

# SYNTHESIS OF NANOCRYSTALLINE SODIUM POTASSIUM FLUOROPHLOGOPITE MICA MINERAL FOR $\text{Cu}^{2+}$ , $\text{Pb}^{2+}$ , AND $\text{Cd}^{2+}$ REMOVAL FROM WASTE WATER

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## Abstract

In the present work, nanocrystalline sodium potassium fluorophlogopite (FGP) was synthesized successfully by hydrothermal method and was characterized by X-ray diffraction, energy dispersive analysis, scanning electron microscope, transmission electron microscopy and FT-IR spectroscopy. This synthesized material was then used for the sorption of metal ions. For all the metal ions sorption was found to increase up to certain time limit which is sufficient for the saturation and then it remains almost constant. Also sorption was found to increase with increase in pH up to certain extent after which it decreases. The maximum sorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  on synthesized materials (FGP) was found at pH between 6.0 & 8.0. Sorption was observed to be enhanced with increase in sorbent concentration.

**Keywords:** *fluorophlogopite; sorption; trace metal ions; 797 VA Computrace ion analyzer*

## Introduction

Mica minerals are capable of removing pollutants from the environment and thereby control their spread in soil and water (Paulus et al., 1992; Franklin and Lee, 1996; Komarneni et al., 2009). These minerals can act as naturally occurring nanomaterials or as nano-reactors for fabrication of nano-species, nanoparticles or nanodevices (Zhou et al., 2006; Tong et al., 2009). Mica minerals are widely used in ceramics, building materials, paper industries, oil drilling, foundry moulds, pharmaceuticals, used as adsorbents, catalysts or catalyst supports, ion exchangers, and decolorizing agents (Konta, 1995; Murry, 2000; Ding et al., 2001; Carretero, 2002; Babel and Kurniawan, 2003; Choy et al., 2007).

Trace metal ions have been discharged into environment as industrial waste, causing serious soil and water pollution (Lin and Juang, 2002).  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  are especially common metals that tend to accumulate in organisms, causing numerous disease and disorders

(Inglezakis et al., 2003). The removal of trace metal ions from drinking water has been carried out by using inorganic and organic ion exchanger. Removal of Cs, Ba and Eu has been carried out using sodium aluminosilicate (Singh et al., 2010). Mica mineral is often reported to exhibit high sorption capacity and selectivity for divalent elements, which makes the mica mineral attractive for environmental applications, such as water softening or removing trace elements from waste water (Apiratikul and Pavasant, 2008; Harold and William, 2007). In our previous studies we have reported a lot on the adsorption of pollutants from wastewater (Gupta et al., 2013; Islam et al., 2017; Khanday et al., 2012, 2017(a), 2017(b); Marrakchi et al., 2016).

Here we report a method to prepare uniform and smaller size sodium potassium fluorophlogopite nanocrystals obtained by hydrothermal heating and its potential use for trace metal sorption from waste water.

## **Experimental**

### ***Synthesis of Nanocrystalline sodium potassium fluorophlogopite***

Sodium potassium fluorophlogopite was synthesized by hydrothermal method and the constituents were taken according to the molar composition. Tetra-ethyl orthosilicate and sodium aluminate were used as silica and alumina sources respectively. Sodium hydroxide was used as alkali source and tetrapropyl ammonium hydroxide (TPAOH, 25wt % in water) was chosen as template or organic structure directing (OSD) agent. Typically, the aluminium source was dissolved in an appropriate amount of TPAOH solution and then NaOH solution was added. TEOS was added dropwise with vigorous stirring and weighed amounts of magnesium nitrate and hydrofluoric acid were added and stirred vigorously until a thick gel was formed. This synthetic gel was magnetically stirred for 2 hours, then placed in 110 mL Teflon lined stainless steel pressure vessel and kept in a pre-heated oven at 175 °C for 48 hours. The synthetic material was recovered by centrifugation at 14,500 rpm. Finally nanocrystalline sodium potassium fluorophlogopite was washed with DM water several times and then dried at 50 °C for 24 h. It was calcined at 450 °C for 5 hrs to remove organic template.

