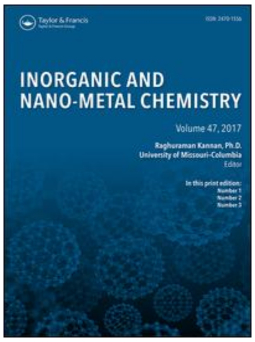

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Comparison of selective oxidation of aromatic alcohols using copper(II) chromite-titanium dioxide nanocomposite at reflux, light irradiation and microwave conditions

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Key words

Copper chromite; nanocomposite; alcohols oxidation; TiO_2, microwave

Abstract

$CuCr_2O_4/TiO_2$ nanocomposites with different TiO_2 contents were synthesized by using sol–gel method. Products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Results demonstrated a cubic normal spinel structure for copper (2+) chromite, with the particle sizes of about 25-40 nm. Activity of synthesized nano powders $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ nanocomposite were tested for oxidation of benzylic alcohols to aldehydes at reflux, light irradiation and microwave condition. The influence of some parameters on the oxidation of alcohol, such as optimum molar ratio of chromite to titanium dioxide, catalyst dosage, type and amount of oxidant and solvents (dichloromethane, acetonitrile and ethanol) were studied to determine the optimal operating conditions for alcohol oxidation in reflux, light irradiation and microwave conditions.

1. Introduction

Carbonyls are one of the important classes of the compounds and intermediates in chemical industries and laboratories. Since alcohol oxidation to the corresponding aldehyde and ketone is of importance because of the extensive usage of these compounds in the synthesis of various chemicals, vitamins, drugs, and fragrances [1-3], numerous methods have been developed using a variety of reagents for this purpose. In spite of the formation of toxic byproducts and large amount of heavy metal wastes, these oxidation reactions have been performed mainly in non-catalytic systems with stoichiometric amount of undesirable environmentally and economically oxidants. Recent demand for eco-friendly chemical processes has encouraged the further development of high yielding, efficient, chemoselective, clean and economical methods for the oxidation of alcohols [4-7]. The copper chromite ($CuCr_2O_4$) with the spinel structure is one of the most efficient materials, has wide commercial application as catalysts being used in the unit processes of organic synthesis, such as C–O hydrogenolysis [8], conversion [9, 10] hydrogenation [11], dehydrogenation [12], oxidation [13], alkylation [14], cyclization [15], with several preparation methods have been established, for instance solid state reaction, co-precipitation, ceramic and sol–gel [16-18]. Three of the most important parameters determining the catalytic activity of the product; crystallinity, surface properties, and specific surface area, are highly dependent on the preparation routes. Citric acid (CA)-assisted sol–gel method (namely Pechini approach) is a facile method for producing homogeneous nanocomposites, in which the intimate mixing of components ensures homogeneity of the final product [19]. Photocatalysis is generally thought of as the catalysis of a photochemical reaction at a solid surface, usually a semiconductor [20]. The nanosized TiO_2 has continued to attract interests in industries and academia due to unique properties that has led to its applications as photocatalysis, solar energy converters, interface in biomaterials, and sensors [21]. Yan and co-workers reported synthesis of $CuCr_2O_4/TiO_2$ heterojunction for hydrogen evolution under simulated sunlight irradiation [19]. Bajaj prepared $BiVO_4/CuCr_2O_4$ for the degradation of methylene blue dye [22]. In addition, $Au/Cu_xCr_yO_z$ mixed oxide and $CuCr_2O_4$ nanoparticle were applied for oxidation of glycerol and aniline, respectively [23-24]. In our previously published research works [25-31], some catalytic systems were synthesized and activities were described in relation to different reactions. In addition, we synthesized $CoCr_2O_4/TiO_2$ nanocomposite via sol–gel method for photodegradation of methylene blue and methyl orange [32]. Herein, we wish to report the preparation of $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ catalysts for oxidation of aromatic alcohols into corresponding aldehyde and ketone in good to high yields under reflux, light irradiation and microwave condition. Products were characterized by XRD, SEM and TEM techniques. The effect of some parameters on the oxidation of alcohol, such as optimum molar ratio of Chromite to titanium dioxide, catalyst dosage, type and amount of oxidant and solvents were studied.

