

REDUCTION OF Cr⁶⁺ BY Fe₃O₄ AND Cr- ROLE IN GLUCOSE CONVERSION TO HMF IN AQUEOUS MEDIUM

Nichapha Senamart¹, Jidapa Watcharakitti¹, Karnjana Atthawilai¹, Kwunkaw Phedlue¹, Pitak Nasomjai², and Sirinuch Loiha^{1*}

Received: June 25, 2018; Revised: December 08, 2018; Accepted: December 13, 2018

Abstract

Magnetite (Fe₃O₄) was synthesized via the hydrothermal method and then used as an adsorbent for Cr⁶⁺ removal from water. Cr-adsorbed Fe₃O₄ (Cr/Fe₃O₄) with various Cr concentrations were then applied as catalysts for glucose dehydration in aqueous solution. The role of Cr-adsorbed species for the catalytic performance was investigated. The absorption ability and reducibility of the Fe₃O₄ for Cr⁶⁺ were investigated. The maximum adsorption ability of 3.3 mg/gFe₃O₄ was determined at 10 ppm Cr⁶⁺ concentration using UV-Visible spectroscopy. The Fe and Cr species on Cr/Fe₃O₄ investigated by X-ray absorption spectroscopy were in trivalent forms of FeOOH and CrOOH which clearly resulted in a reduction of Cr⁶⁺ on the Fe₃O₄ surface. The existent structures corresponded to the Brønsted acidic sites. This result clearly confirmed the reduction ability of Fe₃O₄ to transform Cr⁶⁺ to Cr³⁺. The catalytic performances of the Fe₃O₄ and Cr/Fe₃O₄ acidic catalysts were investigated for glucose dehydration in an aqueous medium under hydrothermal conditions. The presence of the FeOOH and CrOOH species on the Cr/Fe₃O₄ catalyst clearly improved their catalytic performance for glucose dehydration to a 5-hydroxymethylfurfural (HMF) product. About 50% of the HMF yield was reached by 20 ppm Cr/Fe₃O₄. The maximum turnover number was observed by 1 ppm of Cr/Fe₃O₄ catalyst. The improvement of the HMF yield was strongly dependent on the Cr-adsorbed species and dispersion on the Fe₃O₄ surface.

Keywords: Glucose dehydration, chromium, 5-hydroxymethylfurfural, Fe₃O₄, CrOOH

¹ Materials Chemistry Research Center, Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, E-mail: sirilo@kku.ac.th

² Department of Chemistry, School of Science, University of Payao, Payao 56000, Thailand

* Corresponding author

Introduction

The contaminant heavy metals such as Pb (Kumari *et al.*, 2014), As (Iconaru *et al.*, 2016), Cr (Ni *et al.*, 2017), Cd (Guyo *et al.*, 2015), and Ni and Cu (Karami, 2013) in water is still a challenging problem. Chromium is released into the ecosystem from leather tanning, metal processing, electroplating, pigment synthesis, dying, and electrical and electronic equipment. Hexavalent chromium (Cr^{6+}) is a great concern due to its extreme toxicity and carcinogenicity for living organisms. It is a toxic contaminant classified as a group 'A' human carcinogen by the United States Environmental Protection Agency (1998). Normally, the toxic Cr^{6+} may exist in the negative charge forms of hydrochromate (HCrO_4^-), chromate (CrO_4^{2-}), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in a solution (Lazo, 2009).

Recently, magnetite-based adsorbents (Fe_3O_4) have attracted much attention from researchers due to their excellent magnetic properties which affect separation, chemical stability, and non-toxicity (Ianoş *et al.*, 2018; Saksornchai *et al.*, 2018). The Fe_3O_4 has been widely used in drug delivery (Arora *et al.*, 2017), catalysts (Hammiche-Bellal *et al.*, 2018), wastewater treatment (Long *et al.*, 2017), biosensors (Jaime *et al.*, 2017; Samphao *et al.*, 2018), redox materials (Kim *et al.*, 2017), and adsorbents (Alijani and Shariatnia, 2018; Mohammed and Samaka, 2018). Hug *et al.* (1997) suggested that the redox couples of $\text{Fe}^{2+}/\text{Fe}^{3+}$ can catalyze the reduction of Cr^{6+} to the less toxic Cr^{3+} in the form of $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$. In addition, the presence of a trivalent iron (Fe^{3+}) ion in Fe_3O_4 was a good adsorbent for the negative Cr compounds. Hence, Fe_3O_4 is believed to be a superior adsorbent and reducing agent for Cr^{6+} molecules.

As a catalyst application, the Fe_3O_4 generally contains a Brønsted acid site which is suitable for involvement in the dehydration process (Elsayed *et al.*, 2018). The illustrative acidic catalysts of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ (Elsayed *et al.*, 2018) and graphene oxide- Fe_3O_4 (Zhang *et al.*, 2015) have been used for dehydration of glucose. The use of the Cr-adsorbed Fe_3O_4 in glucose dehydration without leaching of the contaminant Cr^{6+} species has attracted much

attention. Wei and Wu (2018) proposed that the Cr^{3+} species could be reacted as a Lewis acid site for glucose dehydration and improved catalytic activity. Hence, an integration of the 2 active species of Fe_3O_4 and Cr^{3+} plausibly help to improve the catalytic performance of glucose dehydration.

The catalytic performance of glucose dehydration proceeds via both the Brønsted and Lewis acid sites contained in the acidic type catalysts (Choudhary *et al.*, 2013; Moreno-Recio *et al.*, 2016). The valuable compound of 5-hydroxymethylfurfural (HMF) has been determined as the main product in the presence of the organic solvent addition. In the presence of high water content, the HMF could be further rehydrated to levulinic acid (LA) (Pedersen *et al.*, 2015; Marianou *et al.*, 2018). Thus, the improvement of the HMF yield which is a critical starting material for the synthesis of other platform chemicals, a precursor for polymers, fuels, or solvents (Corma *et al.*, 2007; Cueto *et al.*, 2017; Obregón *et al.*, 2017) in aqueous media reaction, is the research challenge.