### ***Characterization of nanocrystalline sodium potassium fluorophlogopite***

#### ***X-Ray diffraction***

For X-Ray Diffraction, the samples were sieved in an ABNT n° 200 (0.074 mm) sieve and then placed in an aluminum sample holder for X-ray diffraction assays, using Shimadzu XRD 6000 equipment. The operational details of the technique were set as follows: Copper K $\alpha$

radiation at 40 KV/30 mA, with a goniometer speed of 2°/min and a step of 0.02° in the 2θ range scanning from 10° to 90°.

#### ***Energy dispersion spectroscopy***

The determination of bulk element composition of mica minerals is of importance as this information is used to verify the synthesis formulation, the bulk silics/ alumina ratio, the cation concentration, degree of ion exchange, and the detection of contaminant element. The chemical composition of synthesized material was checked for Na, K, Al, Si, and F using energy dispersive spectrometry. SEM EDS spectra were measured on a JEOL JSM 5800 Scanning microscope equipped with the microprobe analyzer.

#### ***Fourier Transform-Infrared spectroscopy***

FT-IR Spectroscopy was used to identify structural features in the sodium potassium fluorophlogopite samples. The KBr pellet technique was used for the investigation of vibrational transitions within the molecular framework. FT-IR spectra were analyzed before and after calcination. Spectra were collected in the mid – IR range of 400-4000cm<sup>-1</sup>.

#### ***Sorption experiment***

The ion exchange of trace metal ions by sodium potassium fluorophlogopite (FGP) was carried out using batch method. Batch sorption experiments were conducted by taking 100mg of sorbent in 250ml conical flask containing 25ml of solutions containing trace metal ions (Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup>) of desired concentrations at constant temperatures (25°C). The conical flasks were shaken in a thermostated water bath shaker and then the solutions were filtered. Metal ion concentration before and after sorption was determined by 797 computrace ion analyzer (Metrohm). The percentage sorption was calculated by taking initial and final concentration of the metal ions in solution.

$$\% \text{ Sorption} = (C_i - C_f) / C_i \times 100$$

Where, C<sub>i</sub> and C<sub>e</sub> are the initial & equilibrium metal ion concentrations respectively.

K<sub>d</sub> values were calculated as:

$$K_d = \{(C_i - C_e) / C_e\} * (V/W) \text{ mL/g}$$

Where C<sub>i</sub> & C<sub>e</sub> are the metal ion concentration before and after equilibration respectively, V is the volume of solution in mL and W is the weight of exchanger in g.

### Result and Discussion

Fig.1 shows representative XRD pattern of hydrothermally synthesized sodium potassium fluorophlogopite nanocrystal which proved it to be completely crystalline without presence of any impurity. The crystal size is 25nm as calculated from the XRD line widths by applying Scherer's equation. Fig.2 shows, the chemical composition of the synthesized sample obtained from scanning electron microscopy-energy dispersive analysis (SEM-EDX) for the metals F, Na, Si & Al agree well with the weight percentage of these elements. Fig.3 shows the FT-IR spectra of the synthetic material (FGP). The band observed between 1600 to 1800  $\text{cm}^{-1}$  is mainly due to H-O-H bending vibration. The bands at  $\sim 1036 \text{ cm}^{-1}$  and  $\sim 835 \text{ cm}^{-1}$  are due to Si-O-Si and Al-O-Al stretching respectively. The bands at  $\sim 500 \text{ cm}^{-1}$  and  $\sim 600 \text{ cm}^{-1}$  are due to the bending of Si-O-Si and Al-O-Si bonds respectively. A band at  $1639 \text{ cm}^{-1}$  can reasonably be assigned to the (N-H) deformation because vibration for amino salt appear as strong bands near  $1600\text{-}1575 \text{ cm}^{-1}$  and also near  $1639 \text{ cm}^{-1}$ .

