

Preparation and Physicochemical Characterization of Cadmium and Zinc Ferrocyanides as Catalysts and Ion Exchangers

S.A. El-Molla^{a*}, A. M. I. Ali^b, G. M. Mohamed^c

^aChemistry Depart., Faculty of Education, Ain Shams Univ., Roxy, Cairo 11757, Egypt ^b Atomic Energy Authority, Hot Lab. Center, Cairo, Egypt and ^c National Research Centre, NRC, 33Elbohouth St.-Dokki-Giza-Egypt-P.O. 12622 Egypt
This paper is dedicated to the spirit of the late professor G.A. El-Shobaky

CADMIUM and zinc ferrocyanide complexes were prepared then calcined at 100, 400, 600 and 800 °C. The obtained solids were characterized using IR, XRD, N₂-adsorption measurements, H₂O₂ decomposition, and isopropanol conversion. The results showed that the diffractograms of ZnFeCN calcined at 600 -800°C consisted of ZnO, K₂FeO₄, ZnFe₂O₄, K₂O-Fe₂O₃ phases while the CdFCN complexes calcined at 600-800°C composed of K₂CdO₂, K₂Cd₂O₃, K₂FeO₄, K₂O-Fe₂O₃ phases and Fe₂O₃ (Maghemite phase). The S_{BET} of CdFeCN and ZnFeCN compounds were small and decrease with increasing the calcination temperature. CdFeCN and ZnFeCN are ion exchangers for ¹³⁷Cs⁺-removal. The exchange of ion capacity remained almost unaffected by changing the concentration of HNO₃ within 0.05-0.5M. The increase in the acid concentration above this limit brought about a significant decrease in the exchange of ion capacity. The decrease was however more pronounced in case of ZnFeCN complex. The catalytic activity of cadmium and zinc ferrocyanide complexes heated at 100°C and 600 °C towards H₂O₂ decomposition was very small, while the complexes calcined at 800°C behaved as active catalysts. The catalytic activity of cadmium and zinc ferrocyanide complexes was moderate towards alcohol conversion and increased by increasing the calcination temperature. The increase was however much more pronounced in case of CdFeCN which shows better activity than ZnFeCN. CdFeCN and ZnFeCN acted mainly as dehydrogenation catalysts (above 90%).

Keywords: Cadmium ferrocyanide, Zinc ferrocyanide, Cs-ions extraction, Catalytic activity

Insoluble metal ferrocyanides (MFeCN) is an important class of compounds that have several applications as adsorbents for substituted amines and phenols^(1,2). These compounds may also be used as an ion exchanger for ¹³⁷Cs⁺ removal from radioactive wastewater solutions⁽³⁾. The transition metal hexacyanometalates usually have an open-channel framework appropriate for

*Corresponding author E-mail Address: Toonyoprade@yahoo.com, phone: +201003823267

separation and storage of small molecules⁽³⁾. These compounds have been also used in some catalytic processes⁽⁴⁾ and for therapy of animals and humans affected by nuclear accidents⁽⁵⁾. Zinc hexacyanoferrates (II, III) have hexagonal structure in which Zn^{2+} ions are tetrahedral coordinated to four N atoms from CN ligands. Such coordination provides a relatively high thermal stability of these materials and an interesting porous nature⁽⁶⁾. Zinc ferrocyanide is used as ion exchanger for detergents sorption⁽⁷⁾. Cadmium ferrocyanide is an important microporous material although it has no vacant sites in its structure, Cd^{2+} ions have incomplete coordination sphere formed by only three CN ligands, which formed a network of interconnected small channels^(8,9). The free coordination sites of Cd^{2+} are adsorption centers for water and other polar molecules⁽⁹⁾.

It has been reported that cobalt, zinc and cadmium ferrocyanides are water insoluble and amorphous in nature⁽¹⁰⁾. These metal ferrocyanides were characterized based on elemental and spectral studies⁽¹¹⁾. Few published works have been oriented for studying the effect of thermal treatment of cyanometalates on their magnetic properties⁽¹²⁾. The thermal treatment of hexacyanoferrate interlayered hydrotalcite was studied and followed by Raman spectroscopy⁽¹³⁾ and XRD investigation which showed the thermal decomposition of hexacyanoferrate (II) hydrotalcite at 300 °C yielding Fe_3O_4 besides other mixed oxides containing iron⁽¹³⁾. Ferrites may compose an essential product of some metal ferrocyanides.