The pristine Fe_3O_4 was first synthesized via the hydrothermal method and sequentially adsorbed Cr^{6+} ions in water to form Cr/ Fe_3O_4 catalysts. The Cr-adsorption ability was determined using UV-Visible spectroscopy (UV-Vis) and the Cr-adsorbed species was investigated using the X-ray adsorption (XAS) technique. Catalytic performance of the pristine Fe_3O_4 and Cr/ Fe_3O_4 for glucose dehydration was conducted under hydrothermal conditions in a water medium. The final products were analyzed using the high performance liquid chromatography (HPLC) technique.

Materials and Methods

Materials

The Fe^{3+} precursor used was chloride (FeCl_3) from Sigma-Aldrich Corporation (St. Louis, MO USA). Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and sodium acetate (NaOAc) were purchased from LOBA Chemie Pvt. Ltd.

(Mumbai, India). Hydrochloric acid 38% (HCl) and ethylene glycol (EG) were purchased from QR&C (Auckland, New Zealand). 1,5-diphenylcabazide was purchased from Merck & Co., (Kenilworth, NJ, USA). Ethyl alcohol (EtOH) and D-glucose ($C_6H_{12}O_6$) was purchased from CARLO ERBA Reagents S.A.S. (Val-de-Reuil, France).

Preparation of Fe_3O_4

Magnetite (Fe_3O_4) was synthesized using the hydrothermal method, as reported earlier (Pal *et al.*, 2014). Firstly, 1.94 g of $FeCl_3$ was dissolved in 10 mL of ethylene glycol (EG). The solution was added to 40 mL of EG in a 2-necked round-bottom flask under N_2 flow. After 30 min stirring, 10 mL of 1.35 M NaOAc was added into the EG solution and sequentially stirred for 3 h. The mixture was transferred to a Teflon-lined autoclave and heated to 190°C for 24 h. The autoclave was kept at room temperature for cooling down and the Fe_3O_4 black powder was easily separated from the solution using a magnetic bar. The powder was then washed with deionized water and ethanol several times and dried at 50°C overnight.

Cr^{6+} adsorption on Fe_3O_4

The Cr^{6+} -adsorbed on the Fe_3O_4 catalysts (Cr/Fe_3O_4) was carried out via the adsorption process by varying the initial concentration of the Cr^{6+} ions at 1, 5, 10, 15, and 20 ppm. A 100 ppm of $K_2Cr_2O_7$ in 100 mL deionized water was prepared as a stock solution. 0.1 g of Fe_3O_4 powder was added to 50 mL of Cr^{6+} solution at pH 3 with magnetic stirring at 300 rpm for 30 min. The Cr/Fe_3O_4 samples were then separated by centrifugation. The adsorption efficiency was determined by measuring of the Cr^{6+} residue in solution via the colorimetric method, using a UV-Vis spectrophotometer at $\lambda = 540$ nm.

Characterization

The crystal structures of the pristine Fe_3O_4 and Cr/Fe_3O_4 samples were investigated with a powder X-ray diffractometer (XRD), (Empyrean, Malvern Panalytical Ltd., Malvern, UK), using Cu $K\alpha$ (1.5406 Å) radiation with a step size of 0.02° in the 2 θ range of 5-80°. The

crystalline sizes of the catalysts were calculated using Scherrer's equation:

$$\tau = K\lambda/\beta\cos\theta$$

where K is a dimensionless shape factor about 0.9, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle (Scherrer, 1918). The characteristic functional groups on Fe_3O_4 and Cr/Fe_3O_4 were analyzed using the Fourier-transform infrared spectrometer (FT-IR), TENSOR27 model (Bruker Corp., Billerica, MA, USA). The oxidation states and speciation of the metals on the samples were determined by X-ray adsorption spectroscopy (XAS) provided at beamline BL 5.2 Synchrotron Light Research Institute (SLRI). The intermediate photon energy ranges of 5.7-6.7 KeV and 7.0-8.0 KeV for the Cr *K*-edge and Fe *K*-edge, respectively, were conducted. The beam characteristics were the storage ring energy of 1.2GeV, the electron current which varied in the range of 140-70 mA, and the use of a Ge(220) double-crystal monochromator. For the XAS data collection, 3 scans for each sample were conducted for the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra. Athena and Artemis codes as interfaces for IFEFFIT were employed for X-ray absorption fine structure (XAFS) spectra interpretation. The EXAFS fitting was performed with empirical phase shift and amplitude functions derived from the Fe_2O_3 and over the *k* range: 2-8. The glucose conversion and the dehydration products were determined using high-performance liquid chromatography (HPLC) in a LC-20AD model (Shimadzu Corp., Kyoto, Japan).

Catalytic Testing

The glucose dehydration was carried out under hydrothermal conditions in a 25 mL Teflon-lined autoclave. Glucose, 0.04 g, was dissolved in 10 mL of deionized water and then 0.04 g of catalyst was the suspension. The solution was aged at 190°C for 4 h before quenching in an ice bath. The catalyst was separated from the mixture by an external magnet. The mixture was then analyzed by

HPLC coupled with a refractive index detector by primarily being filtrated through a nylon membrane filter with a pore size $0.02\ \mu\text{m}$, $\varnothing = 13\ \text{mm}$ before injection. The catalytic conversion and product yield were investigated.