2. Experimental

2.1. Material

All the chemicals used in the experiments were of analytical grade (Merck) and were utilized as received without further purification.

2.2. Preparation of catalysts

Briefly, 5mmol $Cu(NO_3)_2$ and 10mmol $Cr(NO_3)_3$ were dissolved together in 50 ml deionized water to get a mixed solution. Subsequently, the mixed solution was added into 100 ml 0.3 M citric acid (CA) solution under stirring, and produced a transparent mixed sol. The temperature was controlled at around 50 ^{o}C by using a water bath during this mixing procedure. After that the temperature was further kept at 80 °C until a transparent and viscous gel was obtained. The as-obtained gel was subsequently transferred into an oven and kept at 130 °C for 3 h. The as-prepared precursor was then calcined at 600 º C for 3 h with a heating rate of 6 ºC/min. $CuCr_2O_4/TiO_2$ heterojunction was synthesized via the same route by adding a certain amount of fully anatase phase of TiO_2 in the raw materials preparation when the transparent mixed sol had been obtained.

2.3. Characterization and reactor set up

The crystal phase of the catalysts was identified in a Philips pw1840, X-ray diffractometer using Cu Kα radiation (λ = 1.54 Å). The patterns were collected in the range of (2θ=10-70), and continuous scan mode. A Varian Model Spectra AA 220 flame atomic absorption spectrometer was used for the analysis of metals in the catalysts. Scanning electron microscopy (SEM) images were obtained on Philips XL30 equipped with an energy dispersive X-ray spectroscopy. The grain size and morphology of the catalysts were characterized with a Philips CM10 transmission electron microscope (TEM) operated at 100 kV. The light was provided by a 400 W high pressure Hg lamp without a filter which was placed vertically in the reactor. The temperature of the photo reactor set up was adjusted using a water bath in which heating or cooling water circulated through the jacket of the beaker.

2.4. Catalytic activity testing

The catalytic activity of the prepared catalysts was evaluated by oxidation of aromatic alcohols under reflux, light irradiation and microwave condition at atmospheric pressure. Typically, 0.03

g of prepared catalyst was placed in two necked flasks with (1-3) mmol of alcohols and 10 mL of solvent (acetonitrile, dichloromethane and ethanol) and t-BHP 70%, (0.3-0.5 mL) or hydrogen peroxide 30% (0.3 mL) used as oxidant. The reaction mixture was stirred continuously with a magnetic stirrer and the progress of the reaction was followed using thin layer chromatography. After the reaction was run for the desired time, the products were filtered out of the catalyst and then oxidation products were analyzed using a gas chromatograph with a GC capillary column HP 6890 and a FID detector.

3. Results and Discussion

3.1. Characterization

Fig. 1 (a) describes the XRD patterns of the as-prepared catalysts indicating good crystallinity and small particle size since diffraction peaks of these samples are strong and broad. These diffractions can be indexed to the spinel-type $CuCr_2O_4$ (JCPDS 87-0432) and showed tetragonal structure; these findings are in agreement with the literature reports [9]. The presence of the diffraction peaks of TiO_2 (the patterns of anatase structures shown with A) and $CuCr_2O_4$ in the $CuCr_2O_4/TiO_2$ nanocomposite indicates TiO_2 and $CuCr_2O_4$ crystallite phases separate from each other which showed in Fig. 1 (b). The crystallite sizes for $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ nanocomposite are calculated from Debye Scherrer formula applied to the major intense peak and are found to be about 27 and 24 nm, respectively. The amounts of total copper, chromium and titanium of catalysts were determined by atomic absorption spectroscopy of acid digested samples (Cu, 17.78%, Cr, 32.83%, Ti, 18.98%). SEM results from $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ samples show presence of strong agglomeration with spherical shapes as exhibited in Fig.2 (a) and (b). It can be seen that, $CuCr_2O_4$/ TiO_2 ($nCuCr_2O_4:nTiO_2 = 0.7$) nanocomposite have smaller size than pure $CuCr_2O_4$. Fig.3 shows TEM images of $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ nanocomposite ($nCuCr_2O_4:nTiO_2 = 0.7$) indicating morphology and size of these catalysts calcined at 600 °C. It can be concluded that the particles have minor agglomeration with a relatively narrow particle size distribution. The average particle size of catalysts is about 30 nm. Also, it can be seen that the $CuCr_2O_4$ and TiO_2 crystallite particles in the nanocomposite are homogeneously dispersed.