It is known that ferromagnetic spinel containing Zn, Co and Ni are used as alkylating catalysts for aniline and phenol⁽¹⁴⁾. Ferrites as $ZnFe_2O_4$ had been used for oxidative dehydrogenation of butane⁽¹⁵⁾. Ferrites have been studied also for their magnetic properties and applicability in telecommunication power transformers⁽¹⁵⁾. For all above reasons, this work aimed at studying some physicochemical and catalytic properties of zinc and cadmium ferrocyanide complexes and their decomposition products. The techniques employed in this study were IR, XRD, nitrogen adsorption at -196 °C, $^{137}Cs^+$ removal from aqueous solutions and catalytic measurements using hydrogen peroxide decomposition and conversion of isopropyl alcohol.

Experimental

Materials

Cadmium nitrate, zinc nitrate and potassium ferrocyanide were obtained from Merck and BDH companies. All chemical used were of analytical grade. Zinc hexacyanoferrate (II) and cadmium hexacyanoferrate (II), $(ZnFeCN)_6$ and $(CdFeCN)_6$, were prepared using 0.5M aqueous $K_4Fe(CN)_6$ which was added with stirring to 1M zinc nitrate or cadmium nitrate with 1:2 volume ratio. The precipitate was removed, washed, and dried at 100 °C to constant weight. The dried solids were pulverized and fractionated by

sieving. The finest grain fractions were used for different investigations carried out through this work. The obtained complexes were dried at 100 °C then calcined in air at 400, 600 and 800 °C for 4 hr.

Techniques

The chemical composition of the prepared $M_2Fe(CN)_6 \cdot 3H_2O$, $M=Zn$ or Cd was determined by XRF using XRF Italis structure, Italy. The data obtained showed the ratio between the elements as follows: $Cd/Fe=3.98 \pm 0.23$ and $Zn/Fe=2.17 \pm 0.14$.

The specific surface areas of the samples were determined from nitrogen adsorption isotherms measured at -196 °C using a Micromeritics pore size 9320. All samples were degassed at 200 °C for 3 hr under a reduced pressure of 10^{-5} Torr before undertaking such measurements.

Phase analysis of the various solids calcined in air at 100, 400, 600 and 800 °C was performed by X-ray powder diffraction employing a Shimadzu X-ray Diffractometer Model XD1180-Japan, Patterns were run using Ni-filtered copper radiation ($\lambda = 1.5404 \text{ \AA}$) at 30 kV and 30 mA with scanning rate of 8 degree in $2\theta \cdot \text{min}^{-1}$.

IR measurements were carried out after mixing small amounts of solids with KBr to give disks. The measurements were done using Perkin Elmer 1600 FT-IR spectrometer.

Extraction of Cs ions from solution was carried out using FAA(Flame Atomic Absorption) Spectrometer type Buck scientific 210 VHO(USA) with air/ acetylene flame and hollow cathode lamps were used for determination of Cs ions concentrations(ppm) in the extraction medium of Cs ion concentrations were determined at a resonance line of 852.1 nm with 0.02 mg/l detection limits. The procedure of Cs extraction was as follows: unless otherwise stated batch experiments were carried out by shaking a known weight (0.1 g) of the solid sample with 10 ml of aqueous acid solution having different concentrations containing 100 ppm of Cs at $25 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$. The concentration of Cs element in the aqueous phase before and after shaking was measured by FAA Spectrometer. The extraction % (E%) of Cs ion was calculated from their concentrations in the aqueous phase before and after equilibration C_b and C_a using the relation $E\% = C_b - C_a / C_b \times 100$. The effect of acidity of the aqueous medium on the percentage uptake was studied by changing HNO_3 concentration in the range 0.01-4M and measuring the equilibrium concentration after 3 hr shaking.

The catalytic activities of various investigated solids were determined by using both H₂O₂ decomposition and isopropanol conversion. The catalytic decomposition of H₂O₂ was carried out in presence of the solid catalysts at 30-50 °C, using 0.2 ml volume of 0.45 mol/l H₂O₂ diluted to 20 ml with distilled water. The mass of the catalyst sample taken in each kinetic experiment was fixed at 50 mg in all cases. The reaction kinetics was monitored by measuring the volume of O₂ liberated at different time intervals until O₂ liberated no further.

