**Enhanced Photocatalytic Activity of Mesoporous ZnFe₂O₄ Nanoparticles
toward Gaseous Benzene Under visible Light irradiation**

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Abstract

A mesoporous ZnFe_2O_4 nanoparticles prepared as a visible light responsive catalyst, the morphology, structure and optical property of the spinel oxide are characterised, diligently. Photocatalytic activity of ZnFe_2O_4 nanoparticles assessed toward the oxidation of gaseous benzene. A comparative study conducted, between ZnFe_2O_4 and Fe_2O_3 , in terms of water and benzene adsorption using microcalorimetry as well as photocatalytic benzene oxidation. In this context, ZnFe_2O_4 showed greater activity than Fe_2O_3 . The heats of water adsorption for the spinel and hematite are -270 kJ/mol and -190 kJ/mol, respectively; revealing the dissociative mode of the adsorption, which is crucial for the generation of hydroxyl radicals. Moreover, the heat of benzene adsorption for ZnFe_2O_4 and Fe_2O_3 are -167 kJ/mol and -139 kJ/mol, respectively. Finally, the intermediate (phenol) and products (H_2 & CO_2) of the oxidation reaction is monitored by GC (FID/TCD) and DRIFT: a mechanism is proposed accordingly for the photocatalytic oxidation of the benzene.

Keywords: ZnFe_2O_4 ; Fe_2O_3 ; Gaseous benzene; Visible-light photocatalysis; Adsorption of water; Hydroxyl radicals.

1. Introduction

Over the past few decades, semiconductor photocatalysts have attracted public interest as a promising technology to eradicate the dye pollutants from textile and paper wastewater as well as the volatile organic compounds (VOCs) from the indoor air [1–3]. In this context, benzene is one of the most abundant VOCs found in indoor air, chemical factories (e.g. paint, petrochemicals, etc.), as well as polluted urban atmospheres. It is also one of the eight representative indoor

VOCs with a high oxidation potential and solely stable structure that makes it a proper choice as an organic reactant to evaluate the photocatalytic property of semiconductors, compare to dyes that are easily photo-oxidised due to their lower oxidation potential [4,5]. A limited number of publications are reported about the gas-phase photocatalytic oxidation of benzene under visible light irradiation [6–11]. Consequently, preparation of stable and low-cost semiconductors with narrow bandgap energy to absorb a large number of solar energy is vital [12]. In this context, hematite (Fe_2O_3) is the most thermodynamically stable iron oxide phases at ambient temperature and it has narrow band gap energy (2.2 eV) [13]. However, hematite has its own disadvantages due to poor conductivity, high charge recombination rates and short hole diffusion length (2–4 nm) [14–16]. Encountering these issues, semiconductors consisting of two or more distinct semiconductor components have become a focus of intense research due to their unique and enhanced performances nanoparticle [17–20]. In such case, spinel oxides have attracted great interest for catalytic reactions due to their desirable properties, such as single crystal shape, high thermal stability, and well diffused, etc. [21–24]. ZnFe_2O_4 is an n-type semiconductor and one of the most promising spinel system materials [25]. It has been investigated in many applications, such as photocatalysis, magnetic resonance imaging, drug delivery technology and gas sensor due to its low cost, eco-friendly and photo-corrosion resistant advantages [26–28]. In spite of the great potential, there have been only limited studies of these materials, mainly as a supplementary component of composite photocatalysts with other semiconductor materials [29–34]. Also, there are limited investigations reported regarding the surface's active sites toward pre-adsorption of benzene and water over ZnFe_2O_4 . As a heterogeneous catalyst, it is demonstrated that reactions occurring on the surface of the catalyst and pre-adsorption of the target substrates around catalyst particles are critical for the oxidation process [35,36].

In this paper, the photocatalytic activity of ZnFe_2O_4 and Fe_2O_3 were tested under visible light irradiation toward gaseous benzene as an organic reactant. Also, the surface properties of the catalysts studied by adsorption microcalorimetry of water and benzene. The products of photocatalytic oxidation were monitored by GC (FID/TCD) as well as diffuse reflectance infrared Fourier transform (DRIFT). Eventually, a mechanism is proposed with a main focus on the active species of the surface such as hydroxyl radicals.

2. Experimental

2.1. Preparation of ZnFe_2O_4 nanoparticles

At the first step, the appropriate amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1M, 99.0%) and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.05M, 99.0%) were dissolved in deionized water. Then citric acid (0.3M, 99.8%) was slowly added to the metal-containing solution at room temperature under constant magnetic stirring. Moreover, the mentioned solution mixed for 2 h and heated at 90 °C for 2 h under constant stirring. In the following, the gel was dried in the oven at 120 °C and calcined in a muffle furnace for 1h at 600 °C to obtain the ZnFe_2O_4 sample. In addition, as-prepared ZnFe_2O_4 and purchased Fe_2O_3 (Sigma-Aldrich, BET surface area= 37 m²/g, band-gap; 2.15 eV) were coated using the following method: glass beads were placed in concentrated HCl for 2 h, and washed in hot water consecutively to remove the excess amount of adsorbed Cl which was detected by adding silver nitrate to mother solution. Finally, the glass beads have been dried at 250 °C for 6h. It is noteworthy that the photocatalysts (ZnFe_2O_4 or Fe_2O_3) were homogeneously dispersed in an aqueous solution using an ultrasonic bath. Then the beads were coated with ZnFe_2O_4 and Fe_2O_3 by dip-coating method.