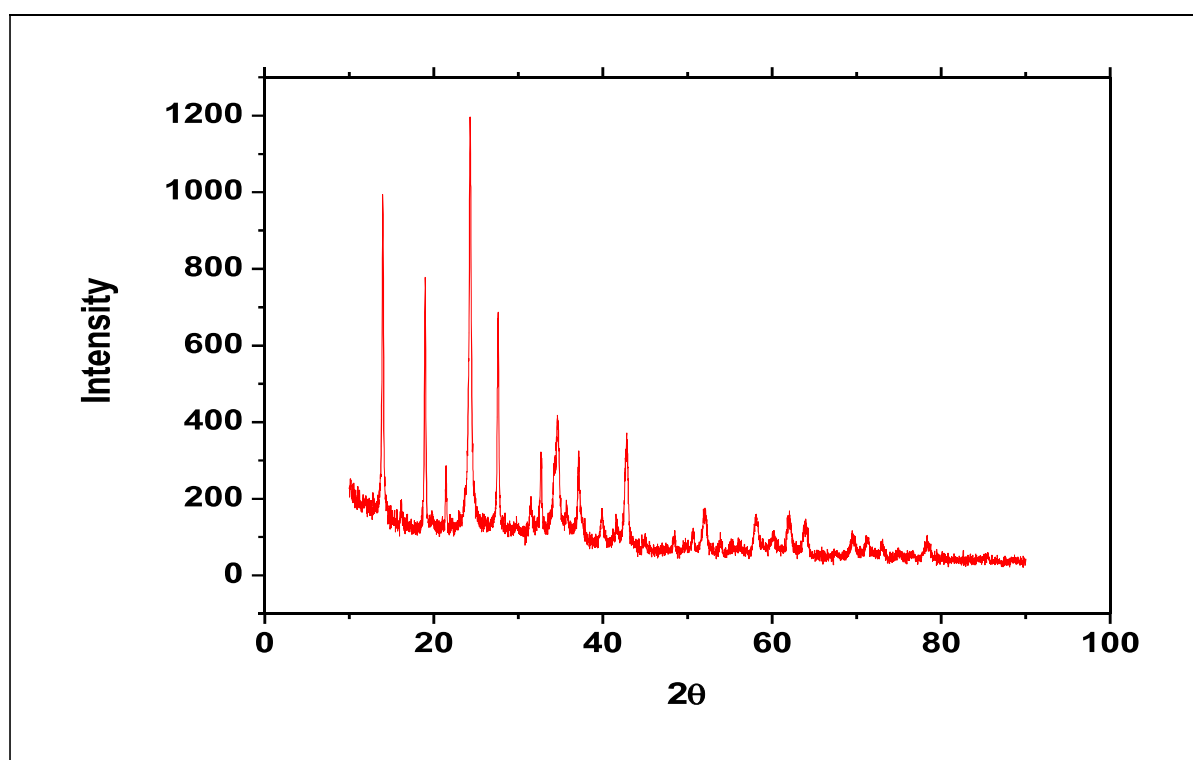


Fig.1: XRD of synthesized sodium potassium fluorophlogopite (FGP).

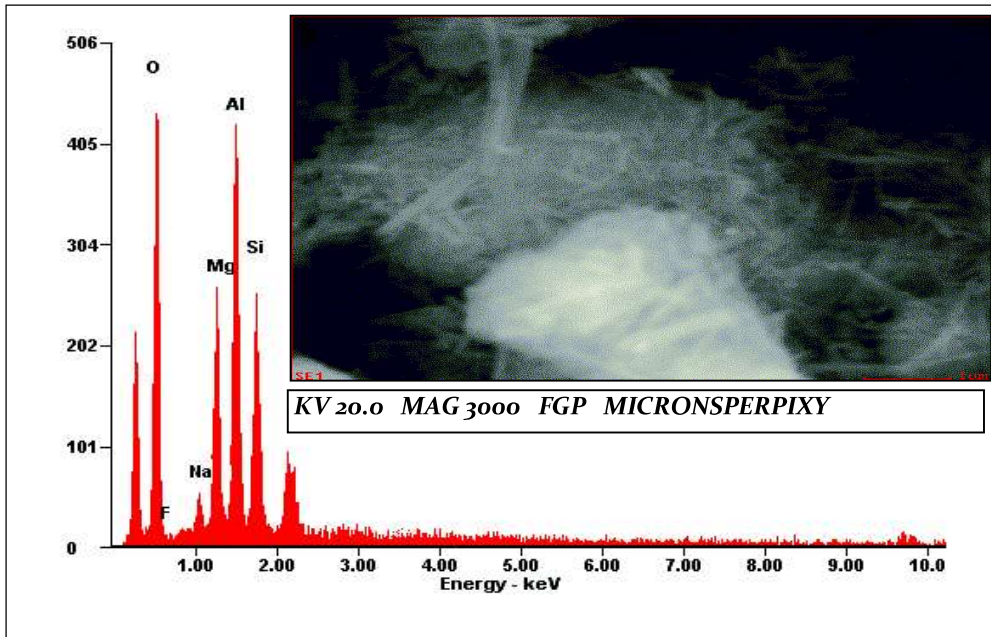


Fig. 2: SEM-EDS spectra of synthesized sodium potassium fluorophlogopite (FGP).