3.2. Activity of the catalytic systems

We studied the oxidation of different types of primary and secondary benzylic alcohols to aldehydes and ketones with $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ nanocomposite as the catalyst and t-BHP as the oxidant. As expect, both of catalysts are able to oxidize alcohol in good conversion and yield. The catalytic oxidation reaction was carried out at reflux, light irradiation and microwave systems. Results are shown in Table one to three, respectively. Generally, it reveals that the selective oxidation of benzylic alcohols to aldehyde with $CuCr_2O_4/TiO_2$ nanocomposite is efficiently higher than $CuCr_2O_4$ in the presence of TBHP. Indeed, 90 and 95 percent conversion of oxidation reaction was achieved for 4-chlorobenzyl alcohol (Tables 1, Entry 2) oxidized by $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ respectively. Halogens are deactivating group which share their free electron pairs in benzylic resonance that dominates on their electron drawing affect and oxidize alcohol in high yield (Tables 1 Entries 2, 3). Among them, accession of halogen groups to hydroxyl is a negative effect (Tables 1 Entry 3). Benzylic alcohol with electron donor groups such as –R, –OR (Tables 1 Entries 4-6) successfully converted to their corresponding aldehyde in good yields. Secondary alcohol has oxidized to ketones in good yield (Tables 1 Entries 7, 8). Benzhydrol with two benzylic rings which participate in hydroxyl electron resonance, oxidize to ketone in short time (Entry 7). The electron drawing groups like -

NO_2, -COR decrease conversion of alcohol to aldehyde and when these groups get closer to hydroxyl, decrease on conversion of alcohol is more (Tables 1 entry 9-11). The distance between hydroxyl group and benzylic ring (Entry 12) also can effect on conversion value. Tables 2 shows oxidation of alcohols catalyzed by $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ (0.7) under light irradiation set up. The results show that the catalytic activity of both catalysts at light irradiation condition, are much lower than that of reflux system reaction. However, traditional heating is not used in light irradiation system. All parameters such as halogen effect, electron donor groups and electron drawing groups are able to effect on conversion and subsequently on yield of oxidation reaction like as reflux condition (Tables 2). Microwave method has shown the best results in shorter time. As shown in Tables 3 compared to reflux procedure, in microwave reaction, benzylic alcohol and its derivatives was successfully converted to their corresponding aldehydes and ketones at very short time. Results showed that good conversions of starting material (90 %) were obtained after 1-3 minute of reaction. The use of microwave reduced times of reaction as well as the conversion of starting material in the oxidation under relatively similar reaction conditions. This demonstrates that the microwave irradiated synthesis is superior to that of conventional methods in terms of reaction time and energy consumption.

3.2.1 Effect of $nCuCr_2O_4$:$nTiO_2$

Access to the best molar ratio of nanocomposite was achieved by using 0.03 g of all catalysts for conversion. Table 4 indicates that the highest conversion was found on the nanocomposite with a $CuCr_2O_4/TiO_2$ molar ratio of 0.7. According to this result, we decided to use ($nCuCr_2O_4:nTiO_2 = 0.7$) molar ratio for the rest of alcohols in oxidation process.