2.2. Microcalorimetry

Measurement of catalyst's active sites; ZnFe_2O_4 and Fe_2O_3 were studied by adsorption microcalorimetry to assess the adsorption properties, whether the differential heat of adsorption or quantity of adsorbed gases. Microcalorimetry experiment was performed on Setaram-C80 heat flow calorimeter coupled to a multiport high-vacuum homemade glass manifold. An appropriate amount of specimen (approx. 500 mg) was taken into a sample cell, which is connected by a "T" shaped Pyrex connector to the empty reference cell. The sample was heated from room temperature to 200°C under vacuum and kept for 2 h, then 3-4 doses of helium gas were introduced into the system to remove any excess residue such as moisture or organic impurity from the system. The system was heated for 4-5 h under vacuum at 200°C and then cooled down to the temperature (50°C) where we want to perform the adsorption study. Small doses of test gas consecutively introduced to the system and gradually increased up to 50 Torr until an equilibrium pressure was reached. Then the obtained differential heats of the test gas adsorption were recorded as a function of its coverage. Further, the manifold degassed under vacuum for almost 30 min; adsorption conducted in the same manner. Finally, the number and strength of active surface are obtained from the difference between the adsorbed gases from the first and second adsorption

Benzene adsorption energy; the adsorption energy of benzene on the surface of the spinel and Fe_2O_3 was measured by microcalorimetry to figure out whether the surface of the materials is capable of adsorbing benzene or not. In addition, adsorption of oxygen on the surface of ZnFe_2O_4 and Fe_2O_3 studied, the heat of oxygen adsorption for both photocatalysts is low and in the range of physical adsorption.

2.3. Photocatalytic reaction

Photocatalytic oxidation of gaseous benzene over ZnFe_2O_4 and Fe_2O_3 under visible-light irradiation carried out in a glass photoreaction cell with an effective volume of 80 ml, which was attached to a homemade glass manifold with a volume of 174 ml (Figure S1), it should be mentioned, the manifold was wrapped with heat tape to maintain the temperature at 125 °C. A vacuum pump was connected to the manifold for evacuation of benzene after every run of the photocatalytic oxidation reaction. First, an adequate amount of coated photocatalyst was located in the photoreaction cell. Second, the manifold was taken under vacuum for 30 min to remove gas from the photoreaction cell completely. Third, 5 μL of liquid benzene and 1.5 μL water were injected to manifold from injection chamber, benzene and water were allowed to evaporate in the manifold for 20 min afterwards air was introduced to the system by opening the air valve. Next, photoreaction cell's valve was opened and subsequently, closed after 10 min to let the benzene and water, as well as air flow into the reaction cell; after the completion of adsorption-desorption of gases on the photocatalyst surface (monitored by GC-FID), Then the reaction cell conducted to visible light exposure (60 W tungsten lamp) for 60 min. The reaction was monitored every 10 min consecutively by recording the concentration of benzene, CO_2 , and H_2 simultaneously using GC-TCD-FID (HP 6890 GC with TCD-FID). In addition, Infrared spectroscopy (DRIFT) was performed using a Perkin-Elmer spectrometer at room temperature. The sample was cleaned by raising the temperature from 25 to 300 °C under concurrent flowing argon gas (30 mL/min); then the system allowed to cool, up to room temperature. Subsequently, the benzene photooxidation was conducted under simultaneous flowing of benzene and air as well as water vapour over the ZnFe_2O_4 nanoparticles.

3. Results and discussion

3.1. Characterization of photocatalyst

The crystallographic structure and phase purity of ZnFe_2O_4 are determined by X-ray diffraction (XRD) (Rigaku, UltimaIV, Japan) analysis (Figure 1a). All the observed diffraction peaks can be ascribed to the cubic spinel structure of ZnFe_2O_4 (JCPDF#65-3111), revealing that a pure ZnFe_2O_4 phase obtained. The crystallite size calculated from the XRD peak broadening of the major peak which is located at 35° by the Scherer's equation (Eq. 1):

$$D_{hkl} = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad (1)$$

where D_{hkl} is the particle size perpendicular to the normal line of the (hkl) plane, β_{hkl} , θ_{hkl} and λ is the full width at half maximum, the Bragg angle of the (hkl) peak and the wavelength of X-ray respectively. The results indicated that the particle size of ZnFe_2O_4 is 38 nm. In addition, X-ray diffraction pattern of Fe_2O_3 is shown in Figure S2; the average particle size of the metal oxide with respect to Scherer's equation is 35 nm.

The textural properties of pure ZnFe_2O_4 studied by SEM, TEM, STM, EDS and BET, demonstrated in Fig. 1b–e. Regarding SEM (LEO 1450 VP) image, Figure 1b shows the rough, loose and porous surface feature of ZnFe_2O_4 ; the large surface area, as well as the numerous pores, which may facilitate mass transport for the reactant diffusion. Corresponding, TEM (LEO 912 AB) image (Figure 1c) of ZnFe_2O_4 nanoparticles mainly consist of particles with irregular shape with an average size of 27 nm. In this context, the STM was also exploited to investigate the morphology, Figure 1d shows the STM (SS1 (NATSYCO), Iran) images (1415 nm x 1113

nm) of ZnFe_2O_4 nanoparticles, which illustrates the size and height of particles. In this image, the bright spots are higher than the dark ones and the distribution of the particles on the surface is mapped in a way that they can be identified. Three particles selected for quantitative measurements and results revealed that their average size and height are 20 nm and 2.3 nm, respectively. Results affirm convergence between STM and SEM; in both cases, the surface does not have homogeneity that can be due to the presence of particles with a different size on the surface. Moreover, the EDS (Inca 400–Oxford Instruments) analysis of pure ZnFe_2O_4 (Fig. 1e) confirms that the spinel is composed of Zn, Fe, O and the Zn/Fe atomic ratio is 0.5. Furthermore, N_2 adsorption–desorption isotherms (Tristar II, Micromeritics) exploited to exhibit surface features in the term of specific surface area and pore distribution of ZnFe_2O_4 . A distinct hysteresis loop obtained (Fig. S3a) that displays the existence of the abundant pores; moreover, the obtained specific surface area from the BET equation is $60.68 \text{ m}^2 \text{ g}^{-1}$. Furthermore, the BJH pore diameter distribution profile (inset in Fig. S3b) indicates a variety of pores 20-40 which is centred and 25 nm corresponds to the mesoporous structure. These structures with a high surface area are essential to enhance the photocatalytic performance by providing sufficient photocatalytic surface sites and facilitating the diffusion of the reactant and product through the surface. Therefore, the microscopic images in Figure 1b-d illustrate the near-spherical shape of ZnFe_2O_4 nanoparticles, which in contribution with a highly porous (from BET analysis) and crystalline structure (from XRD analysis) could facilitate not only the adsorption of the reactants, whether liquid or gas, but also the photocatalytic oxidation of them on the surface.[37].