Results and Discussion

Structural Analysis of Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$

XRD:

The XRD patterns of the Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$ are shown in Figure 1. The synthesized Fe_3O_4 indicates a characteristic structure regarding JCPDS No. 19-0629 as Rajput *et al.* (2016) and Alibeigi and Vaezi (2008) report Main peaks at $2\theta = 30.16^\circ$, 35.40° , 43.23° , 53.51° , 57.09° , and 62.60° found in the Fe_3O_4 and $2\theta = 30.27^\circ$, 35.54° , 43.36° , 54.01° , 57.22° , and 62.86° in the $\text{Cr}/\text{Fe}_3\text{O}_4$ corresponded to the characteristic cubic structure of magnetite. However, the main peak positions of the $\text{Cr}/\text{Fe}_3\text{O}_4$ were systematically shifted to higher values indicating a decrease of the d-spacing. In addition, the peak intensity of the $\text{Cr}/\text{Fe}_3\text{O}_4$ was lower than that of the pristine Fe_3O_4 . The lattice constants (a) of the Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$ were 0.8396 and $0.8359\ \text{nm}$, respectively. The contraction of the lattice parameter in the $\text{Cr}/\text{Fe}_3\text{O}_4$ cubic structure demonstrated ion-exchange of Fe^{3+} (ca. $63\ \text{pm}$) sites by a smaller ion of Cr^{3+} (ca. $62\ \text{pm}$) on the Fe_3O_4 surface.

The crystalline sizes of the materials determined by Scherrer's equation were about $5.0\ \text{nm}$ and $5.6\ \text{nm}$ for Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$,

respectively. An increase in a crystalline size of the $\text{Cr}/\text{Fe}_3\text{O}_4$ indicated the covering of the Cr-species on the Fe_3O_4 surface.

FT-IR:

The FT-IR spectra of the Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$ are shown in Figure 2. The Fe_3O_4 spectrum showed a characteristic sharp band corresponding to Fe-O vibration of the iron oxide mainly in the goethite ($\alpha\text{-FeOOH}$) structure at $575\ \text{cm}^{-1}$ (Feng *et al.*, 2012; Vahur *et al.*, 2010). The peak at $1645\ \text{cm}^{-1}$ represented H-O-H bending of adsorbed water on the Fe_3O_4 surface (Kumari *et al.*, 2014). The peak at $3405\ \text{cm}^{-1}$ corresponded to terminal -OH vibration (Rajput *et al.*, 2016). For $\text{Cr}/\text{Fe}_3\text{O}_4$, the characteristic bands corresponding to Cr-O bonds in chromium (III) oxide were observed at 456 , 575 , and $648\ \text{cm}^{-1}$ (Vahur *et al.*, 2010; Palimi *et al.*, 2014; Gangadharan and Nambi, 2017). The band at $575\ \text{cm}^{-1}$ was also assigned as an overlapping of the Fe-O and Cr-O bands (Borgohain *et al.*, 2010). These characteristic bands clearly indicated the covering of a chromium oxide structure on the Fe_3O_4 surface which was coherent with the XRD results. The sharp bands observed at 2336 and $1387\ \text{cm}^{-1}$ represented the atmospheric CO_2 absorption (McKellar *et al.*, 2016).

Cr^{6+} Uptake on Fe_3O_4

The adsorption ability of Cr^{6+} on the Fe_3O_4 was determined by varying the initial concentration of Cr^{6+} in the range of $1\text{--}20\ \text{ppm}$, and the results are shown in Figure 3. The adsorption ability of the Fe_3O_4 increased with

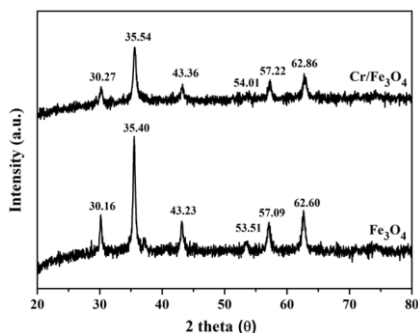


Figure 1. XRD patterns of Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$

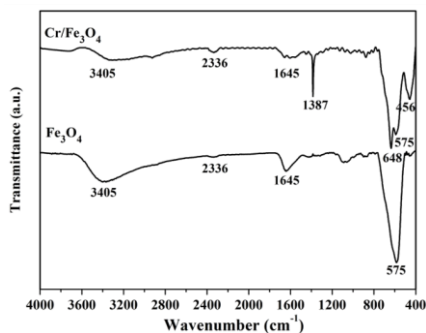


Figure 2. FT-IR spectra of Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$

increasing the Cr^{6+} concentration and reached maximum adsorption ability at about 3.33 mg/g Fe_3O_4 . An increase of the initial concentration of the adsorbate contributed to an increase of the molecular repulsion resulting in low surface binding of the adsorbent and reaching the surface saturation (Zolfaghari *et al.*, 2011; Rahimi *et al.*, 2015).

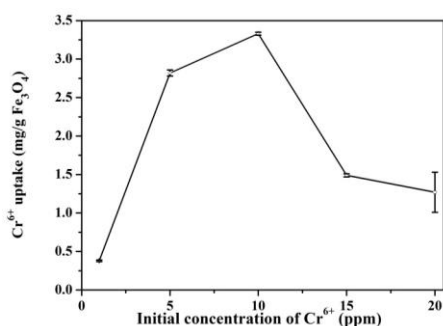


Figure 3. The adsorption ability of Fe_3O_4 to Cr(VI) ions with varying initial concentrations (the adsorption condition: pH = 3, Fe_3O_4 = 0.1 g, time = 30 min)