The catalytic conversion of isopropanol using various solid catalysts was determined at 200-325 °C, the catalytic reaction being conducted in a flow reactor under atmospheric pressure. Thus, a 50 mg catalyst sample was held between two glass wool plugs in a Pyrex glass reactor tube 20 cm long and 1 cm internal diameter packed with quartz fragments 2-3 mm length. The temperature of the catalyst bed was regulated and controlled to within ±1 °C. Argon gas was used as the diluent and carrier of the reactant. Isopropyl alcohol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 35°C. The flow rate of the carrier gas was maintained at 25 ml/min. Before carrying out such catalytic activity measurements, each catalyst sample was activated by heating at 300 °C in a current of argon for 2 hr then cooled to the catalytic reaction temperature. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. The column used was fused silica glass capillary column type PE-CW length 15 m-1.0 UM Perkin-Elmer corp.

Results and Discussion

FTIR Spectra of cadmium and zinc ferrocyanide complexes

The infrared spectra of zinc ferrocyanide (ZnFCN) and cadmium ferrocyanide (CdFCN) complexes were measured and given in Fig. 1 in the range of 500-4000 cm⁻¹. Figure 1 reveals that the prepared cyanoferrate complexes being dried at 100°C show a sharp stretching band located at 2000-2230 cm⁻¹ characteristic for active CN group. So, the appearance of this band is an indicative for the cyano complexes. Figure 1 includes also the spectrum of ZnFCN complex heated at 600 °C. The IR spectra of ZnFCN being dried and calcined at 600 °C show the presence of three main absorption bands at 3600, 2130 and 1610 cm⁻¹. The band at 3600 cm⁻¹ can be assigned to the H₂O stretching vibration in the compound and / or due OH groups⁽¹⁰⁾. While the band at 1610 cm⁻¹ could refer to water that may exist in the bulk of ferrocyanide (bending band). Furthermore, a band at 590 cm⁻¹ is due to Fe-C stretching vibration⁽¹⁷⁾. The band appearing at 450 cm⁻¹ is due to metal-N bond due to polymerization⁽¹⁸⁾. Figure 1 depicts also the FTIR of

CdFCN being dried at 100. It is clear from this figure that all bands observed in case of ZnFCN complex appeared in case of CdFCN complex. The comparison between the FTIR spectra of ZnFCN and CdFCN complexes dried at 100 and those calcined at 600 °C shows that the heat treatment of different complexes led to a complete disappearance of the band of CN group (indicative for cyanocomplexes). This finding suggested clearly an effective decomposition of the investigated ZnFCN and CdFCN complexes.

XRD investigation of different investigated solids

X-Ray powder diffractograms of ZnFCN and CdFCN solids dried at 100 °C then calcined at 400, 600 and 800 °C were determined. Figure 2 depicts the diffractograms of ZnFCN complex and its thermal products being thermally treated at 100, 400, 600 and 800 °C, respectively. It has been reported by several investigators that the prepared metalocyanoferrate (II) that containing Cd or Zn are amorphous in nature^(10,11). So, these compounds could not be identified by XRD investigation. However, their thermal stability or possible crystallization by heating at high temperature could be checked by XRD. Examination of Fig. 2 shows the following: (i) the solid dried at 100 °C consisted of some diffraction lines of K₂O left from the preparation and washing process of the prepared complex. (ii) Heating the prepared solid at 400 °C led to the appearance of K₂FeO₄ and K₂O-Fe₂O₃ mixed oxide. (iii) Increasing the calcination temperature up to 600 °C led to the appearance of ZnO and ZnFe₂O₄ together with the phases detected for solids calcined at 400 °C. (iv) Increasing the calcination temperature up to 800 °C led to the disappearance of ZnFe₂O₄ with subsequent formation of K₂Fe₂O₄ according to:

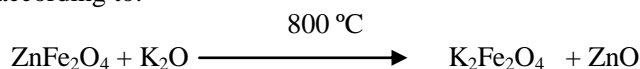


Figure 3 shows the x-ray diffractograms of prepared cadmium cyanoferrate II and its thermal products being thermally treated at 100, 600, and 800 °C, respectively. Examination of Fig.3 shows the following (i) the solid dried at 100°C consisted of the diffraction lines of Cd₂Fe(CN)₆.1.5H₂O with poor degree of crystallinity and K₄Fe(CN)₆ left from preparation process.(ii) Heating the prepared solids at 600 °C led to the appearance of K₂FeO₄, K₂CdO₂, K₂Cd₂O₃ and Fe₂O₃ phases. (iii) Increasing the calcination temperature up to 800 °C led to the disappearance of K₂FeO₄ phase and increasing relative intensity of diffraction lines of K₂Cd₂O₃ and Fe₂O₃ (Maghemite phase). The observed increase in the relative intensity of the diffraction lines of K₂Cd₂O₃ and Fe₂O₃ might be attributed to a better crystallization of these phases according to increasing the calcination temperature to 800°C.

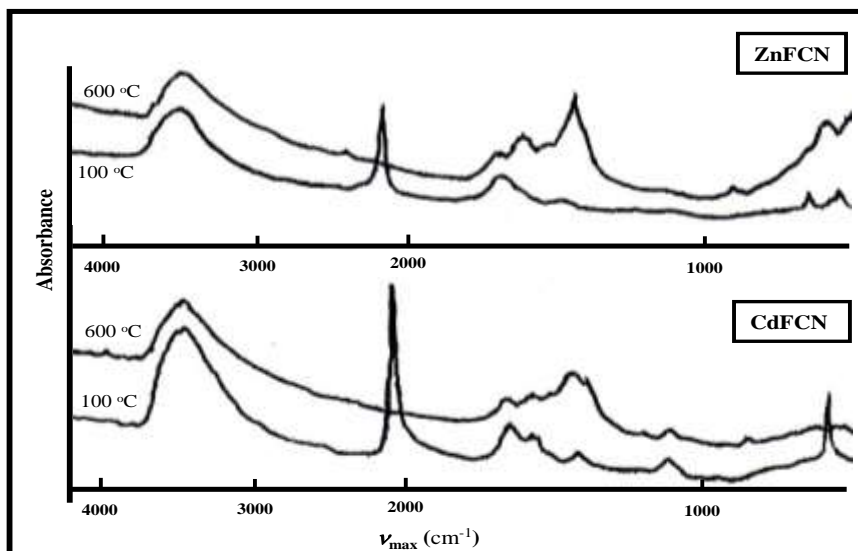


Fig. 1. FTIR spectra of ZnFCN and CdFCN complexes heated in air at different calcination temperatures.

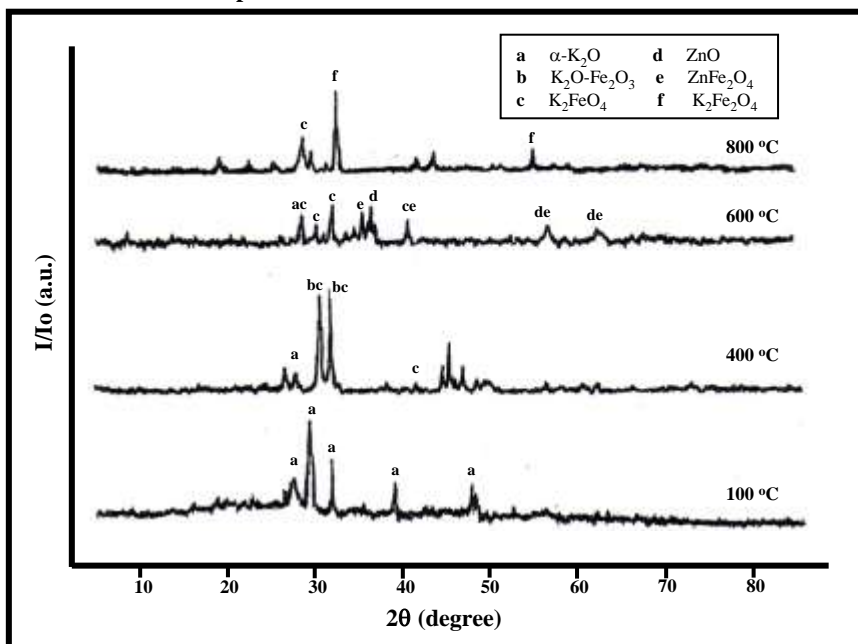


Fig. 2. X-ray diffractograms of ZnFCN complex heated in air at different calcination temperatures.