In order to acquire more details, The UV-vis diffuse reflectance spectrum (Varina-Carry 100) of the ZnFe_2O_4 nanoparticle is investigated (Fig. S4). The ZnFe_2O_4 nanoparticles demonstrate an absorption edge located at 650 nm, however, the adsorption edge for Fe_2O_3 is 580 nm (Fig. S4a).

185 The results reveal the visible activity of ZnFe_2O_4 , which corresponds to dislocation of an excited
 186 electron of O(2p) level to the Fe(3d) level for a spinel-type oxide with brick red colour [22].
 187 Consequently, this property can culminate an efficient contribution to the photocatalytic
 188 reactions due to a wide range of solar energy can be adsorbed. Furthermore, plots of $(ah\nu)^2$
 189 versus photon energy (eV) are illustrated in Fig. S4b, the estimated band gap energy is 1.8 eV,
 190 which is quite lower than the band gap energy of Fe_2O_3 (2.2 eV).
 191 The temperature programmed reduction (H_2 -TPR, Micromeritics Chemisorb 2750 apparatus, 5
 192 vol % H_2/Ar) is presented in Figure 2. This analysis provides an applicable method to study the
 193 reducible oxygen species of the metal oxides. In ZnFe_2O_4 , iron is in a mixed oxidation state
 194 ($\text{Fe}^{+2/+3}$), the reduction of the Fe^{+3} to Fe^{+2} took place in two steps. The first step is a reduction of
 195 Fe^{+3} to an intermediate oxidation state ($\text{Fe}^{+2/+3}$) that observed between 455 and 530 °C.
 196 Moreover, the next step attributes to the main reduction of $\text{Fe}^{+2/+3}$ to Fe^{+2} that occurred between
 197 572 and 675 °C [38]. On the other hand, the first reduction peak of Fe_2O_3 , attributed to α -oxygen
 198 of surface observed in the temperature between 277°C and 388 °C, the Second peak, which,
 199 contains two peaks (separated by a shoulder) occurred at the temperature between 375 and 495
 200 °C corresponds to β -oxygen of the lattice. In comparison with ZnFe_2O_4 the first reduction of iron
 201 in Fe_2O_3 occurred at lower temperatures, however, the second reduction peak took place at the
 202 temperatures between 530 and 811 °C which correspond to γ -oxygen of the Fe_2O_3 's lattice [39].
 203 Even though the Fe^{+3} , which is located in the lattice of the ZnFe_2O_4 at the first reduction step is
 204 more stable than Fe_2O_3 , at the second reduction step the ($\text{Fe}^{+2/+3}$) is more stable in the lattice of
 205 the Fe_2O_3 than ZnFe_2O_4 (the reducibility of lattice oxygen depends on the crystal size of the
 206 metal oxides; the smaller particles of the spinel oxide results shortening the distance for oxygen
 207 migration from the bulk to the surface). Altogether the total reduction of Fe^{+3} to Fe^{+2} in the

lattice of ZnFe_2O_4 carried out at lower temperatures compared to Fe_2O_3 , so it seems that ZnFe_2O_4 shows a better reduction property than Fe_2O_3 , which leads to a greater oxygen mobility of the spinel. The following reaction occurred through the TPR reaction (Equation 2):

the presence of Zn–O–Fe in the ZnFe_2O_4 structure makes an asymmetric electronic environment leads to easier reduction features of the spinel oxide [39]. Corresponding to the TPR results, compare to Fe_2O_3 , the spinel oxide structure shows a higher oxygen mobility along with easier oxygen reducibility that both are crucial for the photocatalytic activity [40].

In summary, the characterizations of ZnFe_2O_4 reveal that the preparation protocol allowed ZnFe_2O_4 to have a smaller particle size, larger specific surface area, high crystallinity as well as a great oxygen mobility.

<Figure 1>, <Figure. 2>

3.2. Microcalorimetry analysis

3.2.1. Water adsorption

As it is known, cations (as a Lewis acid) contributes to the stabilization of anions (as a Lewis base) by attaching one another and creating a Lewis acid-base pair—it actually takes place on the surface of metal oxide as a host and the anion molecule as a guest [41,42]. Furthermore, water is a sorely appropriate molecule in the study of the surface, it is a weak and / or medium ligand in the ligand's spectrochemical series, which is an amphoteric compound that makes it a molecule with the ability to attach to a metal center by the oxygen atom and also to the oxygen of the

231 metal oxide via its hydrogen. However, adsorption of water as a Lewis base (ligand) can
232 exclusively occur from the oxygen of water as an electron donor to metal centre and / or oxygen
233 vacancy as an electron acceptor (Lewis Acid). The adsorption of water on oxides like Al_2O_3 and
234 TiO_2 has been briefly studied by microcalorimetry [43–46]. So, comparative studies of water
235 chemisorption on metal oxides such as ZnFe_2O_4 and Fe_2O_3 may help us to understand about the
236 active sites of the surface in the both case and figure out how existing of Zn–O–Fe can effect on
237 the nature of active surface in ZnFe_2O_4 .

