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Selective oxidation of hydrocarbons under air using recoverable silver ferrite-graphene (AgFeO₂-G) nanocomposite: a good catalyst for green chemistry

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South Marines

Abstract

The selective oxidation of hydrocarbons is a main academic and industrial research challenge. A lot of researches have been done about this issue, but till now relatively little attention has been paid to graphene-complex oxide nanocomposites. Herein, we report our studies on a new catalyst. Silver ferrite-graphene (AgFeO₂-G) as a separable nanocomposite from the reaction solution, was used as an effective oxidizing agent for the oxidation of various hydrocarbons (1- decene, cyclohexene, cis-cycloctene, cyclohexane, cyclooctane etc.) under mild conditions (55 °C, 8h) with high conversion and selectivity using air, that is proper for 'green' chemistry. Metal or metal oxide nanoparticles assembled on graphene sheets revealed high electrocatalytic activity. Indeed, AgFeO₂ with graphene due to low band gap and graphene oxide with large amounts of oxygen-containing groups, provide facility catalytic activity of catalyst-supported system. We also found that, with this catalyst, selective oxidation could be achieved without the need for the addition of solvent, which is appropriate in partcular for 'green' chemistry. The catalysts showed little deactivation and maintained their conversion and selectivity levels duration of the measurements.

Keywords: Oxidation, Silver, Selective, Nanocomposite, Graphene

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1. INTRODUCTION

Oxidation is an important method for the synthesis of fine chemicals and chemical intermediates in the manufacture of high-tonnage goods, pharmaceuticals and agrochemicals [1, 2]. For example, propylene oxide (PO) is a major chemical intermediate with a universal estimated production of 6.7 million tons in 2003 [3], and by volume it is among the top 50 chemicals produced around the world [4]. Nevertheless, the selective oxidation of hydrocarbons is a main academic and industrial investigation challenge and oxidations are often useless [5]. The present of catalytic systems using oxygen from air is preferred for 'green' chemistry [6]. Among the metal-based nanocomposites, nanogold and nanosilver play an important role in catalysis, which have been widely explored in many reactions. Gold catalysis is now displaying potential in selective oxidation processes [7-10]. But, gold-based catalysts are usually costly. Among many metal catalysts, silver is an extremely effective noble metal and has some prominent characteristics such as antimicrobial activity and environmental friendliness [11]. More notably, silver is exclusively appropriate for industrial catalysis and heterogeneous catalysis because of its relatively low prices, for example, less than 1/50 of the price of gold or platinum and about 1/25 of the price of palladium [12,13]. So, silver compounds have been used in different reations such as isomerization [14], substitution [15], oxidation [16-20], antimicrobial agents [21,22], synthesis [23,24], catalytic [25], photocatalytic [26-28], hydrogenation [29], optical [30], biological [31], reduction [32], adsorption [33,34], metathesis [35], polymerization [36], formylation [37], ammonia oxidation [38,39], electron microscopy and EXAFS studies [40], and as sensor [41]. Even though ethene is epoxidized efficiently using molecular oxygen with silver catalysts in a high-scale industrial process [42], but for higher alkenes can only be effectively epoxidized using hydroperoxides [43], hydrogen peroxide [44,45], or stoichiometric oxygen donors. The use of silver alone does not have economically advantageous. On the other hand, the utilize of silver compounds not only increase the efficiency of the reaction, but also work in terms of industrial. Metal and traditional semiconductor nanoparticles are considered as a suitable factor for nanocatalysts (or catalysts support) and have received notable attention in photoreduced oxidation, hydrocarbon selective oxidation, solar water splitting and so on [46,47]. It is well-known that the support plays a vital role in the catalytic performance of a heterogeneous catalyst [48]. In recent years, there has been an increasing attention in the use of nanostructure carbon materials as catalyst supports [49, 50]. Graphene has attracted worldwide interest since it is an appealing support due to its outstanding properties, such as superb mechanical strength, high adsorption capability, easiness of modification large, specific surface area and remarkable electrical conductivity with a single layer of sp²-bonded