3.2.2. Effect of catalyst dosage

Whereas catalyst dosage in catalytic processes is an important factor that can strongly influence in this process, different concentration of $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ (0.7) nanopowders have been tested and showed that the oxidation of benzyl alcohol efficiency increased with an increase in nanopowders concentration up to 0.03 g and then no great change have seen in conversion as showed in Table 5. A small but significant increase in the rate of the catalytic oxidation observed with an increase in the catalyst weight from 0.01 to 0.04 g. On the other hand, the conversion increased from 60% to 82% by increasing the catalyst amount from 0.01 to 0.04 g. In the higher amount of the catalyst, the better the chances for the reactants (benzyl alcohol and TBHP) to react before diffusing out of the catalysts surface. Consequently, the extent of oxidation of benzyl alcohol increases on increasing the catalyst amount and suitable efficiency (80%, after 15 min) of benzyl alcohol was obtained at catalyst dosage of 0.03 g.

3.2.3 Effect of oxidant

The utilizing of oxidants plays a crucial role in the oxidation process. Furthermore, the catalytic efficiency of $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ (0.7) was examined for the alcohol oxidations using t-BHP and H_2O_2 as oxidant. As showed in Table 6, the result of selective oxidation of benzylic alcohols to aldehyde with $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ (0.7) is more efficient in the presence of t-BHP. Maximum conversion and good reaction time was obtained by t-BHP while H_2O_2 is not found to be effective for the oxidation of alcohols. This observation can be explained in terms of decomposition of H_2O_2 into molecular oxygen, and shows its effect on the times of their action which were quite high. Also, in the absence of oxidant, no alcohol oxidation was observed. In addition, concentration of oxidant has been tested and the results revealed that by increasing concentration of t-BHP from 0.2 to 0.5 ml no great changes in conversion has been occurred (Table 7).

3.2.4 Effect of the nature of solvent

To investigate the solvents effect in the catalytic activity of the $CuCr_2O_4/TiO_2$ (0.7), oxidation of the benzhydrol and benzyl alcohol was studied in various other solvents e.g. acetonitrile, ethanol and dichloromethane (Table 8). It can be seen that, acetonitrile is suitable solvent for the oxidation reaction. As shown in Table 8, the best results were obtained when acetonitrile was used as the solvent. However, in the presence of acetonitrile 90% and 80% conversion were achieved for benzhydrol and benzyl alcohol. Ethanol and dichloromethane were also used as the solvent where 80% and 45% of conversion was observed for benzhydrol in 15 min. It can be concluded that the polarity index of acetonitrile (acetonitrile: 5.8, ethanol: 5.2 and dichloromethane: 3.1) is higher than other solvents and strong polarity of solvent may be useful for the oxidation of alcohols.

4. Conclusions

In this work, $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ nanocomposites with normal spinel structure were synthesized by the sol-gel method and their structure and catalytic properties in alcohol oxidation was studied. The result showed that alcohol was not oxidized in the absence of catalysts or oxidant and also the catalytic activity of catalysis at reflux condition is much higher than that of under light irradiation reaction. Pure $CuCr_2O_4$ or TiO_2 displayed poor catalytic activity for alcohol oxidation, whereas, after coupling of $CuCr_2O_4/TiO_2$ heterojunction catalytic activity were improved, because $CuCr_2O_4$ is a semiconductor with a small band gap and TiO_2 has a large band gap, therefore coupling of TiO_2 with $CuCr_2O_4$ improve electron-hole separation.

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Table 1. Oxidation of alcohols catalyzed by $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ under reflux condition[a].