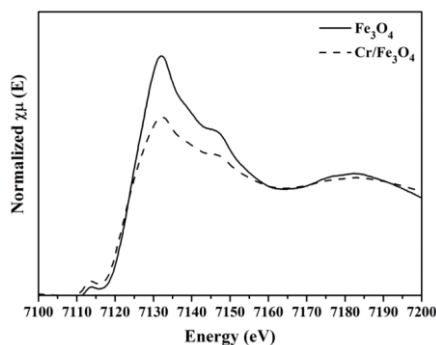


Figure 4. XANES spectra at Fe K-edge in Fe_3O_4 and $\text{Cr/Fe}_3\text{O}_4$

Cr-adsorbed Species on Fe_3O_4 by XAS Analysis

XANES Analysis:

The Fe K-edge energy of the Fe_3O_4 and $\text{Cr/Fe}_3\text{O}_4$ samples were observed at about 7124 eV, as shown in Figure 4 and Table 1, which corresponded to the electron transition $1s \rightarrow 4p$ of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixture. Thus the Fe species on the Fe_3O_4 was not significantly changed with Cr adsorption. However, the normalized XANES intensity of the $\text{Cr/Fe}_3\text{O}_4$ was lower than that of the pristine Fe_3O_4 revealing an increase in the coordination number of the Fe-O bond by an increase of the occupancy in the d-orbital of Fe by oxygen donor atoms. The suggestion on the iron structures will be further described in the EXAFS analysis section.

The XANES spectra in the Cr K-edge of the Cr solution (l) and $\text{Cr/Fe}_3\text{O}_4$ solid (s) compared with the Cr^{3+} and Cr^{6+} standards of CrCl_3 and $\text{K}_2\text{Cr}_2\text{O}_7$, respectively, are shown in Figure 5 and Table 1. Pre-edge and edge energies of the Cr species can be attributed simplistically to transitions between the bound electronic states (e.g. $1s \rightarrow 3d$, $1s \rightarrow 4s$). The pre-edge peak of Cr ions was dramatically dependent on the oxidation state and coordination chemistry. For ions with partially filled d shells, the p-d hybridization changed dramatically as regular octahedra distortion (Cr^{3+}), and is very large for tetrahedral coordination (Cr^{6+}). The energy positions found in the Cr solution (l) (Figure 5(a)) were well correlated with the Cr^{6+} species. Besides, the pre-edge energy of the Cr in the $\text{Cr/Fe}_3\text{O}_4$ (s) clearly presented the Cr^{3+} species (Figure 5(b)) evidencing a reduction of Cr^{6+} to Cr^{3+} by Fe_3O_4 . It was interesting that the XANES profile of the $\text{Cr/Fe}_3\text{O}_4$ (s) was clearly different

Table 1. XANES analysis of Fe K edge and Cr K edge of the samples

Materials		Pre-edge (eV)	Edge (eV)
Fe K-edge	Fe_3O_4	7112.36	7124.56
	$\text{Cr/Fe}_3\text{O}_4$	7112.26	7123.86
Cr K-edge	Std. CrCl_3	-	6000.64
	Std. $\text{K}_2\text{Cr}_2\text{O}_7$	5992.79	5999.62
	$\text{Cr/Fe}_3\text{O}_4$ (l)	5992.94	5998.96
	$\text{Cr/Fe}_3\text{O}_4$ (s)	-	6002.51

from the isolated Cr^{3+} ion in the CrCl_3 standard. The XANES profile was well fitted to the $\alpha\text{-CrOOH}$ structure containing the Cr^{3+} ion in octahedral geometry deduced from the literature (Lee *et al.*, 1995; Ould-Chikh *et al.*, 2014). The presence of this species indicated

a partial ion exchange of the Fe^{3+} sites by the Cr^{3+} ion containing a higher ionic strength and smaller size than the Fe^{3+} ion. The result was well coherent with the XRD and FTIR analysis.

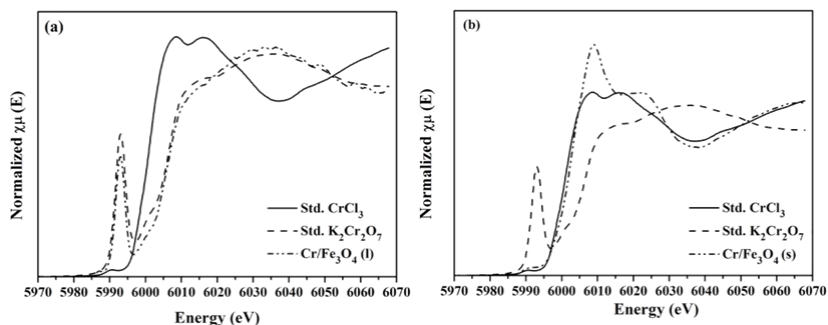


Figure 5. XANES spectra at Cr *K*-edge in solution (a) and on solid catalyst (b)

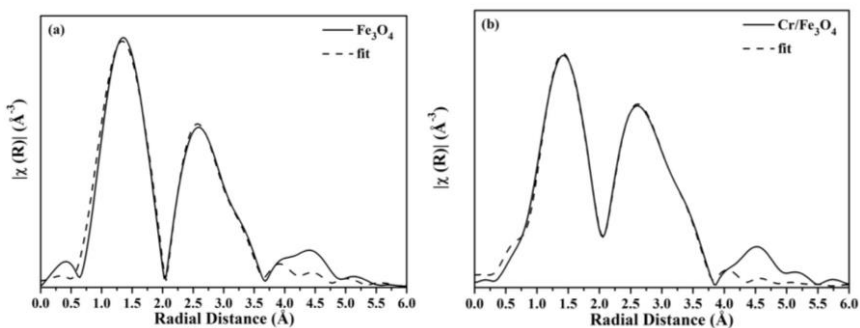


Figure 6. Fourier transform (FT) magnitude of the k^2 -weighted Fe EXAFS with fresh Fe_3O_4 (a) and $\text{Cr}/\text{Fe}_3\text{O}_4$ (b), fitting k -range of $2\text{--}8\text{ \AA}^{-1}$

