

Research Article

Kinetic Interaction of Hexan Conversion and Oxidation on the Surface of an Al_2O_3 Nanocatalyzer at Room Temperature under the Effect of Gamma Radiation

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Received 1 August 2021; Revised 25 September 2021; Accepted 1 October 2021; Published 19 October 2021

Academic Editor: Maria N. D.S. Cordeiro

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The kinetic and temperature dependencies of the conversion of hexane to gas and liquid oxide products on the surface of the nano- Al_2O_3 catalyst in the homo and hetero phase were investigated and compared. The rate of hexane conversion in air in different phases at temperature $\Delta T = 180\text{--}2000\text{ C}$ was determined ((a) 10–15% from the homo phase in the hetero phase; (b) thermal 12–17%; (c) radiation-thermal 14–22%). It is shown that the excess electron density formed in radiation defects migrates from the surface to the adsorbents, thereby weakening the intramolecular chemical bonds of the adsorbent and accelerating the decomposition processes investigated.

1. Introduction

The study of the kinetic interaction of the conversion of hexane to organic oxide products in the low temperature range in the atmosphere with the combined use of radiation technologies and nanocatalysts is of great importance in practice. The application of radiation to oxidation processes saves energy and time and gives high yields [1, 2].

Energy saving requires the creation of new high-quality systems for the production of fuel from organic raw materials. Under the influence of ionizing radiation, it is possible to break various energetic chemical bonds on hydrocarbons of any molecular structure on the surface of the nanocatalyst, to create new molecules by creating an unlimited number and variety of free radicals. Unlike the classical methods, the application of radiation technologies can change the molecular structure of petroleum products and selectively investigate the quality of the product [1–4].

After a long time, nanotechnology has picked up consideration as the oxidation form of vehicle catalyst framework

for the upcoming era due to a few reasons. As shown, the transport segment could be a source of all discussed contaminations due to the utilization of fossil fills [1–5].

Investigation of oxidation processes on the surface of the nanoheterogeneous catalyst modified by the gamma radiation has demand for implementation. The emerged anion centers, influence of hole centers in radiolysis-catalytic transitions, and the working mechanism of these process are today's actual challenge. Adsorption and desorption processes on the surface of the dielectric oxides, emerging of O^- centers, and transmission of CO to CO_2 depend on the amount of atomic oxygen [6].

The stability of nanosystems was investigated using modern analytical methods. It has been established that the role of the Al_2O_3 nanoparticles is dual. A very strong dependence of the concentration of nanoparticles is detected and interpreted in this manuscript. We support our conclusions by employing FT-IR spectroscopy. It was noted that the rheological parameters of carboxymethyl cellulose improved after nanoeffect [7].

However, the use of these metal oxides will be productive and pertinent regarding high costs and less saves [8].

One alternative for decreasing the discussed contamination caused by the transport division is to switch to nanocatalysts, which are more cost effective and easily available for generation. Inquiring shows that the nano- $\text{Al}_2\text{O}_3 + \text{CuO}$ contains a wide run in comparison with other catalysts utilized within the catalyst framework [9–12].

In this paper, the oxidation/conversion process of carbon-monoxide has been investigated on the surface of catalysts (TAI_2O_3 , $\text{TAI}_2\text{O}_3 + \text{CuO}$, and $\text{RTAI}_2\text{O}_3 + \text{CuO}$) which has been modified by radiation. The catalyst samples have been radiated in various absorption doses by the source of a ^{60}Co isotope device in order to analyze the distribution of anion centers on the surface. It was found out by the examples of investigation size and element concentration of anion centers (atoms O^-) depending on absorption dose. The results show that the amount of paramagnetic centers on the surface has increased. The average activation energy of the process decreases, and conversion happens faster. The triangular oxide can also form on the square lattice of the nanocatalyst of Al_2O_3 under CO oxidation conditions, and similar features are observed. Furthermore, oxides are unstable outside the O_2 atmosphere, indicating the presence of active O atoms, crucial for oxidation catalysts [12–17].

Catalytic converters contain replaced metal catalysts inserted on a strong stage bolster. The kinetics of decreasing emissions in various flow rates and temperature ranges of 70–35°C on the surface of catalyst, which is constituted on the $\text{Al}_2\text{O}_3/\text{CuO}$ nanoparticles conversion of CO to CO_2 on the mix-catalysts in the closed nanoflow reactor, has been researched [11–16].