carbon atoms tightly packed into a two-dimensional (2D) honeycomb structure [51, 52]. Also it is well-known that a single graphene layer has a zero-gap semiconductor with a linear Dirac-like spectrum around the Fermi energy. To cut a long story short, graphene has awarded both the Nobel Prize in Chemistry to Robert Curel et al. in 1996 and Physics to Andre Geim et al. in 2010, which illustrate graphene is an exceptional material. Hence, graphene has received late consideration as an ideal catalyst support [53, 54]. Besides, graphene oxide (GO) compared with other supports such as mesoporous silicates (MCM-41 and SBA-15), has unique nanostructure (monolayer), abundant oxygen carrying functionalities on its basal planes and at its edges (hydroxyl, epoxide, and carboxylic groups), excellent mechanical strength and hydrothermal stability, and the viewpoint of various applications such as composite materials, catalysis, optoelectronics, supercapacitors, memory devices, etc [55, 56].

However, based on our knowledge up to now, relatively little attention has been paid to nanocomposites [57, 58], or graphene-complex oxide nanocomposites for oxidation. Of course, a few studies have been conducted on the photocatalyst [59, 60]. It is of great appetite to study the facility of graphene complex oxide nanocomposites, such as AgFeO₂-G systems. If that can be accomplished, then it may be feasible to gain some specific properties as a outcome of the interaction of complex oxide nanoparticles and support as well as the good consequence. Nanocomposite not only has a low band gap [61], due to the AgFeO₂, but also large amounts of oxygen-containing groups, because of the graphene oxide, which cause oxygen easily be transferred to the substrate. Magnetically recoverable nanocatalysts have been used in organic synthesis for a wide range of catalytic processes [62, 63]. For the reason that AgFeO₂ is a magnetic semiconductor substance, thus AgFeO₂-based catalysts can be magnetically separable in a suspension system by virtue of their own magnetic properties without other magnetic materials, which makes we can reuse and recovery catalysts after process. Hence, we for the first time report our work on AgFeO₂-G nanocomposites can perform a good activity for the oxidation of hydrocarbons using air, with excellent selectivity to oxidation products and substantial conversions. Moreover, our catalyst does not need to initiator in contrast to the way in which initiator is required in previous studies for hydrocarbons oxidation [64].

2. EXPERIMENTAL

2.1. Materials

Graphite powder, potassium permanganate, $Fe(NO_3)_3.9H_2O$, H_2SO_4 (98 wt%), H_2O_2 (30%), HCl (37 wt%), silver nitrate, formaldehyde, and ethylene glycol were purchased from Merck. Cyclohexene (99%, Fluka), Cyclohexane (99%, Fluka), 1-methyl-1-cyclohexene (97%, Sigma-Aldrich), alpha-methyl styrene (>99%, Merck), styrene (>99%, Merck), cis-stilbene (>95%, Merck), trans-stilbene (96%,Sigma), 1,2,3,4-tetrahydronaphthalene (>98%, Merck), 1decene and other reagents were obtained from commercial sources and were used as received without further purification. The deionized water used throughout experiments. For obtaining graphene oxide (GO), graphite powder was oxidized using reported procedures Hummers' method [65].

2.2. Characterization

Fourier transform infrared (FT-IR) spectra were recorded using a Perkin-Elmer 597 spectrophotometer in the range of 400-4000 cm⁻¹ as KBr disks. ¹H NMR spectra of a reaction mixture (without purification) were recorded on a Bruker 250 MHz spectrometer. UV-Vis spectra of solutions were recorded with a Shimadzu 160 spectrophotometer. Powder X-ray diffraction (XRD) data were recorded on a Bruker D8ADVANCED diffractometer with a wavelength of 1.5406 Å (Cu K α), a voltage of 40 kV, and a current of 40 mA. Field-emission scanning electron microscopy (FESEM) was performed with a Hitachi F4160 microscope at an accelerating voltage of 15 kV. The resulted suspensions were deposited on a holey carbon film supported by a copper grid. The Brunauer –Emmett–Teller surface area of as-synthesized samples was measured using an ASAP2010C surface aperture adsorption instrument (Micromeritics Instrument Corporation, USA) by N₂ physisorption at 77 K. Raman spectra of graphene-based materials were recorded in the spectral range 200-3500 cm⁻¹ on a BRUKER (SEN-TERRA 2009) Raman spectrometer with laser power 50 mW and 785 nm. The reaction products of the oxidation were determined and analyzed by using an HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenyl methyl siloxane 30 m × 320 µ m × 0.25 µm) with a flame-ionization detector (FID). The magnetization measurement was performed at room temperature using a vibrating sample magnetometer (VSM) device, in the Development Center of the University of Kashan (Kashan, Iran).