Table 2. EXAFS fitting results of Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$

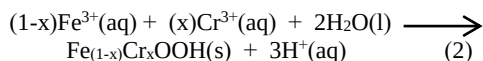
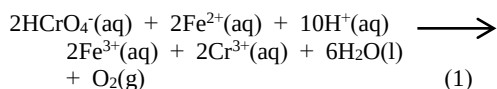
Sample		Distance (Å)	Coordination number (CN)	Debye-Waller factor (σ^2)
Fe_3O_4	Fe-O	1.46 ± 0.37	0.9 ± 1.20	0.003
	Fe-O	1.95 ± 0.01	2.9 ± 1.20	0.005
	Fe-Fe	2.78 ± 0.02	2.5 ± 1.04	0.015
	Fe-Fe	2.99 ± 0.02	3.8 ± 1.04	0.001
	Fe-Fe	4.07 ± 0.37	6.0 ± 1.20	0.021
$\text{Cr}/\text{Fe}_3\text{O}_4$	Fe-O	1.97 ± 0.03	2.2 ± 1.63	0.012
	Fe-O	2.40 ± 0.28	3.8 ± 1.63	0.059
	Fe-Fe	2.76 ± 0.13	0.9 ± 1.63	0.004
	Fe-Fe	3.00 ± 0.02	2.9 ± 1.63	0.008
	Fe-Fe	3.49 ± 0.13	3.2 ± 1.63	0.013

EXAFS Analysis:

Fourier transforms EXAFS of the Fe₃O₄ and Cr/Fe₃O₄ were determined and reported in Figure 6 and Table 2. The 4-fold Fe-O bonds in Fe₃O₄ (Figure 6(a)) were calculated from the first shell. One coordinated Fe-O and 3 coordinated Fe-O bonds were observed with average bond distances at 1.46 and 1.95 Å, respectively. These results corresponded well to the mononuclear [FeO]⁺ species calculated by Choi *et al.* (2003). The result exhibited Fe³⁺ occupancy in the distorted tetrahedral site found in the Fe₃O₄ structure. In addition, the second shell containing 2 distances of the Fe-Fe bonds of 2.78 and 2.99 Å was determined. It was noticed that no octahedral sites which were occupied by both the Fe²⁺ and Fe³⁺ ions were deduced by EXAFS analysis. Hence, the Fe³⁺ ion was the major component found in our sample. The presence of this main species contributed to the enhancement of an acidic strength of the synthesized Fe₃O₄ over the commercial Fe₃O₄ materials. Although, the Fe²⁺ sites could not be determined by EXAFS, probably due to the ion content limit, the XANES analysis clearly revealed the existence of the Fe²⁺/Fe³⁺ mixture in this structure (Table 1).

After Cr⁶⁺ adsorption, the first shell of the Cr/Fe₃O₄ sample indicated 6-fold Fe-O bonds with average distances of 1.97 and 2.40 Å. Besides, 4-fold Fe-Fe bonds were determined in the second shell with average distances of 2.76 and 3.00 Å. An increase of the oxygen surrounding the Fe atoms and extended in the Fe-Fe bond distances compared with the pristine Fe₃O₄ indicated the existent FeOOH structure on the sample surface. The iron species could be formed by the ion exchange Cr pathway proposed in Equations (1) and (2). The proposed reduction pathway of the Cr⁶⁺ molecules by an isolated Fe²⁺ ion had been reported by Niu *et al.* (2005). We involved this reaction pathway to explain a relevant surface reaction of Fe₃O₄ containing Fe²⁺ and Cr⁶⁺-adsorbed molecules. It was proposed to obtain the solid product of the Fe_(1-x)Cr_xOOH. The solid mixture containing the FeOOH and CrOOH structures was determined mainly in the octahedral geometry of the M-O bonds where M = Fe or Cr. The evidence of the

existent CrOOH species was also revealed by XANES analysis. The transformation from a tetrahedral to octahedral geometry of the Fe-O bonds in Fe₃O₄ clearly evidenced the structural rearrangement of iron to the FeOOH species on the Cr/Fe₃O₄ sample. The present structures are suggested to react as the Brønsted acid sites for the negative molecules of the Cr⁶⁺ ion.

**Catalytic Performances for Glucose Dehydration**

The glucose conversion and HMF yield relevant to the initial concentration of Cr compared with the Cr₂O₃ standard are shown in Figure 7(a). The calculated turnover numbers (TON) of each catalyst are plotted in Figure 7(b). A high glucose conversion of about 90% and 41% HMF yield were obtained by the pristine Fe₃O₄ catalyst indicating the presence of the appropriated acidic strength of both the Brønsted and Lewis sites on the catalyst surface (Choudhary *et al.*, 2013; Moreno-Recio *et al.*, 2016). It was noticed that the glucose conversions were approximately high at 90-95 for all Cr/Fe₃O₄ catalysts. Therefore, the high amount of the Lewis acid sites on the catalysts was remained after the Cr loading on Fe₃O₄. The HMF yield of Cr/Fe₃O₄ was varied in the range of 20-45% depending on the Cr content on the catalysts. However, in comparison to the glucose conversion of other metal oxide catalysts performed in aqueous media from the literature, as shown in Table 3, the Cr/Fe₃O₄ catalysts reached a higher HMF yield. The greatest enhancement of the HMF yield of about 50% was found on the catalyst of 20 ppm Cr/Fe₃O₄. This result clearly evidenced the increase of the Brønsted acid sites over the Fe₃O₄ surface by Cr adsorption (Elsayed *et al.*, 2018). The plausible active species on the Cr/Fe₃O₄ catalysts, evidenced by XANES and EXAFS analysis, were chemisorption species