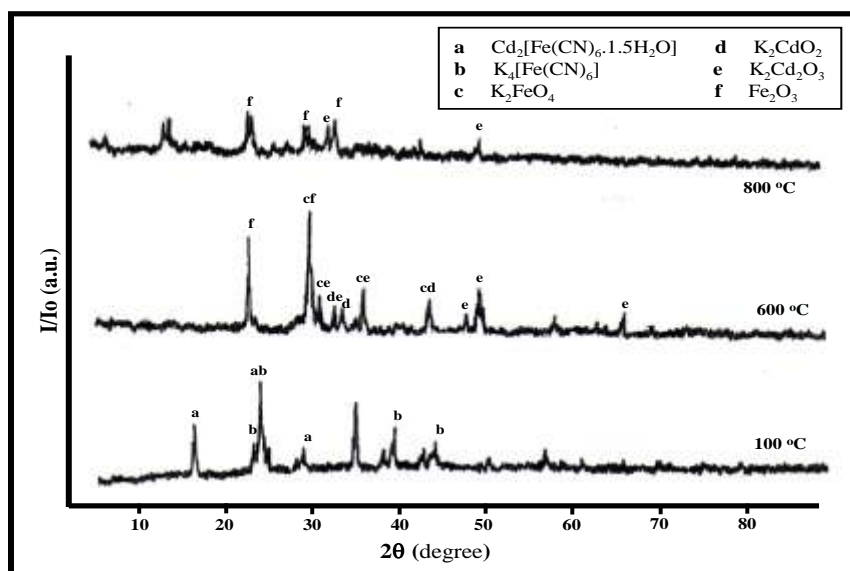


Fig. 3. X-ray diffractograms of CdFCN complex heated in air at different calcination temperatures.

Specific surface areas of different investigated solids

The S_{BET} of the various prepared and thermally treated solids were determined and given in Table 1. Inspecting the data of Table 1, one can conclude that (i) The prepared complexes have relatively small S_{BET} values. The specific surface area of cadmium complex is greater than that of zinc complex. (ii) Increasing the calcination temperature from 100 to 400 °C decreased the specific surface areas of the prepared solids. This decrease is due to their thermal decomposition. (iii) The further increase of the calcination temperature up to 600 °C led to a more pronounced decrease in the S_{BET} . This decrease is due to the formation of mixed oxides with small surface area containing metal ferrites as $\text{K}_2\text{Fe}_2\text{O}_4$, ZnFe_2O_4 beside K_2CdO_2 formation. (iv) Increasing the calcination temperature to 800 °C resulted in a drastic decrease in the S_{BET} indicating an effective sintering of some phases obtained and also due to the transformation of the obtained phases to free oxides as ZnO and Fe_2O_3 with small surface areas.

TABLE 1. The specific surface areas of different investigated adsorbents.

Solids	S_{BET} (m^2/g) at			
	100 °C	400 °C	600 °C	800 °C
CdFCN	44.4	32.4	12.01	2.4
ZnFCN	27.8	24.6	5.8	1.03

Extraction of radioactive cesium ($^{137}\text{Cs}^+$) using various investigated solids

Inorganic ion exchangers exhibit a broad variety of advantageous properties when compared to synthetic organic ion exchangers. The main advantage is their high selectivity for the capture of certain ions. The good chemical stability even in strongly acidic media is another advantage. These exchangers are promising offering advanced new technologies that should ensure greater safety and lower cost⁽¹⁹⁾. The effect of the concentration of nitric acid on the uptake capacity for $^{137}\text{Cs}^+$ -removal by prepared zinc and cadmium ferrocyanide complexes was determined. The effect of acidity of the aqueous medium on the percentage uptake was studied by increasing the concentration of HNO_3 in the range of 0.01-4M and measuring the equilibrium concentration after 3 hr shaking. The extraction percentage E % of Cs was calculated from their concentration in aqueous phase before and after equilibration C_b and C_a using the relation ($E\% = \frac{C_b - C_a}{C_b} \times 100$). The obtained results are given in Tables 2&3 which indicate the extraction percentage of cesium remained un-effected by using HNO_3 concentration within 0.01 up to 0.5M then decreased progressively by increasing the acid concentration above this limit falling to a value about 50% of that formed in case of small acid concentration. It is also shown in this table the cadmium ferrocyanide complex has slightly higher activity for removal of Cs ions more than zinc ferrocyanide complex under various concentrations of HNO_3 .