238 In this context, water adsorption microcalorimetry was carried out to determine the number and
239 the strength of the surface active sites. Figure 3a and Figure 3b represent the differential heats of
240 water adsorption versus the amount of adsorbed gas and the amount of adsorbed water versus
241 pressure (Torr), respectively. The initial heats of water adsorption, with an exothermic nature,
242 observed for ZnFe_2O_4 (-270 kJ/mol) is greater than Fe_2O_3 (-190 kJ/mol), which indicates the
243 tendency of both samples to adsorb water; however, the spinel mixed oxide shows much more
244 activity toward it. Also, the dissociative species that produced after water adsorption on the
245 surface of the metal oxide can adsorb on the surface and could consequence a new set of
246 reactions—the protonation of an anion O^{2-} and the formation of the hydroxyl group on the cations
247 are due to the dissociation of water. Furthermore, first layer coverage of water on the surface of
248 ZnFe_2O_4 and Fe_2O_3 are 463 $\mu\text{mol/g}$ and 63 $\mu\text{mol/g}$, respectively, which indicate the adsorbed
249 amount on spinel surface is almost 7 times higher than Fe_2O_3 . Nevertheless, Menetrey, et. al.,
250 suggested, as the heat of water adsorption on the surface of metal oxide is higher than -120
251 kJ/mol, the adsorption mode is dissociative; however, when it is lower than -120 kJ/mol,
252 correlates with molecular mode [47]. Thus, in our cases, water adsorption on the surface of
253 ZnFe_2O_4 and Fe_2O_3 are dissociative. These results correlate with spinel's nanoparticle; smaller

particle and mesoporous structure which may lead to higher adsorption ability in comparison by Fe_2O_3 .

<Figure 3>

3.2.2. Benzene adsorption

Figure 4a shows the differential heat of benzene adsorption on the surface of the samples, which for ZnFe_2O_4 and Fe_2O_3 are -167 kJ/mol and -139 kJ/mol, respectively. Figure 4b shows coverage amounts of benzene on the surface of samples that the obtained results for the ZnFe_2O_4 and Fe_2O_3 are 54 $\mu\text{mol/g}$ and 27 $\mu\text{mol/g}$, respectively. These results comply with the obtained results from water adsorption on the surface of the samples. It seems, the number of the active sites of ZnFe_2O_4 is the double magnitude of Fe_2O_3 , which may lead to greater photocatalytic activity of the spinel. These results demonstrate that the surface of spinel is more favourable than Fe_2O_3 for adsorption of benzene and water molecules. Furthermore, the surface of the catalysts did not show any tendency toward adsorption of oxygen (Figure 4c), in other words, oxygen has not been adsorbed strongly with surface's active sites. It seems the surface has shown greatest activity toward the water and the lowest activity against oxygen.

<Figure 4>

3.3. Photocatalytic benzene oxidation

Figure 5 exhibits time course of photocatalytic oxidation of benzene over ZnFe_2O_4 and Fe_2O_3 . No proceed were detected for reaction occurred without a catalyst, the absence of air and in darkness. In addition, a reaction in the absence of water was conducted, which showed **negligible oxidation after 40 min light illumination**. On the other hand, in the presence of catalyst, water,

air, and visible light, almost 70% conversion of benzene is observed for ZnFe_2O_4 nanoparticle, and almost 32% conversion was obtained in the case of Fe_2O_3 , indicating ZnFe_2O_4 is excellent visible-light photocatalytic performance. In the presence of ZnFe_2O_4 , after 30 min irradiation, initial conversion reached to 60%, and then the conversion percentage slightly increased. In the case of Fe_2O_3 , after 40 min irradiation 37% conversion is obtained and it slightly decreased for the next 20 min of the reaction. Furthermore, H_2 and CO_2 were monitored by GC-TCD (Figure 6) to realise that in which manner the benzene is decreasing under illumination, whether photocatalytic oxidation or adsorption. Moreover, Figure 6a demonstrates the amount of CO_2 evolved within the illumination of the photoreaction cell, the concentration rises steeply within 20 min of the reaction, and then raised slightly for the next 40 min. Also, this figure indicates that the hydrogen amount is increasing slightly at the first 10 min, which is followed by the persistence of the photooxidation reaction. In addition, production of carbon dioxide corroborates with decreasing of benzene concentration in the photocatalytic oxidation manner. Thus, phenol production was observed carefully as a possible product of benzene photooxidation; for 30 min, the rise in phenol concentration is simultaneous by a decrease in benzene concentration. Afterwards, its concentration gradually decreases in the next half of the reaction. It seems, phenol is the intermediate of photocatalytic oxidation of benzene, which it consumed by active species to generate CO_2 and / or H_2 . Furthermore, Figure 6b illustrated CO_2 and H_2 production on Fe_2O_3 versus time of irradiation, which demonstrates, consumption of benzene in the photocatalytic process; however, Fe_2O_3 is less active than the spinel counterpart. In addition, phenol generation over Fe_2O_3 was investigated diligently; moreover, on Fe_2O_3 , phenol production detected as the intermediate of the oxidation. It is noteworthy that carbon monoxide concentration was as equal as its concentration in the air, therefore, we assume that the

CO was not produced by photooxidation reaction and the concentration was constant all over the reaction.

In addition, benzene photooxidation on ZnFe_2O_4 was studied by in-situ FTIR technique (Figure S5) to assert the phenol production. The bands at 1114, 1479, 1700 and 3033 cm^{-1} were correspond to bending of the C-H aliphatic group, C=C bond of aromatic, the stretching of CO_2 and the stretching of C-H bond of the aliphatic group, respectively. The stretching of hydroxyl groups due to adsorption of water on the surface appeared as a broadband at $3200\text{--}3500\text{ cm}^{-1}$, as well as, the narrow band at 3750 cm^{-1} attributed to stretching of OH groups that formed by dissociative chemisorption of phenol. The specific band of benzene at 1479 cm^{-1} is recognisable in Figure S5, the intensity of this band is decreasing within the reaction and disappeared at the end of the reaction. In this context, a decrease in this peak is in convergence with the raising of new bands correspond to phenol and carbon dioxide. A dramatic rise in CO_2 intensity detected due to oxidation of benzene and phenol for 30 min, and then it increased slightly. DRIFT data support the results obtained by GC; both showed production of phenol and CO_2 as the intermediate and product of the benzene photooxidation, respectively. With respect to the absence of carbon monoxide peaks in both DRIFT and GC as well as the production of phenol, we introduce the mechanism of the reaction in the following manner.