The main objective of the work is to investigate the catalytic conversion of hexane on the surface of the nano- Al_2O_3 catalyst and the generation of oxide items of gases [18–21].

2. Experimental Part

Preparation of samples: at room temperature $m = 0.21$ g, $d = 20$ nm size nano- Al_2O_3 is drawn and filled into ampoules of 15 ml. Different amounts of pure hexane are taken, filled into ampoules on the catalyst and gasified in a vacuum device, and then, refrozen and sealed at nitrogen temperature by giving oxygen prepared from the system to the catalyst. In this work, dose rate $P = 10.05$ rad/sec in the ^{60}Co isotope unit at room temperature at intervals $D = 0$ –72 hours. Nanocatalysts used were purchased from USA Sky-springNanomaterials Inc. The concentration of gas products obtained by radiolysis was analyzed in “Gazachrome-3101” and “Svet-101” devices. The sensitivity of the device to H_2 is $K = 8.6 \cdot 10^{13}$ molecules/($\text{cm}^3 \cdot \text{mm}$).

The amount of hydrocarbons in the fluid phase was analyzed on the Varian 450-GC (USA) chromatograph.

Column: 15 mm x 0.25 mm, ID x 0.25 mm CP-Sil 5CB, carrier gas: nitrogen (constant pressure 15.0 psi), injector: 300°C, auto sampler: CP-8410 Variant, and injection volume: 1 μL .

Functional changes in the sample were analyzed on infrared (IR) and ultraviolet ((UB) $l = 200 \div 800$ nm UV-Visible, Cary-50) spectrometers.

3. Results and Discussion

The kinetic interactions of gaseous and liquid products resulting from the oxidation of n-hexane on the surface of a nanosized Al_2O_3 catalyst under the influence of radiation have been studied. The transformation processes were carried out under static conditions. The dependence of the resulting gas products on the size of the nanocatalyst taken was studied. Table 1 shows the amount of gaseous products formed from a mixture of n-hexane and air at room temperature on the surface of nano- Al_2O_3 of different sizes under the influence of radiation.

It shown in Table 1 that the concentration of carbon dioxide in the gaseous products of radiolysis of n-hexane and air mixture on the surface of nano- Al_2O_3 is higher, which is due to the oxidation process. Thus, the presence of hydrogen and unsaturated hydrocarbons in the system is a complete dehydrogenation process.

The dependence of the formation of methane and ethylene, which are the main products of the dehydrogenation process, on the nanoparticle size is shown in Figure 1.

As can be seen from the figure, depending on the nanoscale in the system, the formation of methane and ethylene decreases as the nanoscale grows. In short, the process of formation of light gases occurs at a greater speed on the surface of the catalyst size $d = 5, 20$ nm, so it will be more interesting to study the subsequent processes on catalysts size $d = 20$ nm.

The kinetic dependences of n-hexane at room temperature in the form of gas (CH_4 , C_2H_6 , C_2H_4 , ΣC_3 , and ΣC_4) formed by the conversion of radiation on the surface of nano- Al_2O_3 are also investigated. Figure 2 shows the kinetic dependence curves of the accumulated CH_4 , C_2H_4 , and C_2H_6 gases controlled in the system, which show that the number of gases generated by the conversion of n-hexane exposed to radiation on the catalyst surface increases with the absorbed dose.

As can be seen from the kinetic dependence, the formation of light hydrocarbons (CH_4 , C_2H_4 , and C_2H_6) increases depending on the absorbed dose. After an interval of $\Delta\tau \geq 50$ hours, after the value of the absorbed dose $\Delta D = 18$ –20 kGy, the formation of light hydrocarbons slows down. Saturation curves are visible, which cause the product in the system to decompose again under the influence of radiation to form relatively heavier-molecular-weight hydrocarbons (ΣC_3 , ΣC_4 , and ΣC_5). Under the influence of long-term radiation, hexane breaks down to form larger-molecular-weight compounds or new fragments.

Thus, the formation of hydrocarbon gases other than hydrogen and propane gases was less than that of pure hexane, which is an indicator of the formation of heavy hydrocarbons in the liquid phase. In addition to the redecomposition of large-molecular-weight hydrocarbons that have been exposed to radiation for a long time, the share

TABLE 1: The amount of gaseous products formed from a mixture of n-hexane and air at room temperature on the surface of nano- Al_2O_3 of different sizes under the influence of radiation.