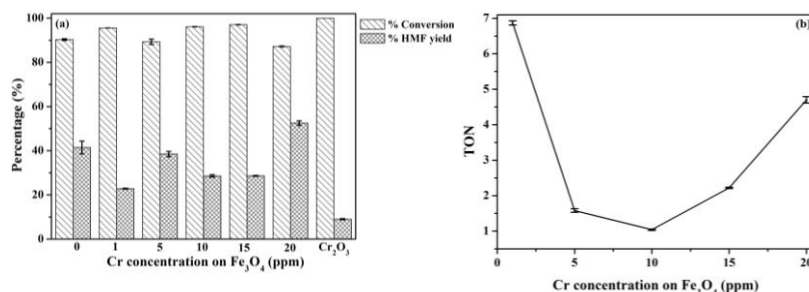


Figure 7. The glucose conversion and HMF yield of the pristine Fe_3O_4 and $\text{Cr}/\text{Fe}_3\text{O}_4$ catalysts (a) (reaction condition: 0.04 g of glucose, 0.04 g catalyst, 190 °C for 4 h) and TON of the catalysts (b)

Table 3. Comparison of HMF yield and conversion of glucose on different heterogeneous catalysts in aqueous media

Catalysts	Condition	HMF yield (%)	Conversion of glucose (%)	Ref.
1. Sn 20/ γ - Al_2O_3	150 °C, 1h	12	88	Marianou <i>et al.</i> (2018)
2. ZnPO-700	125 °C, 3 h	7	58	Villanueva and Marzioletti, (2018)
3. Nb(0.05)-Beta18	180 °C, 24 h	22*	47	Candu <i>et al.</i> (2018)
4. Fe_3O_4	190 °C, 4 h	42	90	This work
5. 20 ppm Cr/ Fe_3O_4	190 °C, 4 h	53	89	This work

* Selectivity of HMF

of $\text{Fe}_{(1-x)}\text{Cr}_x\text{OOH}$ which contained Brønsted acid of the FeOOH and CrOOH structures.

Considering the TON of the $\text{Cr}/\text{Fe}_3\text{O}_4$ catalysts (Figure 7(b)), the highest TON of about 6.9 was found by the 1 ppm $\text{Cr}/\text{Fe}_3\text{O}_4$ catalyst. The TON values were dramatically decreased with increasing the Cr concentration to 10 ppm. The TON values were then again increased with increasing the Cr concentrations to 15 and 20 ppm. These results correlated well with the Cr-uptake in Figure 3. An increase of the Cr content decreased dispersion of the Cr-active phases on the catalyst surfaces by the presentation of particle accumulation. Moreover, the increase of the TON on 15 and 20 ppm $\text{Cr}/\text{Fe}_3\text{O}_4$ might be due to the presence of various Cr active species by physical adsorption covered on the Fe_3O_4 surface when the Cr concentrations were high. Those species could enhance the Cr active sites on the catalysts and improve the TON. However, the observed TON on the 20 ppm $\text{Cr}/\text{Fe}_3\text{O}_4$ was less than that

achieved by 1ppm $\text{Cr}/\text{Fe}_3\text{O}_4$. Therefore, the most active species on the $\text{Cr}/\text{Fe}_3\text{O}_4$ catalyst was the ionic structure of $\text{Fe}_{(1-x)}\text{Cr}_x\text{OOH}$.

Conclusions

The cubic crystalline of a Fe_3O_4 structure with an approximate lattice parameter of 0.8396 nm was performed via the hydrothermal method. The lattice parameter of the Fe_3O_4 was slightly decreased by Cr^{6+} adsorption that might be due to an ion exchange of the small ion size of Cr^{3+} in the Fe^{3+} sites. The highest Cr^{6+} uptake of about 3.33 mg/g Fe_3O_4 conducted by UV-Vis analysis was observed at 10 ppm Cr concentration. The active species of Fe and Cr on the $\text{Cr}/\text{Fe}_3\text{O}_4$ catalysts determined by XAS were trivalent Fe and Cr in a $\text{Fe}_{(1-x)}\text{Cr}_x\text{OOH}$ structure. In comparing with the pristine Fe_3O_4 , the present $\text{Fe}_{(1-x)}\text{Cr}_x\text{OOH}$ structure on the $\text{Cr}/\text{Fe}_3\text{O}_4$ catalyst could improve the HMF

yield of the glucose dehydration in aqueous media. This catalytic improvement might be due to the existence of the Brønsted acid sites of the CrOOH and FeOOH structures on the catalyst surfaces. Meanwhile, the pristine Fe₃O₄ contained only a strong acidic site of tetrahedral Fe-O which was more favorable for the isomerization process of glucose to a fructose product. The dehydration product yield of the HMF was less.

Acknowledgements

The authors are grateful for the Science Achievement Scholarship of Thailand, Center for Innovation in Chemistry, Materials Chemistry Research Center, Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand, and Synchrotron Light Research Institute, BL5.2, Nakhon Ratchasima, Thailand.