The effect of increasing calcination temperature of the prepared sorbents to 200, 400, 600, and 800°C on the extraction properties of Cs was studied as shown in Table 3. According to the data given in this table, one can conclude the following: (i) Cadmium complex and its thermal products at different calcination temperatures have higher extraction efficiencies more than zinc complex. (ii) Increasing the calcination temperature from 100 to 200°C decreases relatively the extraction % for Cs. Further increasing the calcination temperature led to a progressive decrease in the sorption properties. Increasing of the calcination temperature from 100 to 800 °C resulted in a decrease of 69 and 73 % in the efficiency of extraction for cadmium and zinc ferrocyanate II complexes, respectively.

TABLE 2. Effect of nitric acid on the extraction (E) % and extraction capacity of Cs ions by CdFCN and ZnFCN complexes.

Molarity of HNO ₃	CdFCN E%	Capacity of CdFCN mg/g	ZnFCN E%	Capacity of ZnFCN mg/g
0.01	85	100	83	98
0.05	85	100	82	98
0.1	84	99	83	98
0.5	85	100	84	98
1	80	90	82	85
2	76	85	75	75
3	72	80	70	68
4	69	66	64	57

TABLE 3. Effect of temperature on the extraction (E) % of Cs ions after thermal treatment the sorbents.

Temperature	(E%)CdFCN	(E%)ZnFCN
100	85	82
200	65	62
400	56	53
600	35	32
800	26	22

*Catalytic activity measurements of different investigated solids**Catalytic decomposition of H₂O₂ on the investigated solids*

The catalytic decomposition of H₂O₂ was conducted at 30– 50 °C over cadmium and zinc ferrocyanide compounds thermally treated at 100, 600 and 800°C. First-order kinetics was observed in all cases^(20,21), the values of the reaction rate constant (k) and the rate constant per unit surface area of the solids (k⁻) of H₂O₂ decomposition conducted at 30– 50 °C over the investigated solids were calculated and shown in Table 4. According to the data in Table 4, one can observe the following: (i) Cadmium and zinc ferrocyanide compounds dried at 100°C exhibited very small catalytic activity towards H₂O₂ decomposition, their catalytic activity increases slightly by increasing the calcination temperature to 600°C. (ii) A considerable increase in the catalytic activity was observed upon increasing the calcination temperature up to 800°C. (iii) The catalytic activity for cadmium ferrocyanide compounds is much bigger than that of zinc

ferrocyanide compounds calcined at the same temperature. The maximum increase in the catalytic activity, expressed as $k_{30}^{\circ\text{C}}$ (min^{-1}) due to increasing the calcination temperature from 100 to 800°C attained 39 and 5.3-fold for cadmium and zinc ferrocyanide, respectively.

These results could be attributed to the formation of new compounds devoted with very big catalytic activity such as ZnFe_2O_4 , K_2FeO_4 , $\text{K}_2\text{Fe}_2\text{O}_4$, and $\text{K}_2\text{O-Fe}_2\text{O}_3$ for zinc ferrocyanide-containing compounds and K_2CdO_2 , $\text{K}_2\text{Cd}_2\text{O}_3$, and Fe_2O_3 (Maghemite phase) for cadmium ferrocyanide-containing compounds as shown in X-ray section. The latter compound is responsible for the big catalytic activity of cadmium ferrocyanide-containing compounds calcined at 800°C.

The apparent activation energy of the catalyzed reaction was calculated from plotting $\log k$ as function of $1/T$ (reciprocal of reaction temperature) by direct application of the Arrhenius equation. The computed ΔE values for different solids dried at 100°C, those calcined at 600, and 800°C are given in Table 4. Examination of Table 4 shows the following: (i) ΔE values ran parallel to k -values. In fact, the solids having maximum catalytic activity showed minimum ΔE values and vice versa. Table 4 includes also $\ln A$ -values (pre-exponential factor in the Arrhenius equation for different solids. (ii) The change in $\ln A$ -values for cadmium-containing compounds are more pronounced as compared to zinc-containing compounds. This finding may indicate that the Cd-containing compounds are more heterogeneous than the other compounds. This heterogeneity might also account for the bigger catalytic activity of Cd-containing compound as compared to that of Zn-containing ones. However, one cannot overlook the enhanced existence of Fe_2O_3 (Maghemite phase) in the decomposition of cadmium containing compounds being calcined at 800°C. This phase exhibited an outstanding big catalytic activity towards H_2O_2 decomposition.