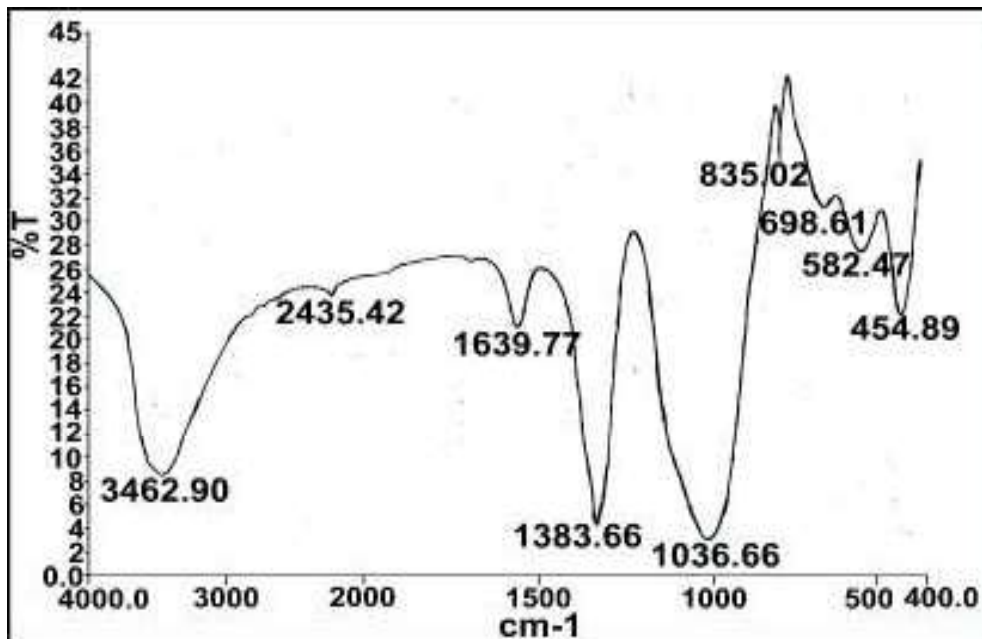


Fig. 3: FT-IR spectra for synthesized sodium potassium fluorophlogopite (FGP).

Differential pulse mode was employed to obtain the voltammograms as shown in Fig.6 which showed that the sensitive, stability and reliability of peak height could be reached in the potential range depending on the metal ion under determination. The voltammogram is recorded using parameters given in table 1. Fig.4 shows that Peak potential of Cd is -0.60 V, Pb is -0.40V and Cu is -0.21V.

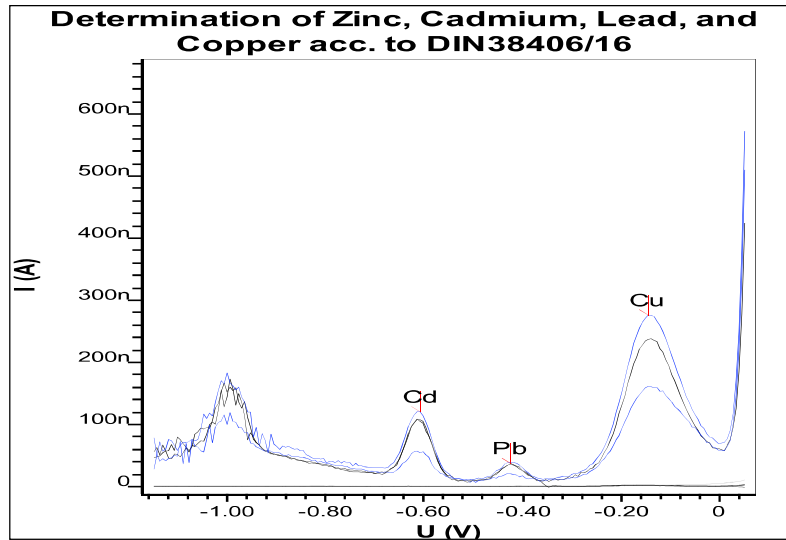


Fig. 4: Determination of cadmium, lead and copper according to DIN38406/16 by 797 VA computrace ion analyzer in waste water.