	$CuCr_2O_4$					$CuCr_2O_4/TiO_2$		
Entry	Yield %[b]	Conversion %	Time (min)	Substrate	Product	Time (min)	Conversion %	Yield %[b]
1	70	80	45	$C_6H_5CH_2OH$	C_6H_5CHO	15	80	75
2	87	90	30	$4\text{-}ClC_6H_5CH_2OH$	$4\text{-}ClC_6H_5CHO$	15	95	92
3	70	85	45	$2\text{-}BrC_6H_5CH_2OH$	$2\text{-}BrC_6H_5CHO$	30	85	80
4	80	90	90	$4\text{-}(CH_3)_2CHC_6H_5CH_2OH$	$4\text{-}(CH_3)_2CHC_6H_5CHO$	60	90	80
5	80	90	90	$2\text{-}CH_3C_6H_5CH_2OH$	$2\text{-}CH_3C_6H_5CHO$	60	95	92
6	70	85	60	$CH_3(O)C_6H_5CH_2OH$	$CH_3(O)C_6H_5CHO$	30	85	80
7	85	90	45	$C_6H_5CHOHC_6H_5$	$C_6H_5COC_6H_5$	15	90	84
8	85	90	60	$C_6H_5CHOHCH_2CH_3$	$C_6H_5COCH_2CH_3$	30	90	84
9	34	40	90	$2\text{-}NO_2C_6H_5CH_2OH$	$2\text{-}NO_2C_6H_5CHO$	60	40	35
10	40	50	90	$4\text{-}NO_2C_6H_5CH_2OH$	$4\text{-}NO_2C_6H_5CHO$	60	50	40
11	45	50	30	$C_6H_5(O)C_6H_5CH_2OH$	$C_6H_5(O)C_6H_5CHO$	15	50	45
12	43	50	60	$C_6H_5(CH_2)_3OH$	$C_6H_5(CH_2)_2CHO$	30	50	40

[a] Reactions were performed using 0.03 g of catalyst, 0.2 mL TBHP and 3 mL acetonitrile.

[b] GC yield.

Table 2. Oxidation of alcohols catalyzed by $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ under UV irradiation system [a].

		$CuCr_2O_4$					$CuCr_2O_4/TiO_2$	
Entry	Yield %	Conversion %	Time (min)	Substrate	Product	Time (min)	Conversion %	Yield %
1	75	80	90	$C_6H_5CH_2OH$	C_6H_5CHO	60	80	75
2	92	95	90	$4\text{-}ClC_6H_5CH_2OH$	$4\text{-}ClC_6H_5CHO$	60	95	90
3	75	85	90	$2\text{-}BrC_6H_5CH_2OH$	$2\text{-}BrC_6H_5CHO$	90	90	85
4	80	85	90	$4\text{-}(CH_3)_2CHC_6H_5CH_2OH$	$4\text{-}(CH_3)_2CHC_6H_5CHO$	90	95	90
5	70	80	90	$2\text{-}CH_3C_6H_5CH_2OH$	$2\text{-}CH_3C_6H_5CHO$	90	85	80
6	70	80	90	$CH_3(O)C_6H_5CH_2OH$	$CH_3(O)C_6H_5CHO$	60	80	75
7	80	85	90	$C_6H_5CHOHC_6H_5$	$C_6H_5COC_6H_5$	60	90	82
8	70	80	120	$C_6H_5CHOHCH_2CH_3$	$C_6H_5COCH_2CH_3$	90	90	80
9	28	30	120	$2\text{-}NO_2C_6H_5CH_2OH$	$2\text{-}NO_2C_6H_5CHO$	90	30	28
10	30	40	120	$4\text{-}NO_2C_6H_5CH_2OH$	$4\text{-}NO_2C_6H_5CHO$	60	40	36
11	36	40	120	$C_6H_5(O)C_6H_5CH_2OH$	$C_6H_5(O)C_6H_5CHO$	90	40	30
12	35	40	120	$C_6H_5(CH_2)_3OH$	$C_6H_5(CH_2)_2CHO$	90	40	30

[a] Reactions were performed using 0.03 g of catalyst, 0.2 mL TBHP and 3 mL acetonitrile.

[b] GC yield.

Table 3. Oxidation of alcohols catalyzed by $CuCr_2O_4$ and $CuCr_2O_4/TiO_2$ under microwave irradiation[a].