No.	Radiation time, hours	Particle size, nm	The obtained gas products, Ni.10-16, molecules/ml						
			CO_2	H_2	CH_4	C_2H_6	C_2H_4	ΣC_3	ΣC_4
1	6	5	1,89	2,65	0,043	0,011	0,034	0,002	-
3	6	20	1,81	4,29	0,036	0,015	0,029	0,007	-
5	6	40	3,54	3,17	0,028	0,015	0,031	0,006	-
7	6	50	5,15	5,74	0,021	0,014	0,023	0,006	0.002

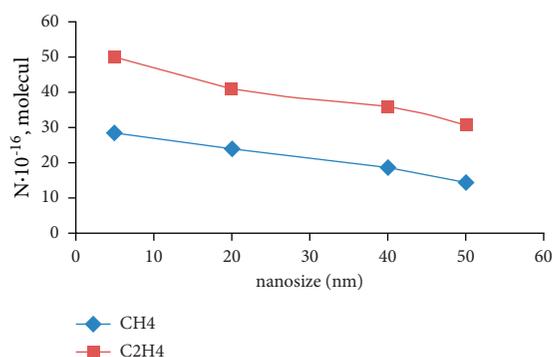


FIGURE 1: Dependence of gases from radiation catalytic decomposition of hexane on the size of the nanocatalyst.

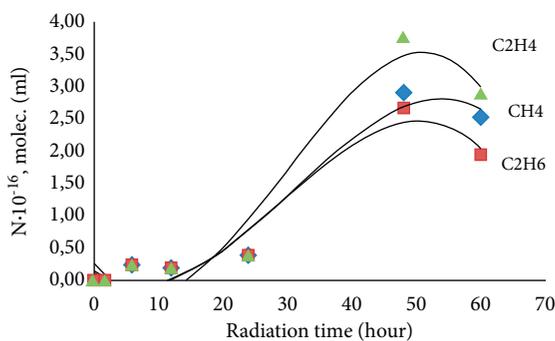


FIGURE 2: Kinetic dependence of methane, ethane, and ethylene from radiolysis of hexane and nano- Al_2O_3 systems (20 nm nano- Al_2O_3 + 5 ml hexane, $T = 24^\circ\text{C}$, $P = 0$, 36 kGy/h).

of gaseous products in the radiation-chemical emission has little effect on the total emission.

Figure 3 shows the temperature dependence of the conversion of hexane to oxide products in different phases. Oxidation processes, thermal, and radiation-thermal conversion processes of normal hexane in air atmosphere in both homo and hetero phase have been studied.

As can be seen from the figure, in the homo and hetero phase, the process of hexane conversion in the air differs more sharply in the upper temperature ranges. Thus, if the homo-phase conversion at $\Delta T = 150\text{--}160^\circ\text{C}$ is 4%, we have added a nanocatalyst to the system, and the thermal processes increase to 5%, and the radiation-thermal processes increase to 7%. When the temperature is increased to 200°C , this conversion rate increases to pure hexane- 22,

hexane + catalyst thermal- 25, and hexane + catalytic radiation-thermal- 33%.

The dependence of the degree of conversion in the linear region of the temperature dependence of radiation-thermal conversion processes on the amount of absorbed dose is shown in Figure 4. Comparative dependencies show that, in all cases, the rate of conversion of hexane increases linearly depending on the amount of dose absorbed and the temperature (see Figures 3 and 4).

As can be seen (Figure 4), the rate of hexane conversion in the air medium (by %) increases linearly depending on the amount of dose absorbed in the temperature ranges $\Delta T = 180\text{--}200^\circ\text{C}$. Thus, if the conversion rate is 7–15% of the absorbed dose at $D = 10$ kGy, it increases to 22–32% at $D = 25$ kGy.

Figure 5 shows a comparison of the percentage of hexane in the atmosphere in the homo and hetero phases in the temperature range $\Delta T = 180\text{--}200^\circ\text{C}$.

A comparative analysis of this histogram shows that a high conversion rate can be obtained by the combined effect of temperature and the absorbed dose, which depends on the value of the absorbed dose.

Structural changes of organic oxide products in the liquid phase were studied as a result of infrared (IR) spectra and liquid-gas chromatograph analyzes. IR spectra of heavier hydrocarbons and oxide products formed from the radiolysis of the hexane fraction in the liquid phase on the surface of nano- Al_2O_3 at room temperature were obtained, and it was found that the intensity of CO bonds in the air increases.