2.3. Synthesis of magnetic AgFeO₂-graphene nanocomposite

A typical condition for the synthesis of AgFeO₂-graphene nanocomposite, is as follows: 50 mg of GO was added into 50 ml ethylene glycol (EG) with ultrasonication for 1 h to form a steady GO colloid. Afterward, 0.808 g of Fe(NO₃).9H₂O and 0.340 g of AgNO₃ were added in 10 ml EG and added slowly into the above colloid with magnetic stirring for 1 h. Then, formaldehyde was added as reducing agent into the mixture followed by stirring for another 20 min, yielding a stable bottle-green homogeneous emulsion. The resulting mixture was then transferred to a 100 ml teflon-lined stainless steel autoclave and heated in an oven at 200 °C for 14 h, and cooled to room temperature. The resulting product were separated by filtration and washed with absolute ethanol and deionized water, then dried at 55 °C for 10 h. The product was labeled as AgFeO₂-G. The formation of AgFeO₂-G composite is schematically illustrated in Fig. 1.

2.4. Catalytic aerobic oxidation with AgFeO₂-graphene

The oxidation processes were performed in a glass inlay of a 32 ml steel autoclave. The autoclave was conditioned by discharge and replenish with dioxygen. All autoclave loading was carried out under air and heated to the required temperature (55 °C) in an oil bath. In a generic test, 2.0 mmol of substrate was added to the reactor with 0.01 g AgFeO₂-G, 3.0 mmol isobutyraldehyde as a co-oxidant. After purgation with O₂, the reactor was pressurized to 1.5 bar. The stirring rate was 350 rpm. At the end of 8 h the reactor was depressurized, the catalyst deleted via an external magnet (1.2 T) and the product mixture was analyzed by gas chromatography and ¹H NMR. The products were identified with authentic samples and ¹H NMR. Conversions and yields were computed about the starting substrate. The reaction products were measured by gas chromatography and recognized by comparison with the retention time and spectral data to those of an authentic sample. To ensure reproducibility, each catalytic reaction was performed at least three times. For recycling experiments, after finishing the process, the nanocomposite was recollected using a magnet, washed with acetonitrile, dried and reused. GC circumstances with column Hp-5: carrier gas N₂ flow = 0.7 ml min⁻¹, inlet temp 250 °C, initial column temp 90 °C, final column temp 190 °C, sleep 10 °C min⁻¹.

3. Results and discussions

3.1. Characterization of composite

Fig. 2, shows FT-IR spectra of GO and AgFeO₂-G. For GO, the stretching vibrations of carbonyl functional group was indicated clearly at round 1730 cm⁻¹ and ether/epoxide functional groups were at 1232 cm⁻¹ [66]. The carbonyl and ether/epoxide groups demonstrate that the original extended conjugated π -orbital system of the natural graphite was destroyed and oxygen-containing groups were inserted into carbon skeleton during the oxidation of graphite powder [67]. Also there is a C-O peak at 1420 cm⁻¹ which is ascribed of carboxy groups in these structures [68]. The spectra of graphene oxides also show a C=C peak at 1622 cm⁻¹ and a C-O peak at 1060 cm⁻¹ corresponding to the remaining sp² character and alkoxy group, respectively [69]. The peaks at 2923 and 2853 cm⁻¹ can be assigned to a methylene stretch and represents the existence of CH₂ or CH groups [70]. Furthermore, O-H groups are seen for graphene oxides about 3600 cm⁻¹ as shoulder. The obvious peak at 3433 cm⁻¹ assigned to the stretching vibration of hydroxy group indicates that both graphite and graphene oxide had a certain amount of adsorbed water. As can be seen, all the characteristic peaks of GO vanished after the hydrothermal process. For AgFeO₂-G, the adsorption peak around 1530 cm⁻¹ may be assigned to the stretching vibrations of the unoxidized carbon backbone [71] and the two strong absorption peaks at lower frequency (around 475 and 553 cm⁻¹) can be assigned to the stretching vibrations of the Ag-O bonds in tetrahedral positions and the Fe-O bonds, respectively [72]. This indicates that there is reduced GO in the AgFeO₂-G composite.