<Figure 6>

3.3.1. Mechanism of benzene photooxidation

The inclusion of ZnO in the structure of ZnFe_2O_4 changes electronic structure of iron as well as the oxygen of metal oxide due to the formation of Zn–O–Fe. It causes a fundamental difference in the nature of the active surfaces (acidity and basicity) in comparison with Fe_2O_3 . There are

qualitative models to explain how the acidic feature of a metal oxide may change/or even generate by adding another metal oxide to its structure with the aim to the formation of a new structure (in this case is spinel type oxide) [48,49]. Mismatch in cation valence and coordination number along a heterogeneous linkage (M-O-M') originates an excess charge at minor component cation; thus, Fe-O-Fe and Zn-O-Fe lead to different acidic and / or basic properties in Fe₂O₃ and ZnFe₂O₄, respectively. In this context, with considering polarising power, Fe³⁺ prevails over Zn²⁺ and consequently contributes more toward Lewis bases, so the surface charge of ZnFe₂O₄ is lower than Fe₂O₃. From TPR data, the presence of Zn-O-Fe increases reducibility and consequently, decrease the strength of Lewis acidity of ZnFe₂O₄. In addition, the basic strength of a surface oxide is stronger with more unsaturated coordinative and weaker with the greater polarising power to which it is bonded. Thus, moderate or strong sites would arise from structures where surface oxide ions bridge over two or three bivalent ions. Thus, it is highly plausible that the basic sites of ZnFe₂O₄ are stronger than Fe₂O₃. Regarding microcalorimetry result; ZnFe₂O₄ with moderate acidic and basic active sites on the surface shows greater capacity toward adsorption of water and benzene, whether the heat of adsorption or coverage amount. The dissociative mode of water adsorption is preferable for the generation of hydroxyl radicals. Upon visible light excitation of ZnFe₂O₄ by the energy equal to or greater than the bandgap of the semiconductor, electrons are excited from the valence band (VB) to the conduction band (CB). Then, the photogenerated electrons (e⁻) and holes (h⁺) migrate from the bulk to the surface. The electron (e⁻) leads to a reduction of the electron acceptors such as oxygen and produce active oxygen species. Also, the holes (h⁺) oxidise donors such as hydroxyl or adsorbed H₂O and /or adsorbed benzene molecule to produce hydroxyl radical and positively charged

benzene molecules, respectively [50]. Hence, we introduce the mechanism regarding hydroxyl radicals:

the reactions of benzene with OH radicals were investigated in liquid and gaseous phase [51,52]. According to the reports, benzene can absorb hydroxyl radicals and can make cyclohexadienyl radicals that are subsequently oxidised to peroxy radicals in the presence of oxygen (Equation 7-8).

the surface hydroxyl groups that captured in the photoreaction can be regenerated, which leads to a successive catalytic cycle. It can be deduced that the OH radicals produced from the hydroxyl groups play a most significant role in the decomposition reaction. Alternatively, benzene may adsorb directly by the hole and produce benzene with a positive charge (Equation 9).

Moreover, the formation of the benzene cation radical on the solid surface, which has strong electron acceptor sites was reported [53]. It subsequently causes the addition reaction to benzene (Equation 10).

As ZnFe₂O₄ has not strongly acidic sites the formation of the intermediate for the spinel is not appropriate. Furthermore, the proper intermediates are consuming with photogenerated species to produce hydrogen;

Finally, the phenol as the main intermediate and other possible intermediates oxidised on the surface of the catalyst to generate CO₂. Furthermore, DRIFT reveals the formation of an aliphatic intermediate with the bands obtained at 1114 cm⁻¹ and 3033 cm⁻¹ as well as 3700 cm⁻¹. Therefore, the enhance photocatalytic activity of ZnFe₂O₄ is regards to the formation of hydroxyl radicals on the surface.

Conclusion

ZnFe₂O₄ with high surface area was prepared by the sol-gel method, it shows the great adsorption and enhances photocatalytic activity. Compare to Fe₂O₃, existing of Zn–O–Fe causes a change in the electronic structure of the spinel oxide, resulting in a different strength of acidic and basic sites. Consequently, as it has known: the adsorption is more facile on the surfaces where higher heats are released; thus, the enhanced photocatalytic activity of ZnFe₂O₄ is due to its greater water and / or benzene adsorption capacity. This work shows carbon monoxide may not be the intermediate of the reaction; it indicates, oxidation of benzene proceeds by the formation of phenol and persisted with oxidation of phenol to carbon dioxide. This work highlighted the major role of hydroxyl groups in the photocatalytic oxidation of benzene, which is generated by adsorption of water on the surface of the photocatalyst. Moreover, it reveals the convergence of photocatalytic property with surface area, particle size and adsorption ability of

the ZnFe_2O_4 . Accordingly, this work is expected to provide a simple synthesis route and a synthesis concept for composites with various functions.

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References

- [1] H. Tavakkoli, D. Beiknejad, T. Tabari, Fabrication of perovskite-type oxide $\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_{3-\delta}$ nanoparticles and its Dye removal performance, *Desalination Water Treat.* 52 (2014) 7377–7388. doi:10.1080/19443994.2013.825881.
- [2] C.H. Ao, S.C. Lee, Enhancement effect of TiO_2 immobilized on activated carbon filter for the photodegradation of pollutants at typical indoor air level, *Appl. Catal. B Environ.* 44 (2003) 191–205. doi:10.1016/S0926-3373(03)00054-7.
- [3] S.G. Kumar, K.S.R.K. Rao, Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO_2 , WO_3 and ZnO), *Appl. Surf. Sci.* 391 (2017) 124–148. doi:10.1016/j.apsusc.2016.07.081.
- [4] Z. Junbo, J. Weidong, X. Bin, H. Xiyang, L. Jianzhang, C. Yaoqiang, Gas-phase photocatalytic oxidation of benzene over titanium dioxide loaded on $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$, *Environ. Prog. Sustain. Energy.* 28 (2009) 519–524. doi:10.1002/ep.10342.
- [5] Y. Ma, Y. Li, M. Mao, J. Hou, M. Zeng, X. Zhao, Synergetic effect between photocatalysis on TiO_2 and solar light-driven thermocatalysis on MnO_x for benzene purification on $\text{MnO}_x/\text{TiO}_2$ nanocomposites, *J Mater Chem A.* 3 (2015) 5509–5516. doi:10.1039/C5TA00126A.
- [6] L. Luo, Y. Li, J. Hou, Y. Yang, Visible photocatalysis and photostability of Ag_3PO_4 photocatalyst, *Appl. Surf. Sci.* 319 (2014) 332–338. doi:10.1016/j.apsusc.2014.04.154.