References

- Alibeigi, S. and Vaezi, M.R. (2008). Phase transformation of iron oxide nanoparticles by varying the molar ratio of Fe²⁺:Fe³⁺. *Chem. Eng. Technol.*, 31:1591-1596.
- Alijani, H. and Shariatnia, Z. (2018). Synthesis of high growth rate SWCNTs and their magnetite cobalt sulfide nanohybrid as super-adsorbent for mercury removal. *Chem. Eng. Res. Des.*, 129:132-149.
- Arora, V., Sood, A., Shah, J., Kotnala, R.K., and Jain, T.K. (2017). Synthesis and characterization of pectin-6-aminohexanoic acid- magnetite nanoparticles for drug delivery. *Mater. Sci. Eng. C.*, 80:243-251.
- Borghain, C., Senapati, K.K., Mishra, D., Sarma, K.C., and Phukan, P. (2010). A new CoFe₂O₄-Cr₂O₃-SiO₂ fluorescent magnetic nanocomposite. *Nanoscale*, 2:2250-2256.
- Candu, N., El Fergani, M., Verziu, M., Cojocaru, B., Jurca, B., Apostol, N., Teodorescu, C., Parvulescu, V.I., and Coman, S.M. (2018). Efficient glucose dehydration to HMF onto Nb-BEA catalysts. *Catal. Today*. (In press).
- Choi, S.H., Wood, B.R., Ryder, J.A., and Bell, A.T. (2003). X-ray absorption fine structure characterization of the local structure of Fe in Fe-ZSM-5. *J. Phys. Chem. B*, 107:11843-11851.
- Choudhary, V., Mushrif, S.H., Ho, C., Anderko, A., Nikolakis, V., Marinkovic, N.S., Frenkel, A.I., Sandler, S.I., and Vlachos, D.G. (2013). Insights into the interplay of Lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media. *J. Am. Chem. Soc.*, 135:3997-4006.
- Corma, A., Iborra, S., and Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.*, 107:2411-2502.
- Cueto, J., Faba, L., Díaz, E., and Ordóñez, S. (2017). Performance of basic mixed oxides for aqueous-phase 5-hydroxymethylfurfural-acetone aldol condensation. *Appl. Catal. B-Environ.*, 201:221-231.
- Elsayed, I., Mashaly, M., Eltoweel, F., Jackson, M.A., and Hassan, E.B. (2018). Dehydration of glucose to 5-hydroxymethylfurfural by a core-shell Fe₃O₄@SiO₂-SO₃H magnetic nanoparticle catalyst. *Fuel*, 221:407-416.
- Feng, L., Cao, M., Ma, X., Zhu, Y., and Hu, C. (2012). Superparamagnetic high-surface-area Fe₃O₄ nanoparticles as adsorbents for arsenic removal. *J. Hazard. Mater.*, 217-218:439-446.
- Gangadharan, P. and Nambi, I.M. (2017). Feasibility study of disposed LCD monitor and carbon cloth electrodes for synchronized removal/recovery of Cr⁶⁺ by microbial fuel cells. *Int. J. Environ. Sci. Dev.*, 8 (8): 557-560.
- Guyo, U., Makawa, T., Moyo, M., Nharingo, T., Nyamunda, B.C., and Mugadza, T. (2015). Application of response surface methodology for Cd(II) adsorption on maize tassel- magnetite nanohybrid adsorbent. *J. Environ. Chem. Eng.*, 3:2472-2483.
- Hamliche-Bellal, Y., Benadda-Kordjani, A., Benrabaa, R., Djadoun, A., and Meddour-Boukhobza, L. (2018). Efficiency of magnetite as nanocrystalline bulk catalyst for the reduction of 4-nitrophenol. *J. Environ. Chem. Eng.*, 6: 2355-2362.
- Hug, S.J., Laubscher, H.U., and James, B.R. (1997). Iron(III) catalyzed photochemical reduction of chromium(VI) by oxalate and citrate in aqueous solutions. *Environ. Sci. Technol.*, 31:160-170.
- Ianoș, R., Păcurariu, C., Muntean, S.G., Muntean, E., Nistor, M.A., and Nižňanský, D. (2018). Combustion synthesis of iron oxide/carbon nanocomposites, efficient adsorbents for anionic and cationic dyes removal from wastewaters. *J. Alloy. Compd.*, 741:1235-1246.
- Iconaru, S.L., Guégan, R., Popa, C.L., Motelica-Heino, M., Ciobanu, C.S., and Predoi, D. (2016). Magnetite (Fe₃O₄) nanoparticles as adsorbents for As and Cu removal. *Appl. Clay Sci.*, 134:128-135.
- Jaime, J., Rangel, G., Muñoz-Bonilla, A., Mayoral, A., and Herrasti, P. (2017). Magnetite as a platform material in the detection of glucose, ethanol and cholesterol. *Sensor. Actuat. B-Chem.*, 238:693-701.
- Karami, H. (2013). Heavy metal removal from water by magnetite nanorods. *Chem. Eng. J.*, 219:209-216.
- Kim, Y., Yuan, K., Ellis, B.R., and Becker, U. (2017). Redox reactions of selenium as catalyzed by magnetite: Lessons learned from using electrochemistry and spectroscopic methods. *Geochim. Cosmochim. Ac.*, 199:304-323.
- Kumari, M., Pittman Jr, C.U., and Mohan, D. (2014). Heavy metals [chromium(VI) and lead(II)] removal from water using mesoporous magnetite (Fe₃O₄)