	$CuCr_2O_4$					$CuCr_2O_4/TiO_2$		
Entry	Yield %[b]	Conversion %	Time (min)	Substrate	Product	Time (min)	Conversion %	Yield %[b]
1	80	90	4	$C_6H_5CH_2OH$	C_6H_5CHO	3.5	90	80
2	92	90	2	$4\text{-}ClC_6H_5CH_2OH$	$4\text{-}ClC_6H_5CHO$	1	90	87
3	82	85	3	$2\text{-}BrC_6H_5CH_2OH$	$2\text{-}BrC_6H_5CHO$	2.5	90	80
4	78	80	2	$4\text{-}(CH_3)_2CHC_6H_5CH_2OH$	$4\text{-}(CH_3)_2CHC_6H_5CHO$	1	90	86
5	80	90	3	$2\text{-}CH_3C_6H_5CH_2OH$	$2\text{-}CH_3C_6H_5CHO$	2.5	90	80
6	64	70	2.5	$CH_3(O)C_6H_5CH_2OH$	$CH_3(O)C_6H_5CHO$	1.5	70	67
7	90	95	4	$C_6H_5CHOHC_6H_5$	$C_6H_5COC_6H_5$	3.5	90	85
8	85	90	2	$C_6H_5CHOHCH_2CH_3$	$C_6H_5COCH_2CH_3$	1.5	90	85
9	30	40	3	$2\text{-}NO_2C_6H_5CH_2OH$	$2\text{-}NO_2C_6H_5CHO$	2	40	35
10	35	40	2	$4\text{-}NO_2C_6H_5CH_2OH$	$4\text{-}NO_2C_6H_5CHO$	1.5	50	40
11	40	50	2	$C_6H_5(O)C_6H_5CH_2OH$	$C_6H_5(O)C_6H_5CHO$	1.5	50	40
12	30	40	2.5	$C_6H_5(CH_2)_3OH$	$C_6H_5(CH_2)_2CHO$	2	50	43

[a] Reactions were performed using 0.03 g of catalyst, 0.2 mL TBHP and 3 mL acetonitrile.

[b] GC yield.

Table 4. Effect of molar ratio ($nCuCr_2O_4/nTiO_2$)

Catalyst molar ratio	0.3	0.5	0.7	1
Conversion(%)	70	75	80	83

Reactions were performed using 0.03 g of catalyst, 0.2 mL TBHP and 3 mL acetonitrile compared in 15 min.

Table 5. Effect of different concentration of $CuCr_2O_4/TiO_2$(7:10) in acetonitrile

Catalyst dosage(mg)	10	20	30	40
Conversion(%)	60	75	80	82

Reactions were performed using 0.01, 0.02, 0.03,0.04 g catalysts, 0.2 mL TBHP and 3 mL acetonitrile compared in 15 min.

Table 6. Nature of the oxidant over $CuCr_2O_4/TiO_2$(7:10) in acetonitrile under reflux condition

Oxidant	t-BHP		H_2O_2		No oxidant	
Alcohol	Time	Conversion(%)	Time	Conversion(%)	Time	Conversion(%)
Benzyl alcohol	15	80	30	30	-	NR[a]
Benzhydrol	15	90	30	40	-	NR

[a] No Reaction

Reactions were performed using 0.03 g of catalyst, 0.2 mL oxidant, and 3 mL acetonitrile.

Table 7. Effect of TBHP concentration on oxidation of benzyl alcohol by $CuCr_2O_4/TiO_2$ (7:10)

TBHP concentration(ml)	0.1	0.2	0.3	0.4	0.5
Conversion(%)	70	80	80	80	85

Reactions were performed using 0.03 g of catalyst, 0.1, 0.2, 0.3, 0.4 and 0.5 mL TBHP and 3 mL acetonitrile compared in 15 min.

Table 8. Effect of solvent in the oxidation reaction over $CuCr_2O_4/TiO_2$ (7:10) under reflux condition

solvent	acetonitrile	dichloromethane	ethanol
Alcohol	Conversion(%)[a]	Conversion(%)	Conversion(%)
Benzyl alcohol	80	40	70
Benzhydrol	90	45	80

[a] Time (min) needed to 100% conversion

Reactions were performed using 0.03 g of catalyst, 0.2 mL TBHP and 3 mL solvent.