Fig. 3A gives the nitrogen adsorption-desorption isotherms (inset) and pore size distribution plots for AgFeO₂-G. The N₂ isotherm of the AgFeO₂-G composite is close to Type IV, revealing the existence of mesopores. It is wellknown that the mesoporous structure is a more efficient photocatalyst structure for degrading organic pollutants in water. The specific surface area of the AgFeO₂-G sample was determined to be 252.35 m².g⁻¹, with the Brunauer–Emmett–Teller (BET, nitrogen, 77 K) method. The Barrett–Joyner–Halenda (BJH) desorption average pore diameter was 1.95 nm with a very narrow pore size distribution, and the pore volume was 0.23 m².g⁻¹.

Raman spectroscopy gives useful information related to the electronic and structural properties of graphene. Fig. 3B, displays Raman spectra of GO and AgFeO₂-graphene. The D band (~1363 cm⁻¹) is related to the defect induced breathing mode of A_{1g} symmetry and the G band (~1605 cm⁻¹) is of E_{2g} symmetry, representing the relative degree of graphitization [73]. Both GO and AgFeO₂-G exhibit two bands at about 1363 and 1605 cm⁻¹, which are associated with the D and G bands of carbon-based materials, respectively. Also, compared with GO (curve a), AgFeO₂-G (curve b) shows relative higher intensity of D to G band. These observations offer a decline in the average size of

the sp² domains from AgFeO₂-G and further affirm the formation of new graphitic domains after the reduction [74]. Furthermore, an increase in D/G intensity ratio (ID/IG = 1.24) of AgFeO₂-G illustrated increased defects in graphene sheets after reduction, which is likely because smaller but more numerous graphitic sp² domains were manufactured compared with the ones previously present in graphite oxide [75].

The XRD diffraction patterns of the as-prepared AgFeO₂-graphene nanocomposite and graphene oxide (GO) are shown in Fig. 4A, It can be seen that nearly all the diffraction peaks of AgFeO₂-graphene may be pertained to spinel-type AgFeO₂ (JCPDS 21-1081) [76]. The peaks at 20 values of 12.3 , 25.1 , 27.3 , 31.4 , 34.2 , 42.8 , 48.5, 56.3 , 60.1 , 63.2 and 77.1 can be indexed to (003), (006), (101), (102), (104), (009), (108), (0012), (110), (116), and (202) crystal planes of spinel AgFeO₂, respectively. The average diameter of the AgFeO₂ nanoparticles was surveyed by the Scherrer equation, which is about 45.78 nm. No typical diffraction peak of graphene (002) or GO (001) is observable in the XRD pattern for AgFeO₂-graphene, due to the fact that GO can be destroyed by the presence of AgFeO₂ among the interlayers during the hydrothermal process, leading to the exfoliation of GO. On the other hand, and the reduced GO sheets show no visible sign of the (002) peak [77].

UV-vis spectroscopy is an instructive and important method to recognize the change in the absorption of the semiconductors. As seen in Fig. 4B, the UV-vis absorbance spectra of GO shows an distinct characteristic absorption peak at about 230 nm that pertain to the π - π * transition of aromatic C=C bonds. For AgFeO₂-G, the absorption peak of GO at 230 nm vanishes and the absorption is much stronger than that of the pure AgFeO₂ particles coating the entire visible region because of the presence of graphene.