- [7] H. Huang, D. Li, Q. Lin, W. Zhang, Y. Shao, Y. Chen, M. Sun, X. Fu, Efficient Degradation of Benzene over $\text{LaVO}_4/\text{TiO}_2$ Nanocrystalline Heterojunction Photocatalyst under Visible Light Irradiation, *Environ. Sci. Technol.* 43 (2009) 4164–4168. doi:10.1021/es900393h.
- [8] H. Zhuang, Q. Gu, J. Long, H. Lin, H. Lin, X. Wang, Visible light-driven decomposition of gaseous benzene on robust Sn^{2+} -doped anatase TiO_2 nanoparticles, *RSC Adv.* 4 (2014) 34315. doi:10.1039/C4RA05904B.
- [9] B. Gao, X. Luo, H. Fu, B. Lin, Y. Chen, Z. Gu, Visible-light-driven photocatalytic performance of nitrogen-doped $\text{Ti}_{1-x}\text{Zr}_x\text{O}_2$ solid solution, *Mater. Res. Bull.* 48 (2013) 587–594. doi:10.1016/j.materresbull.2012.11.044.
- [10] M. Li, W. Song, L. Zeng, D. Zeng, C. Xie, Synthesis of a novel NHTiO_2 photocatalyst by annealing in NH_3 and H_2 for complete decomposition of high concentration benzene under visible light irradiation, *Mater. Lett.* 136 (2014) 258–261. doi:10.1016/j.matlet.2014.08.061.
- [11] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, Nanocomposite of Ag-AgBr-TiO_2 as a photoactive and durable catalyst for degradation of volatile organic compounds in the gas phase, *Appl. Catal. B Environ.* 106 (2011) 445–452. doi:10.1016/j.apcatb.2011.06.002.
- [12] S.U.M. Khan, Efficient Photochemical Water Splitting by a Chemically Modified n-TiO_2 , *Science*. 297 (2002) 2243–2245. doi:10.1126/science.1075035.
- [13] H. Liang, X. Jiang, Z. Qi, W. Chen, Z. Wu, B. Xu, Z. Wang, J. Mi, Q. Li, Hematite concave nanocubes and their superior catalytic activity for low temperature CO oxidation, *Nanoscale*. 6 (2014) 7199. doi:10.1039/c4nr00552j.
- [14] W.-H. Hung, C.-J. Peng, C.-R. Yang, C.-J. Li, J.-J. Shyue, P.-C. Chang, C.-M. Tseng, P.-C. Juan, Exploitation of a spontaneous spatial charge separation effect in plasmonic polyhedral $\alpha\text{-Fe}_2\text{O}_3$ nanocrystal photoelectrodes for hydrogen production, *Nano Energy*. 30 (2016) 523–530. doi:10.1016/j.nanoen.2016.10.050.
- [15] X.-M. Song, X. Zhou, C. Yuan, Y. Zhang, Q. Tong, Y. Li, L. Cui, D. Liu, W. Zhang, One-dimensional $\text{Fe}_2\text{O}_3/\text{TiO}_2$ photoelectrode and investigation of its photoelectric properties in photoelectrochemical cell, *Appl. Surf. Sci.* 397 (2017) 112–118. doi:10.1016/j.apsusc.2016.11.143.
- [16] L. Xia, J. Bai, J. Li, Q. Zeng, L. Li, B. Zhou, High-performance BiVO_4 photoanodes cocatalyzed with an ultrathin $\alpha\text{-Fe}_2\text{O}_3$ layer for photoelectrochemical application, *Appl. Catal. B Environ.* 204 (2017) 127–133. doi:10.1016/j.apcatb.2016.11.015.
- [17] L. Ouyang, K.N. Maher, C.L. Yu, J. McCarty, H. Park, Catalyst-Assisted Solution–Liquid–Solid Synthesis of CdS/CdSe Nanorod Heterostructures, *J. Am. Chem. Soc.* 129 (2007) 133–138. doi:10.1021/ja066243u.
- [18] R. Agarwal, Heterointerfaces in Semiconductor Nanowires, *Small*. 4 (2008) 1872–1893. doi:10.1002/smll.200800556.
- [19] D.J. Milliron, S.M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang, A. Paul Alivisatos, Colloidal nanocrystal heterostructures with linear and branched topology, *Nature*. 430 (2004) 190–195. doi:10.1038/nature02695.
- [20] X. Xia, J. Tu, Y. Zhang, X. Wang, C. Gu, X. Zhao, H.J. Fan, High-Quality Metal Oxide Core/Shell Nanowire Arrays on Conductive Substrates for Electrochemical Energy Storage, *ACS Nano*. 6 (2012) 5531–5538. doi:10.1021/nn301454q.