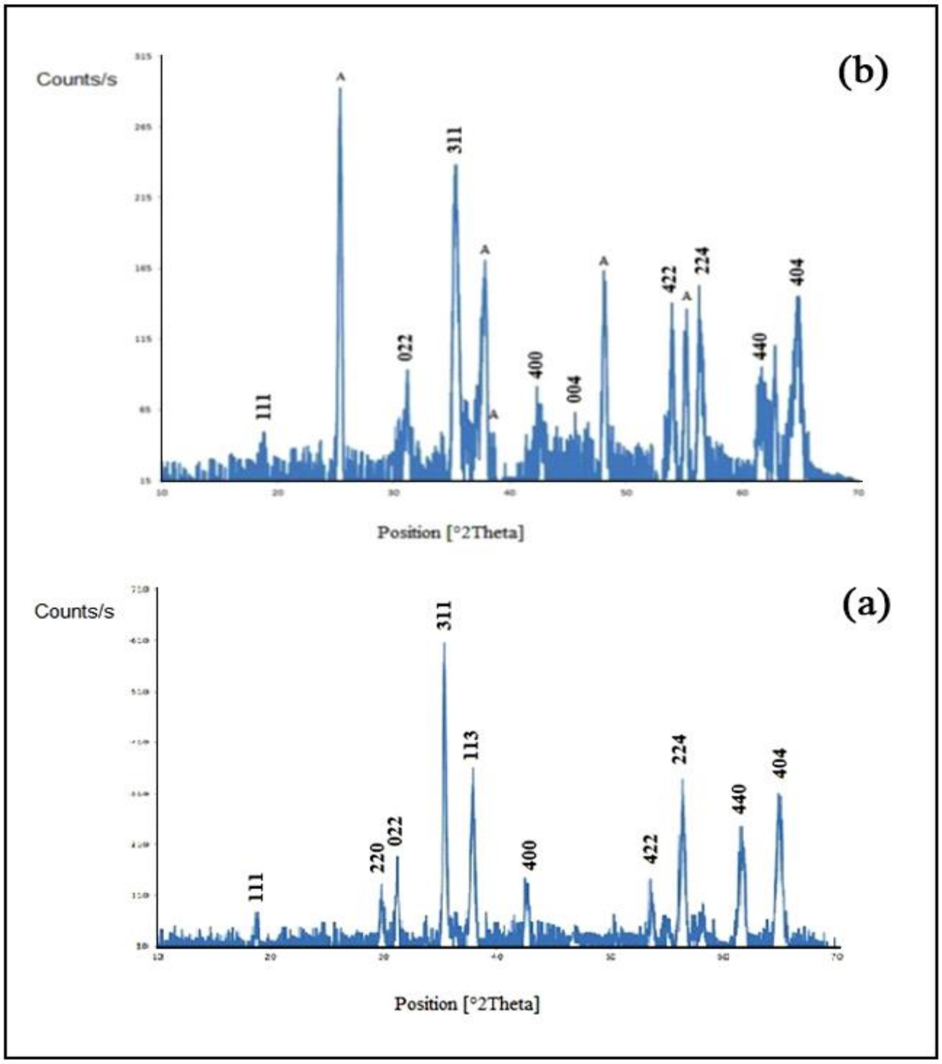

Figure 1 XRD patterns of (a) $CuCr_2O_4$ (b) $CuCr_2O_4/TiO_2$ composite ($nCuCr_2O_4:nTiO_2 = 0.7$)