Changes in the amount of hydrocarbon gases in the liquid phase of the system, the occurrence of isomerization and oxidation processes, and the control of the output of these products are carried out on the basis of IR spectra (Figure 6), and results obtained from gas-liquid chromatograph devices are given in Table 2.

A comparative analysis of Figure 4 and Table 2 shows that the proportion of organic oxides in the liquid phase increases with the absorbed dose.

Changes in the amount of oxide products of hydrocarbons in the liquid phase and the occurrence of isomerization and oxidation can be observed with the results obtained from the gas-liquid chromatograph. Under the influence of gamma rays at room temperature, the hexane-air ratio changes on the surface of nano- Al_2O_3 and the share of newly formed products changes. The initial radiation in the atmosphere creates additional anion centers on the surface of the nanocatalyst, which accelerates the conversion of hexane and increases the rate of conversion. Initially

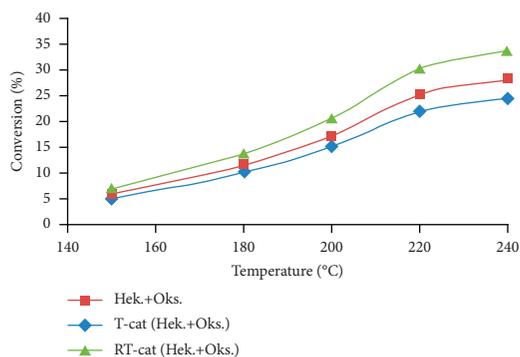


FIGURE 3: Temperature dependence of the conversion of hexane in air at different phases.

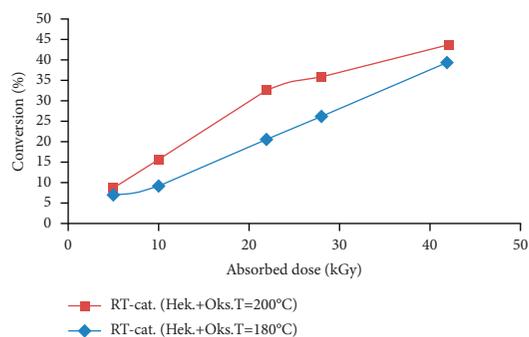


FIGURE 4: Dependence of the conversion rate of hexane on the surface of the nano- Al_2O_3 catalyst on the initial absorbed dose in air.

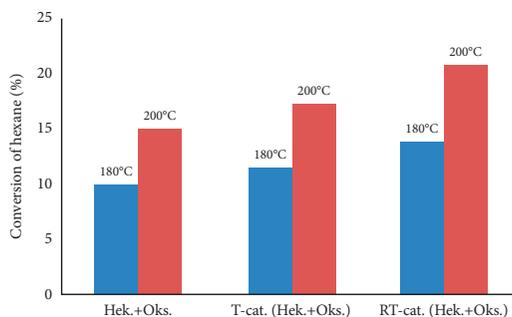


FIGURE 5: Comparison of the conversion of hexane in air in homo and hetero phases at different temperatures.