- [21] Z. Zhu, X. Li, Q. Zhao, S. Liu, X. Hu, G. Chen, Facile solution synthesis and characterization of porous cubic-shaped superstructure of ZnAl_2O_4 , *Mater. Lett.* 65 (2011) 194–197. doi:10.1016/j.matlet.2010.09.085.
- [22] T.M. Sankaranarayanan, R.V. Shanthi, K. Thirunavukkarasu, A. Pandurangan, S. Sivasanker, Catalytic properties of spinel-type mixed oxides in transesterification of vegetable oils, *J. Mol. Catal. Chem.* 379 (2013) 234–242. doi:10.1016/j.molcata.2013.08.027.
- [23] Z. Zhu, Q. Zhao, X. Li, H. Li, M. Tade, S. Liu, Photocatalytic performances and activities in Ag-doped ZnAl_2O_4 nanorods studied by FTIR spectroscopy, *Catal Sci Technol.* 3 (2013) 788–796. doi:10.1039/C2CY20377D.
- [24] K. Yan, X. Wu, X. An, X. Xie, Facile synthesis and catalytic property of spinel ferrites by a template method, *J. Alloys Compd.* 552 (2013) 405–408. doi:10.1016/j.jallcom.2012.11.054.
- [25] M. Zhao, J. Huang, Y. Zhou, X. Pan, H. He, Z. Ye, X. Pan, Controlled synthesis of spinel ZnFe_2O_4 decorated ZnO heterostructures as peroxidase mimetics for enhanced colorimetric biosensing, *Chem. Commun.* 49 (2013) 7656. doi:10.1039/c3cc43154a.
- [26] W. Zhang, M. Wang, W. Zhao, B. Wang, Magnetic composite photocatalyst $\text{ZnFe}_2\text{O}_4/\text{BiVO}_4$: synthesis, characterization, and visible-light photocatalytic activity, *Dalton Trans.* 42 (2013) 15464. doi:10.1039/c3dt52068d.
- [27] Y. Hou, X. Li, Q. Zhao, G. Chen, ZnFe_2O_4 multi-porous microbricks/graphene hybrid photocatalyst: Facile synthesis, improved activity and photocatalytic mechanism, *Appl. Catal. B Environ.* 142–143 (2013) 80–88. doi:10.1016/j.apcatb.2013.04.062.
- [28] Y. Cao, D. Jia, P. Hu, R. Wang, One-step room-temperature solid-phase synthesis of ZnFe_2O_4 nanomaterials and its excellent gas-sensing property, *Ceram. Int.* 39 (2013) 2989–2994. doi:10.1016/j.ceramint.2012.09.076.
- [29] S. Boumaza, A. Boudjemaa, A. Bouguelia, R. Bouarab, M. Trari, Visible light induced hydrogen evolution on new hetero-system $\text{ZnFe}_2\text{O}_4/\text{SrTiO}_3$, *Appl. Energy.* 87 (2010) 2230–2236. doi:10.1016/j.apenergy.2009.12.016.
- [30] J. Cao, J. Xing, Y. Zhang, H. Tong, Y. Bi, T. Kako, M. Takeguchi, J. Ye, Photoelectrochemical Properties of Nanomultiple $\text{CaFe}_2\text{O}_4/\text{ZnFe}_2\text{O}_4$ *pn* Junction Photoelectrodes, *Langmuir.* 29 (2013) 3116–3124. doi:10.1021/la304377z.
- [31] Y. Hou, X.-Y. Li, Q.-D. Zhao, X. Quan, G.-H. Chen, Electrochemical Method for Synthesis of a $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ Composite Nanotube Array Modified Electrode with Enhanced Photoelectrochemical Activity, *Adv. Funct. Mater.* 20 (2010) 2165–2174. doi:10.1002/adfm.200902390.
- [32] E.S. Kim, N. Nishimura, G. Magesh, J.Y. Kim, J.-W. Jang, H. Jun, J. Kubota, K. Domen, J.S. Lee, Fabrication of $\text{CaFe}_2\text{O}_4/\text{TaON}$ Heterojunction Photoanode for Photoelectrochemical Water Oxidation, *J. Am. Chem. Soc.* 135 (2013) 5375–5383. doi:10.1021/ja308723w.
- [33] K.J. McDonald, K.-S. Choi, Synthesis and Photoelectrochemical Properties of $\text{Fe}_2\text{O}_3/\text{ZnFe}_2\text{O}_4$ Composite Photoanodes for Use in Solar Water Oxidation, *Chem. Mater.* 23 (2011) 4863–4869. doi:10.1021/cm202399g.
- [34] A. Sheikh, A. Yengantiwar, M. Deo, S. Kelkar, S. Ogale, Near-Field Plasmonic Functionalization of Light Harvesting Oxide-Oxide Heterojunctions for Efficient Solar Photoelectrochemical Water Splitting: The $\text{AuNP}/\text{ZnFe}_2\text{O}_4/\text{ZnO}$ System, *Small.* 9 (2013) 2091–2096. doi:10.1002/sml.201202140.