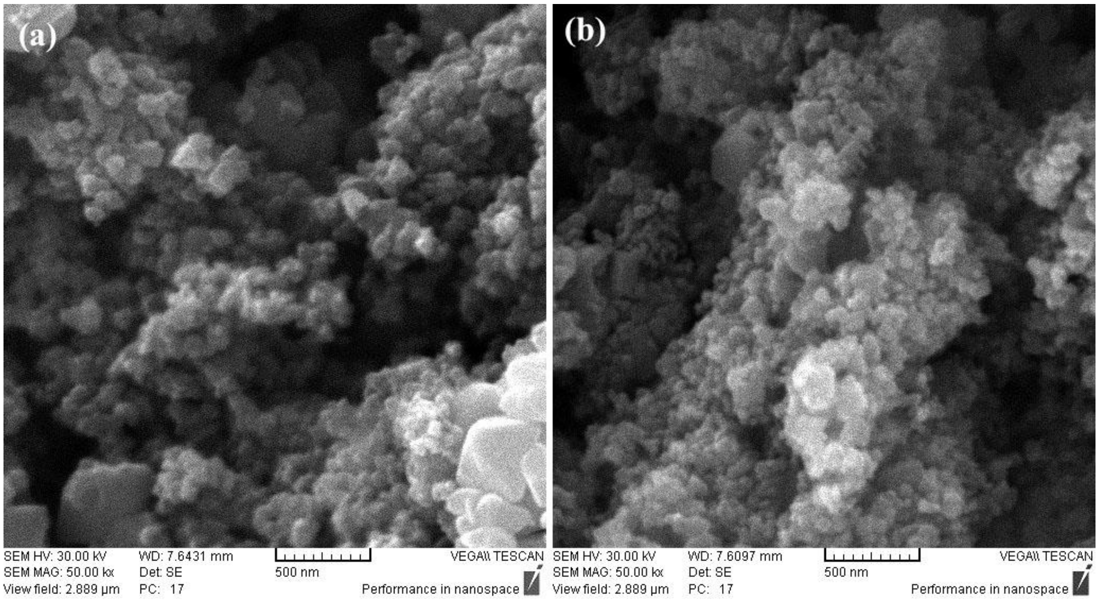

Figure 2 SEM images of (a) pure $CuCr_2O_4$ (b) $CuCr_2O_4/TiO_2$ composite ($nCuCr_2O_4:nTiO_2 = 0.7$)

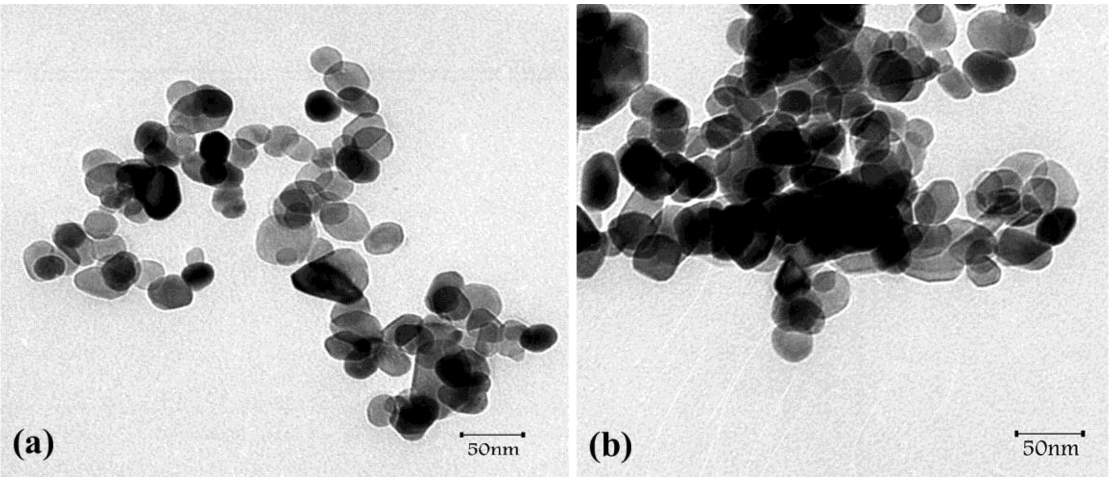

Figure 3 TEM images of (a) pure $CuCr_2O_4$ (b) $CuCr_2O_4/TiO_2$ composite ($nCuCr_2O_4:nTiO_2 = 0.7$)