3.2. Structure and morphology of AgFeO₂-graphene nanocomposite

The size, shape and size distribution of the nanoparticles of $AgFeO_2$ and GO were examined by field-emission scanning electron microscopy (FESEM). The as-synthesized $AgFeO_2$ nanoparticles Fig. 5A have good spherical shape and have a mean diameter of 50 nm. As can be seen in Fig. 5B, the approximately transparent graphene sheets are totally exfoliated and decorated homogeneously with $AgFeO_2$ nanocrystals having an average diameter of 50 nm and a narrow particle size distribution.

3.3. Magnetic separation properties of AgFeO₂-graphene nanocomposite

The magnetic properties of the synthesized AgFeO₂ and AgFeO₂-G were analyzed by vibrating sample magnetometry (VSM). Fig. 6A shows the room-temperature magnetization hysteresis loops of the AgFeO₂-G composite and pure AgFeO₂ particles. The saturation magnetization of the AgFeO₂-G composite is 50.5 emu/g, which is lower than that of pure AgFeO₂ particles (62.2 emu/g), chiefly attributing to the presence of graphene. The hysteresis loops of the powdered material showed no magnetic hysteresis, with both the magnetization and demagnetization curves passing through the origin, which clearly indicates the superparamagnetic nature of the material. Moreover, the synthesized heterogeneous nanocomposite possess strong magnetic features due to a high saturation magnetic separation for the AgFeO₂-graphene nanocomposite. Also, we surveyed magnetic separation properties of the AgFeO₂-graphene nanocomposite. As shown in Fig. 6B, the catalyst can be easily separated from the reaction mixture by a magnetic field after 30 seconds.

3.4. Catalytic activity of the catalyst

For select the optimum solvent, we examined the reaction using magnetite nanocomposite as catalysts into oxidation of 1-decene in the presence of air under the optimized conditions (55 °C, 8h and isobutyraldehyde as cooxidant) for various solvents by a stirred non-pressurized glass reactor (Table 1). The highest conversion for 1decene (69%) was observed with acetonitrile (Table 1, entry 10). Also, highest selectivity (97%) was obtained in the oxidations of 1-decene with DMSO (Table 1, entry 8). As you can see, under relatively mild conditions, the most significant finding with these solvents is that the products distribution is dependent on the solvent. In a further set of experiments, to confirm the general applicability of this oxidation catalyst, different hydrocarbons were used as substrates, using acetonitrile as solvent and $AgFeO_2$ -graphene nanocomposite as catalyst, and a high selectivity for the epoxide products were achieved (Table 2). The high selectivity for the epoxide, in particular for unsaturated hydrocarbons (for example, cyclohexene), demonstrates that direct oxidation of the carbon = carbon double bond is happening with this catalyst structure.

In a final set of experiments, we investigated the oxidation of 1-decene in the absence of solvents. We found that, selective oxidation could be achieved without the need for the addition of solvent (Table 3), which is a main principle of 'green' chemistry. Also we tested aerobic oxidation of 1-decene in the absence of support and AgFeO₂. As you can see, catalyst or support unaccompanied don't have a proper act, whereas it is possible to improve the

efficiency of AgFeO₂ by coupling it with another semiconductor (graphene oxide), resulting in high catalytic performance.

3.5. The possible oxidation mechanism

The proposed mechanism is presented in Fig. 7, in which the conversions of an olefin in the presence of AgFeO₂graphene nanocomposite and isobutyraldehyde as a co-oxidation are plotted. The initiation starts with the conversion of the O_2 to the corresponding superoxide radical catalysted by the nanocomposite. (Fig. 7A) Afterward this radical reacts with aldehyd producing an acyl radical (Fig. 7B), subsequently this radical reacts with O_2 to that produces acylperoxy radical (Fig. 7C) which is the intermediate, responsible for the convey of oxygen from its molecular form in the gaseous phase to the products of olefin oxidation. This observation and the mechanism were similar to those of graphitic carbon nitride (g- C_3N_4) [78], which were used as catalysts for the selective allylic oxidation. The reaction then proceeds on the surface of nanocomposite by the attack of the acylperoxy radical on the coordinated olefin (Fig. 7D), which consequences finally in the epoxide and isobutyric acid.