- [35] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, Photoassisted Degradation of Dye Pollutants. 3. Degradation of the Cationic Dye Rhodamine B in Aqueous Anionic Surfactant/TiO₂ Dispersions under Visible Light Irradiation: Evidence for the Need of Substrate Adsorption on TiO₂ Particles, *Environ. Sci. Technol.* 32 (1998) 2394–2400. doi:10.1021/es9707926.
- [36] Q. Wang, C. Chen, D. Zhao, W. Ma, J. Zhao, Change of Adsorption Modes of Dyes on Fluorinated TiO₂ and Its Effect on Photocatalytic Degradation of Dyes under Visible Irradiation, *Langmuir*. 24 (2008) 7338–7345. doi:10.1021/la800313s.
- [37] S. Wang, J. Zhang, J. Yang, X. Gao, H. Zhang, Y. Wang, Z. Zhu, Spinel ZnFe₂O₄ nanoparticle-decorated rod-like ZnO nanoheterostructures for enhanced gas sensing performances, *RSC Adv.* 5 (2015) 10048–10057. doi:10.1039/C4RA14033H.
- [38] M. Liang, W. Kang, K. Xie, Comparison of reduction behavior of Fe₂O₃, ZnO and ZnFe₂O₄ by TPR technique, *J. Nat. Gas Chem.* 18 (2009) 110–113. doi:10.1016/S1003-9953(08)60073-0.
- [39] M.A. Valenzuela, P. Bosch, J. Jiménez-Becerrill, O. Quiroz, A.I. Páez, Preparation, characterization and photocatalytic activity of ZnO, Fe₂O₃ and ZnFe₂O₄, *J. Photochem. Photobiol. Chem.* 148 (2002) 177–182. doi:10.1016/S1010-6030(02)00040-0.
- [40] O. Ola, M.M. Maroto-Valer, Synthesis, characterization and visible light photocatalytic activity of metal based TiO₂ monoliths for CO₂ reduction, *Chem. Eng. J.* 283 (2016) 1244–1253. doi:10.1016/j.cej.2015.07.090.
- [41] M. Badlani, I.E. Wachs, Methanol: A “Smart” Chemical Probe Molecule, *Catal. Lett.* 75 (2001) 137–149. doi:10.1023/A:1016715520904.
- [42] C. Chizallet, G. Costentin, H. Lauron-Pernot, J.M. Krafft, P. Bazin, J. Saussey, F. Delbecq, P. Sautet, M. Che, Role of Hydroxyl Groups in the Basic Reactivity of MgO: a Theoretical and Experimental Study, *Oil Gas Sci. Technol. - Rev. IFP.* 61 (2006) 479–488. doi:10.2516/ogst:2006023a.
- [43] J. Serranorui, G. Huber, M. Sanchezcastillo, J. Dumesic, F. Rodriguezreinoso, A. Sepulvedaescribano, Effect of Sn addition to Pt/CeO₂–Al₂O₃ and Pt/Al₂O₃ catalysts: An XPS, ¹¹⁹Sn Mössbauer and microcalorimetry study, *J. Catal.* 241 (2006) 378–388. doi:10.1016/j.jcat.2006.05.005.
- [44] D. Uner, I. Bayar, T. Tabari, The influence of relative humidity on photocatalytic oxidation of nitric oxide (NO) over TiO₂, *Appl. Surf. Sci.* 354 (2015) 260–266. doi:10.1016/j.apsusc.2015.07.045.
- [45] G. Li, L. Li, J. Boerio-Goates, B.F. Woodfield, High Purity Anatase TiO₂ Nanocrystals: Near Room-Temperature Synthesis, Grain Growth Kinetics, and Surface Hydration Chemistry, *J. Am. Chem. Soc.* 127 (2005) 8659–8666. doi:10.1021/ja050517g.
- [46] G. Li, L. Li, J. Boerio-Goates, B.F. Woodfield, Grain-growth kinetics of rutile TiO₂ nanocrystals under hydrothermal conditions, *J. Mater. Res.* 18 (2003) 2664–2669. doi:10.1017/S0884291400065936.
- [47] M. Menetrey, A. Markovits, C. Minot, Reactivity of a reduced metal oxide surface: hydrogen, water and carbon monoxide adsorption on oxygen defective rutile TiO₂(γ), *Surf. Sci.* 524 (2003) 49–62. doi:10.1016/S0039-6028(02)02464-0.
- [48] T.L. Silbaugh, J.S. Boaventura, M.A. Barteau, Surface acidity scales: Experimental measurements of Brønsted acidities on anatase TiO₂ and comparison with coinage metal surfaces, *Surf. Sci.* 650 (2016) 64–70. doi:10.1016/j.susc.2015.11.022.

- [49] H.V. Lee, Y.H. Taufiq-Yap, Optimization study of binary metal oxides catalyzed transesterification system for biodiesel production, *Process Saf. Environ. Prot.* 94 (2015) 430–440. doi:10.1016/j.psep.2014.10.001.
- [50] J. Zhong, J. Wang, M. Gong, T. Lin, Z. Liu, X. Zhang, Y. Chen, Kinetic and degradation mechanism study on Sr₂CeO₄-promoted photo-oxidation of gaseous benzene, *Sep. Purif. Technol.* 57 (2007) 57–62. doi:10.1016/j.seppur.2007.01.021.
- [51] C.H. Cho, M.H. Han, D.H. Kim, D.K. Kim, Morphology evolution of anatase TiO₂ nanocrystals under a hydrothermal condition (pH=9.5) and their ultra-high photo-catalytic activity, *Mater. Chem. Phys.* 92 (2005) 104–111. doi:10.1016/j.matchemphys.2004.12.036.
- [52] R. Volkamer, B. Klotz, I. Barnes, T. Imamura, K. Wirtz, N. Washida, K.H. Becker, U. Platt, OH-initiated oxidation of benzene, *Phys. Chem. Chem. Phys.* 4 (2002) 1598–1610. doi:10.1039/b108747a.
- [53] H. Einaga, T. Ibusuki, S. Futamura, Photocatalytic Oxidation of Benzene in Air, *J. Sol. Energy Eng.* 126 (2004) 789. doi:10.1115/1.1687402.

Figure captions

Fig. 1. Characterization of ZnFe_2O_4 , XRD pattern (a), Scanning Electron Microscopy (b), Tunneling Electron Microscopy (c), Scanning Tunneling Microscopy (d), Energy Dispersive Spectroscopy (e).

Fig. 2. Hydrogen temperature-programmed reduction, ZnFe_2O_4 (a), Fe_2O_3 (b).

Fig. 3. Adsorption microcalorimetry analysis on ZnFe_2O_4 , Fe_2O_3 ; Differential heats of water adsorption (kJ/mol) (a), Coverage (μmol water vapor adsorbed per gram of catalyst) (b), Oxygen adsorption microcalorimetry on ZnFe_2O_4 and Fe_2O_3 (c). Adsorption condition: mass (500 mg) and temperature (50 °C).

Fig. 4. Adsorption microcalorimetry analysis on ZnFe_2O_4 , Fe_2O_3 ; Differential heats of benzene adsorption (kJ/mol) (a), Coverage (μmol benzene vapor adsorbed per gram of catalyst) (b) and (μmol oxygen adsorbed per gram of catalyst). Adsorption condition: mass (500 mg) and temperature (50 °C).

Fig. 5. Time dependent photocatalytic benzene oxidation on ZnFe_2O_4 and Fe_2O_3 . Reaction condition: catalyst's mass (28 and 31 mg for ZnFe_2O_4 and Fe_2O_3 , respectively), benzene (5 μL), water (1.5 μL), volume 80 ml and room temperature.

Fig. 6. Monitoring of hydrogen and carbon dioxide evolution; ZnFe_2O_4 (a) and Fe_2O_3 (b).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Enhanced Photocatalytic Activity of Mesoporous ZnFe_2O_4 Nanoparticles toward Gaseous Benzene Under visible Light irradiation

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