Fig.5 shows kinetic study of the trace metal ion sorption on synthesized material. From figure it can be clearly seen that for all the metal ions that sorption increases up to certain time limit (8 hrs) which is sufficient for the saturation and then it remains almost constant. An increase in sorption with increase in time can be attributed to greater contact time between sorbent and sorbate. However, after the initial period, slower sorption may be due to slower diffusion of cations into the interior channels of sodium potassium fluorophlogopite.

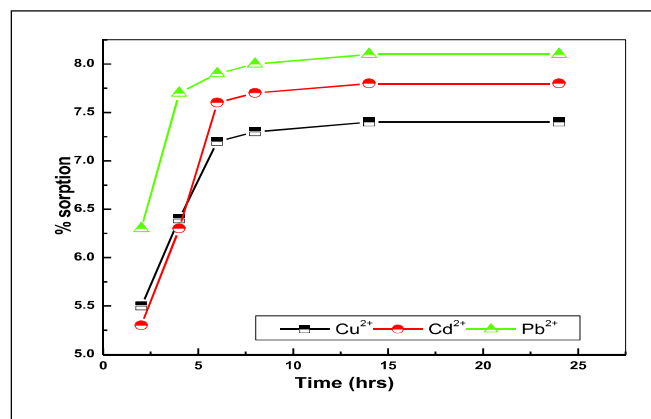


Fig. 5: Kinetic study for sorption of metal ions by sodium potassium fluorophlogopite

The sorption of metal ions as a function of pH is given Fig.6. The maximum sorption of  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  on synthesized materials (FGP) was found at pH between 6.0 & 8.0 that may be explained as the formation of bulky hydroxide complexes at higher pH. At low pH values, the

surface of the sorbent would be closely associated with hydronium ions ( $H_3O^+$ ) which hinder the access of metal ions to the surface functional group. Since surfaces of the sorbent and the metal ions both have the same charge and hence, because of repulsion, the sorption was found to be decreased. As pH is increased there is a decrease of positive surface charge, which results in lower Columbic repulsion of the sorbing metal ions and hence sorption was found to be increased.

Fig.7 shows the effect of sorbent concentration (FGP) variation on the sorption metal ions. The sorption was observed to be enhanced with increase in sorbent concentration which may be due to increase in number of surface sites into the suspension by increasing sorbent concentration. It was observed that sorption of metal ions decreased with increase in metal ion concentration ( $10^{-8}$  to  $10^{-5}$  mol/l) which could be explained in terms of limited number of surface sites available in the suspension at higher metal ions concentrations.

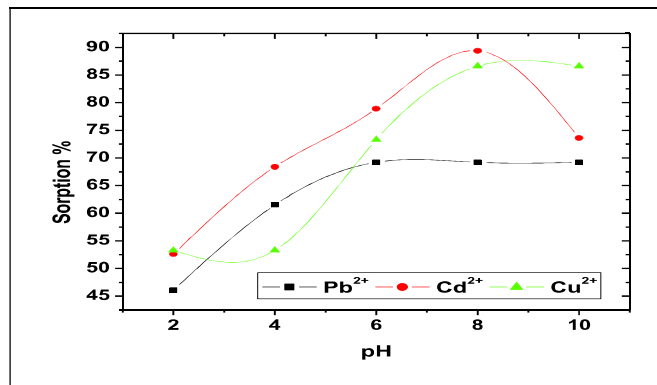


Fig. 6: Effect of pH on sorption of metal ions by sodium potassium fluorophlogopite.