Although detailed considerations on the transition state are not yet clear, the mediation of the co-oxidant (isobutyraldehyde) in the oxidation process could be via a interaction with the nanocomposite surface, particularly influencing the ease of electron transfer from the nanocomposite to establish the active carrier. As matter of fact, as mentioned in the introduction, nanocomposite properties are also vital in this process.

3.6. Catalyst recycling

The AgFeO₂-G catalysts can be used repeatedly for the catalytic oxidation of hydrocarbons. The reusability of AgFeO₂-G catalysts for the oxidation of hydrocarbons using molecular oxygen was investigated under identical conditions. After the required time, the catalyst was filtered and washed with methanol and acetonitrile and dried. The recovered solid was used for another consecutive run without further treatment. Also, as shown in Fig. 8, the catalytic activity of the AgFeO₂-G nanocomposite does not show any clear loss after ten recycles for the oxidation of 1-decene, illustrating the composite has fine stability.

4. Conclusions

In a nutshell, to the best of our knowledge, this is the first report on graphene-complex oxide nanocomposites aerobic oxidation by inexpensive and easily prepared magnetite nanoparticles and O_2 , allowing for general oxidation of a relatively wide variety of hydrocarbons in good conversion and selectivity. Moreover, the synthesized heterogeneous nanocatalysts bear strong magnetic features due to a high saturation magnetization value (~60 emu g⁻¹). After completion of the reaction, the catalysts can be collected by magnet. In addition, the heterogeneous nanocatalysts are stable and can be reused frequently. Also, the method represents a number of highly desirable practical specifications: mild temperature reaction, oxygen can be used as the oxidant, ethyl acetate, a normal organic solvent which is not as unsafe as halogenated compounds, is the reaction medium and all of the catalyst components are almost low-cost, steady, and commercially on hand reagents. Above all, oxidation could be gained without the need for the addition of solvent, which is a major tenet of 'green' chemistry. Eventually, if nanostructured carbon materials are often considered as model supports, the real driving force for the fast development of these materials in catalysis has been the increasing demand for new catalysts that should be more affective, energy-saving, resource-saving and environment-friendly, together with an increasing request for renewable and alternative energies needed for the sustainable development of our society.

Acknowledgment

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Figures and tables captions:

Fig. 1. Schematic illustration of the synthesis procedure of the AgFeO₂-graphene composite.

Fig. 2. Fourier transform infrared (FT-IR) spectra of (a) graphene oxide (GO), (b) AgFeO₂-G.

Fig. 3. (A) Nitrogen Adsorption-Desorption isotherm (inset) and corresponding pore size distribution curves for AgFeO₂-G. (B) Raman spectra of graphene oxide (GO) and AgFeO₂-G composite.

Fig. 4. (A) XRD pattern of (a) graphene oxide (GO) and (b) AgFeO₂-G in the range of 5-80. (B) UV-vis absorbance spectra of graphene oxide (GO), AgFeO₂-G and pure AgFeO₂.

Fig. 5. SEM image of (A) AgFeO₂, (B) AgFeO₂-G and (C) AgFeO₂-G after 10 cycles of reaction.

Fig. 6. (A) Room-temperature magnetization hysteresis loops of (a) AgFeO₂-G composite, and (b) AgFeO₂. (B) Images of AgFeO₂-G suspension with (a) and without (b) a magnetic field.

Table 1. 1-decene oxidation using G-AgFeO2 in different solvents

Table 1. oxidation of hydrocarbons using G-AgFeO₂

Table 3. 1-decene oxidation with molecular oxygen in the absence of a solvent

Fig. 7. The possible mechanism for the oxidation of hydrocarbons by oxygen in the presence of AgFeO₂-G and isobutyraldehyde.

