Ukrainian Gasoline

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<th>Characteristic</th>
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<td>Octane number</td>
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<tr>
<td>-motor octane number</td>
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<td>-at 15°C evaporated, max (% v/v)</td>
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<td>-at 150°C evaporated, max (% v/v)</td>
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<td>-maximum distillation residue (%)</td>
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