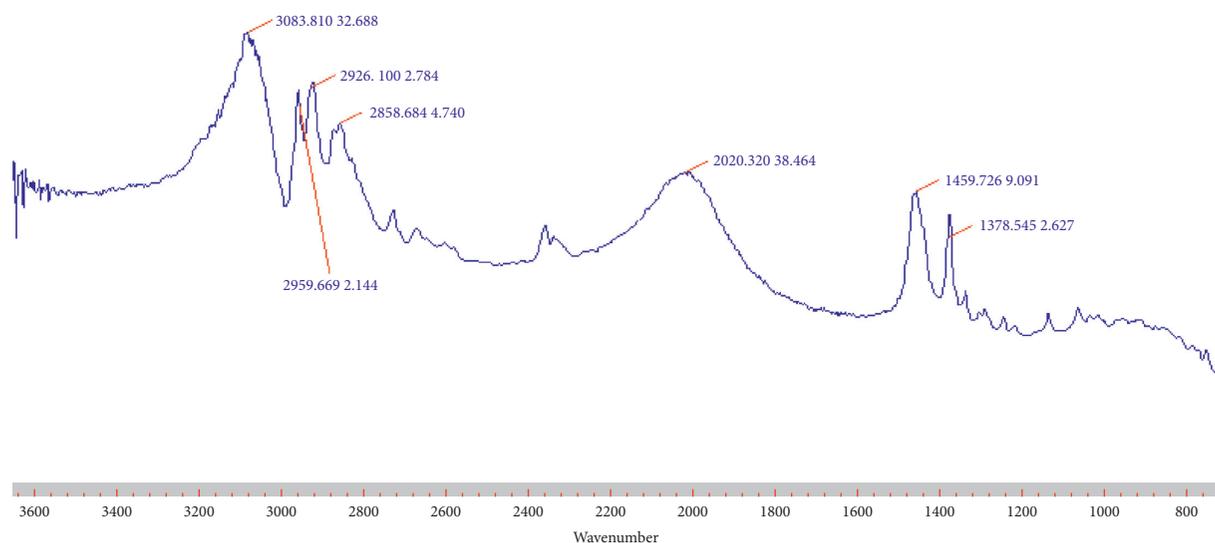


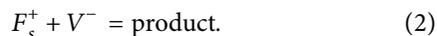
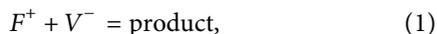
FIGURE 6: IR spectrum of hexane oxide products formed in the liquid phase from the radiolysis of hexane and air in the nano- Al_2O_3 surface at room temperature ($d = 20$ nm, $m = 0.2$ g nano- $\text{Al}_2\text{O}_3 + 5$ ml solution, $T = 24^\circ\text{C}$, $P = 0$, 36 kGy/h).

TABLE 2: Hexane oxidation products.

Obtained products	Identification
Hexaldehyde	1
Hexanon-2	2
Oktanon-2	3
Oktanol-2	4
Oktanol-3	5
$C_n < C_8$	6
$C_n > C_8$	7
$n-C_{16}, \Sigma_i-C_{16}$	8

modified catalysts under the influence of surface radiation have a higher activity, and the rate of conversion on its surface is 15–20% higher than that of others. The average activation energy of the transformation process decreases, and the speed of the transformation process increases [4–6].

When a nanocatalyst is introduced into the system, the absorbed radiation is mainly absorbed by the catalyst, as a result of which additional energy is transferred to the system in the order of the energy of the restricted zone of the oxide catalyst. Under the influence of ionizing radiation, one or two valence electrons (F^+ and F) and hole centers (V , V^+ , and V^{-2}) are formed in aluminum oxide crystals [7]. In macro-sized catalysts, as the electrons in volume migrate to the surface, they are captured on the side of the holes formed on the surface and recombine.



While the size of the catalysts decreases, the volume defects in nanosizes easily migrate to the surface, and additional defects appear on the catalyst surface, which accelerates the process of energy transfer and conversion to the system. Electrons formed on the surface migrate to the environment and accelerate additional transformations. Radiation plays a key role in the occurrence of surface defects, adsorption, and decomposition processes in catalytic reactions and, as a result, increases the yield of the final product.

Excess electron density formed in radiation defects migrates from the surface to the adsorbents, thereby weakening the intramolecular chemical bonds of the adsorbent and accelerating the decomposition processes.

4. Conclusions

The kinetic and temperature dependencies of the conversion of hexane to gas and liquid oxide products on the surface of the nano- Al_2O_3 catalyst in the homo and hetero phase were investigated and compared. The kinetic dependences of n-hexane at room temperature in the form of gas (CH_4 , C_2H_6 , C_2H_4 , ΣC_3 , and ΣC_4) formed by the conversion of radiation on the surface of nano- Al_2O_3 are also investigated. Thus, the formation of hydrocarbon gases other than hydrogen and propane gases was less than that of pure hexane, which is an indicator of the formation of heavy hydrocarbons in the liquid phase. Radiation plays a key role in the

occurrence of surface defects, adsorption, and decomposition processes in catalytic reactions and, as a result, increases the yield of the final product. The rate of hexane conversion in air in different phases at temperature $\Delta T = 180\text{--}200^\circ\text{C}$ was determined ((a) 10–15% from the homo phase in the hetero phase; (b) thermal 12–17%; and (c) radiation-thermal 14–22%).

Data Availability

The data used to support the findings of this study are included within the article, and any data in the full-text can be quoted and does not involve the situation of leakage.

Conflicts of Interest

The authors declare no conflicts of interest.

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