- nanospheres. *J. Colloid Interf. Sci.*, 442:120-132.
- Lazo, P. (2009). Determination of Cr(VI) in environmental samples evaluating Cr(VI) impact in a contaminated area. *J. Int. Environ. Appl. Sci.*, 4:207-213.
- Lee, J.F., Bajt, S., Clark, S.B., Lamble, G.M., Langton, C.A., and Oji, L. (1995). Chromium speciation in hazardous, cement-based waste forms. *Physica B*, 208-209:577578.
- Long, Y., Xiao, L., and Cao, Q. (2017). Co-polymerization of catechol and polyethylenimine on magnetic nanoparticles for efficient selective removal of anionic dyes from water. *Powder Technol.*, 310:24-34.
- Marianou, A.A., Michailof, C.M., Pineda, A., Iliopoulou, E.F., Triantafyllidis, K.S., and Lappas, A.A. (2018). Effect of Lewis and Brønsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media. *Appl. Catal. A-Gen.*, 555: 75-87.
- McKellar, S.C., Sotelo, J., Mowat, J.P.S., Wright, P.A., and Moggach, S.A. (2016). Perfluorocarbon liquid under pressure: a medium for gas delivery. *CrystEngComm*, 18:1273-1276.
- Mohammed, A.A. and Samaka, I.S. (2018). Bentonite coated with magnetite Fe_3O_4 nanoparticles as a novel adsorbent for copper (II) ions removal from water/wastewater. *Environ. Technol. Innov.*, 10: 162-174.
- Moreno-Recio, M., Santamaría-González, J., and Maireles-Torres, P. (2016). Brønsted and Lewis acid ZSM-5 zeolites for the catalytic dehydration of glucose into 5-hydroxymethylfurfural. *Chem. Eng. J.*, 303:22-30.
- Ni, C., Liu, S., Wang, H., Liu, H., and Chen, R. (2017). Studies on adsorption characteristics of Al-free and Al-substituted goethite for heavy metal ion Cr(VI). *Water Air Soil Poll.*, 228:1-10.
- Niu, S., Liu, Y., Xu, X., and Lou, Z. (2005). Removal of hexavalent chromium from aqueous solution by iron nanoparticles. *J. Zhejiang Univ. Sci. B*, 6:1022-1027.
- Obregón, I., Gandarias, I., Ocio, A., García-García, I., Alvarez de Eulate, N., and Arias, P.L. (2017). Structure- activity relationships of Ni- Cu/ Al_2O_3 catalysts for γ - valerolactone conversion to 2-methyltetrahydrofuran. *Appl. Catal. B-Environ.*, 210:328-341.
- Ould-Chikh, S., Proux, O., Afanasiev, P., Khrouz, L., Hedhili, M.N., Anjum, D.H., Harb, M., Geantet, C., Basset, J.M., and Puzenat, E. (2014). Photocatalysis with chromium-doped TiO_2 : bulk and surface doping. *ChemSusChem*, 7:1361-1371.
- Pal, U., Madrid, S.I.U., and De-jesus, F.S. (2014). Controlling size and magnetic properties of Fe_3O_4 clusters in solvothermal process. *Adv. Nano Res.*, 2:187-198.
- Palimi, M.J., Rostami, M., Mahdavian, M., and Ramezanzadeh, B. (2014). Surface modification of Cr_2O_3 nanoparticles with 3-amino propyl trimethoxy silane (APTMS). Part 1: Studying the mechanical properties of polyurethane/ Cr_2O_3 nanocomposites. *Prog. Org. Coat.*, 77:1663-1673.
- Pedersen, A.T., Ringborg, R., Grotkjær, T., Pedersen, S., and Woodley, J.M. (2015). Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose-fructose mixtures. *Chem. Eng. J.*, 273:455-464.
- Rahimi, S., Moattari, R.M., Rajabi, L., Derakhshan, A.A., and Keyhani, M. (2015). Iron oxide/hydroxide (α, γ - FeOOH) nanoparticles as high potential adsorbents for lead removal from polluted aquatic media. *J. Ind. Eng. Chem.*, 23:33-43.
- Rajput, S., Pittman, C.U., and Mohan, D. (2016). Magnetic magnetite (Fe_3O_4) nanoparticle synthesis and applications for lead (Pb^{2+}) and chromium (Cr^{6+}) removal from water. *J. Colloid Interf. Sci.*, 468:334-346.
- Saksornchai, E., Kavinchan, J., Thongtem, S., and Thongtem, T. (2018). Simple wet-chemical synthesis of superparamagnetic CTAB- modified magnetite nanoparticles using as adsorbents for anionic dye Congo red removal. *Mater. Lett.*, 213:138-142.
- Samphao, A., Butmee, P., Saejueng, P., Pukahuta, C., Švorc, L., and Kalcher, K. (2018). Monitoring of glucose and ethanol during wine fermentation by bienzymatic biosensor. *J. Electroanal. Chem.*, 816: 179-188.
- Scherrer, P. (1918). Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachrichten von der Gesellschaft der Wissenschaften Zu Göttingen, Mathematisch-physikalische Klasse*, 26:98-100. (in German)
- United States Environmental Protection Agency. (1998). Chromium (VI); CASRN 18540- 29- 9. Integrated Risk Information System (IRIS) Chemical Assessment Summary. National Center for Environmental Assessment, US Environmental Protection Agency, Cincinnati, OH, USA, 33p.
- Vahur, S., Teearu, A., and Leito, I. (2010). ATR-FT-IR spectroscopy in the region of 550-230 cm^{-1} for identification of inorganic pigments. *Spectrochim. Acta A*, 75:1061-1072.
- Villanueva, N.I. and Marzialetti, T.G. (2018). Mechanism and kinetic parameters of glucose and fructose dehydration to 5-hydroxymethylfurfural over solid phosphate catalysts in water. *Catal. Today*, 302:100-107.
- Wei, W. and Wu, S. (2018). Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst. *Fuel*, 225:311-321.
- Zhang, M., Su, K., Song, H., Li, Z., and Cheng, B. (2015). The excellent performance of amorphous Cr_2O_3 , SnO_2 , SrO and graphene oxide-ferric oxide in glucose conversion into 5-HMF. *Catal. Commun.*, 69:76-80.
- Zolfaghari, G., Esmaili-Sari, A., Anbia, M., Younesi, H., Amirmahmoodi, S., and Ghafari-Nazari, A. (2011). Taguchi optimization approach for Pb(II) and Hg(II) removal from aqueous solutions using modified mesoporous carbon. *J. Hazard. Mater.*, 192:1046-1055.