Fig. 8. Bar plot showing the oxidation of 1-decene in acetonitrile for 10 cycles using AgFeO₂-G in the presence of air.



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1-decene oxidation using G-AgFeO ₂ in different solvents							
Entry	/ Solvent	Conv. ^a (%)			Product Selec	tivity (%)	
		/	~~~~	°7			
1	1,4-dioxane	8	(100)	(0)	(0)	(0)	
2	Methanol	14	(24)	(19)	(22)	(35)	
3	THF	Trace	(0)	(0)	(0)	(0)	
4	Ethylacetate	61	(75)	(4)	(5)	(16)	
5	Chlorobenzene	60	(66)	(0)	(34)	(0)	
6	DMF	8	(95)	(0)	(5)	(0)	
7	Chloroform	46	(97)	(0)	(3)	(0)	
8	DMSO	3	(100)	(0)	(0)	(0)	
9	Mesitylene	Trace	(0)	(0)	(0)	(0)	
10	Acetonitrile	69 ^b	(100)	(0)	(0)	(0)	

Table 1

Reaction conditions: 0.01 g catalyst, 0.002 mol hydrocarbon, 55 °C, 8 h, solvent (3 ml), isobutyraldehyde (0.003 mol). ^aConversions were determined by GC. ^bEvaluated from ¹H-NMR.

Entry	Hydrocarbon	Conv. ^a (%)		Products	Selectivity (%)	
1	\bigcirc	96	(98)		OH (1) OH	
2	$\langle $	97	(80)			(5)
3		23	(73)		(0)	(27)
4		100	(100)	O (0)	OH (0)	O O (0)
5	$\sim \sim \sim$	66			HO (8)	(9)
6		10	(0)	(0)		HO (0)
7		99		(57)	(25)	HO (00)
8	Ph Ph	87		(20)	(15)	(15)
9	~~~~	69	(78)		H0 (4)	
10		27		OH (100)		
11	ss	58	(88)	SOH (3)	s(9)	

Table 2oxidation of hydrocarbons using G-AgFeO2 in CH_3CN as solvent

Reaction conditions: 0.001g catalyst, 0.002 mol hydrocarbon, 55 °C, 8 h, solvent (3 ml), isobutyraldehyde (0.003 mol). ^aConversions were determined by GC and are an average of at least three runs

Catalyst	Conv. ^a (%)	Selectivity (%)				
			°	НО		
AgFeO ₂	4	(70)	(0)	(30)	(0)	
GO	4	(70)	(0)	(30)	(0)	
AgFeO ₂ -G	8	(19)	(0)	(81)	(0)	

Table 3

1-decene oxidation with molecular oxygen in the absence of a solvent

Reaction conditions: 0.01 g catalyst, 0.002 mol hydrocarbon, , 55 °C, 8 h, solvent (3 ml), isobutyraldehyde (0.003 mol). ⁴Conversions were determined by GC and are an average of at least three runs

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Fig. 7. The possible mechanism for the oxidation of hydrocarbons by oxygen in the presence of AgFeO₂-G and isobutyraldehyde.



Fig. 8. Bar plot showing the oxidation of 1-decene in acetonitrile for 10 cycles using AgFeO₂-G in the presence of air. Reaction conditions: 0.01 g catalyst, 0.002 mol hydrocarbon, 55 °C, 8 h, solvent (3 ml), isobutyraldehyde (0.003 mol), Conversions were determined by GC and are an average of at least three runs

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Highlights

- Silver ferrite-graphene is a semiconductor with a relatively narrow bandgap which was applied for the oxidation of hydrocarbons.
- Graphene oxide was used as a support for improvement of catalytic activity.
- High catalytic activity for the oxidation of various hydrocarbones (1- decene, cyclohexene, cis-cycloctene, etc.) was under mild conditions (55 °C, 8h) with high conversion and selectivity using air. We found that selective oxidation could be achieved without the need for the addition of solvent, which is appropriate for 'green' chemistry.