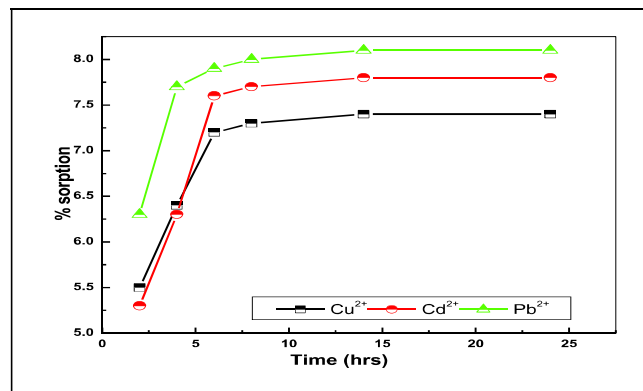


Fig. 7: Effect of sorbent dose on sorption of metal ions by sodium potassium fluorophlogopite.

### Conclusion

Synthesis of nanocrystalline sodium potassium fluorophlogopite (FGP) was carried out successfully and characterized properly by various techniques. This synthesized material was

then used for the sorption of metal ions. For all the metal ions sorption was found to increase up to certain time limit which is sufficient for the saturation and then it remains almost constant. Also sorption was found to increase with increase in pH up to certain extent after which it decreases. The maximum sorption of  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  on synthesized materials (FGP) was found at pH between 6.0 & 8.0. Sorption was observed to be enhanced with increase in sorbent concentration.

### References

1. Apiratikul, R. and Pavasant, P. (2008). *Chem. Eng. J.* **144**: 245.
2. Babel, S. and Kurniawan, T. A. (2003). *J. Hazard. Mater.* **97**: 219.
3. Carretero, M.I. (2002). *Appl. Clay. Sci.* **21**: 155.
4. Choy, J.H., Choi, S.J., Oh, J.M. and Park, T. (2007). *Appl. Clay. Sci.* **36**: 122.
5. Ding, Z., Klopogge, J.T., Frost, R.L., Lu, G.Q. and Zhu, H.Y. (2001). *J. Porous. Mater.* **8**: 273.
6. Franklin, K.R. and Lee, (1996). *J. Mate. Chem.* **6**: 109.
7. Gupta, P., Khanday, W.A., Majid, S.A., Kushwa, V., Tomar, S.S. and Tomar, R. (2013). *J. Environ. Chem. Eng.* **1**: 510.
8. Harold, H.S. and William, A. (2007). *Handbook on the Toxicology of Metals (Third Edition)*.
9. Inglezakis, V.J., Loizidou, M.M. and Grigoropoulou, H. (2003). *J. Coll. Interf. Sci.* **261**: 49.
10. Islam, M.A., Ahmed, M.J., Khanday, W.A., Asif, M. and Hameed, B.H. (2017) *Ecotoxicol. Environ. Saf.* **138**: 279.
11. Khanday, W.A., Asif, M. and Hameed, B.H. (2017a). *Int. J. Biol. Macromol.* **95**: 895.
12. Khanday, W.A., Marrakchi, F., Asif, M. and Hameed, B.H. (2017b). *J. Taiwan Inst. Chem. Eng.* **70**: 32.
13. Khanday, W.A., Singh, S.K., Bhaudoriya, J., Majid, S.A., Tomar, S.S. and Tomar, R. (2012). *Coll. J.* **74**: 573.
14. Komarneni, S., Ravello, R., Noh, Y.D. and Mackenzie, K.J.D. (2009). *Appl. Clay Sci.* **42**: 524.
15. Konta, (1995). *J. Appl. Clay. Sci.* **10**: 275.
16. Lin, S.H. and Juang, R.S. (2002) *J. Hazard. Mater.* **92**: 315.
17. Marrakchi, F., Khanday, W.A., Asif, M. and Hameed, B.H. (2016). *Int. J. Biol. Macromol.* **93**: 1231.
18. Murry, H.H. (2000). *Appl. Clay. Sci.* **17**: 207.
19. Paulus, W.J., Komarneni, S. and Roy, R. (1992). *Nature* **357**: 571.
20. Singh, B.K., Tomar, R., Kumar, S., Jain, A., Tomar, B.S. and Manchanda, V.K. (2010). *J. Hazard. Mater.* **178**: 771.
21. Tong, D.S., Xia, H.S. and Zhou, C.H. (2009). *China .J. Catal.* **30**: 1170.
22. Zhou, C.H., Tong, D.S., Bao, M., Du, Z.X., Ge, Z.H. and Li, X.N. (2006). *Top. Catal.* **39**: 213.