Catalytic conversion of isopropyl alcohol on investigated solids

The catalytic conversion of isopropyl alcohol was carried out using the flow technique^(22, 23) over cadmium and zinc ferrocyanide compounds precalcined at 100 and 800°C. Table 5 shows the behavior of cadmium and zinc ferrocyanide compounds precalcined at 100 and 800°C towards the total conversion of alcohol as a function of reaction temperature. It is noticed from Table 5 that: (i) Cadmium and zinc ferrocyanide compounds dried at 100°C exhibited small catalytic activities for the reaction carried out at 200–275°C. The pronounced increase in the catalytic activity, expressed as total conversion of isopropyl alcohol was observed when the reaction temperature increased to 325 °C. (ii) Increasing the calcination temperature from 100 to 800°C increases the catalytic activity of cadmium and zinc ferrocyanides. (iii) The catalytic activity of cadmium ferrocyanide compound is bigger than that of zinc ferrocyanide compound calcined at the same temperature. (iv) The investigated ferrocyanides are highly selective to dehydrogenation process (formation of acetone). The selectivity to acetone formation decreases slightly with increasing reaction temperature. (v) The small dehydration selectivity increased slightly by increasing the calcination

temperature up to 800°C in case of CdFCN compound while in case of ZnFCN the selectivity % of dehydration has not been much affected.

TABLE 4. Reaction rate constant k (min^{-1}), reaction rate constant per unit area k^- ($\text{min}^{-1} \cdot \text{m}^{-2}$) of solid, frequency factor ($\ln A$), activation energies for catalytic decomposition of H_2O_2 over ferrocyanide compounds being calcined at 100, 600 and 800 °C.

Solid	Calcination Temp. °C	$k_{30}^{\circ\text{C}}$	$k^-_{30}^{\circ\text{C}}$	$k_{40}^{\circ\text{C}}$	$k^-_{40}^{\circ\text{C}}$	$k_{50}^{\circ\text{C}}$	$k^-_{50}^{\circ\text{C}}$	$\ln A$	ΔE
CdFCN	100	0.003	0.001	0.01	0.002	0.02	0.01	23.8	74.3
	600	0.004	0.004	0.02	0.01	0.03	0.03	27.6	82.9
	800	0.12	0.52	0.18	0.77	0.31	1.3	15.2	43.8
ZnFCN	100	0.003	0.001	0.01	0.003	0.14	0.01	21.9	69.2
	600	0.003	0.005	0.01	0.014	0.15	0.03	23.7	74.3
	800	0.019	0.18	0.04	0.35	1.06	1.0	24.9	72.4

TABLE 5. Total conversion of isopropyl alcohol and the selectivity to various products over ferrocyanide compounds calcined at 100 °C and 800 °C, at various reaction temperatures.

The solid	Calcination Temp. °C	Reaction Temp. °C	T.C.%	S_1 %	S_2 %
ZnFCN	100	200	0.14	0	100
		275	3.81	0.8	99.2
		325	25.4	3.5	96.5
CdFCN	100	200	0.45	0	100
		275	5.9	1.1	98.9
		325	16	2.9	97.1
ZnFCN	800	200	0.67	0	100
		275	5.13	0.6	99.4
		325	17.8	0.4	99.6
CdFCN	800	200	0.82	1.8	98.2
		275	21	5.5	94.5
		325	22	6.9	93.1

T.C., total conversion

S_1 , selectivity towards propene (dehydration).

S₂, selectivity towards acetone (dehydrogenation).

Conclusions

The following are the main conclusions that may be drawn from the obtained results:

Cadmium and zinc ferrocyanide complexes were prepared and thermally treated at 100, 400, 600 and 800 °C. The thermal stability of these compounds were investigated using FTIR, which indicated the complete disappearance of CN band of all solids calcined at 600 and 800 °C. CdFCN and ZnFCN start to decompose by heating at 400 °C and the decomposition yielded various mixed oxides upon heating at temperature of 600 and 800 °C. The decomposition products of ZnFCN solid calcined at 600–800 °C consists of ZnO, K₂FeO₄, ZnFe₂O₄ and K₂O-Fe₂O₃ phases. The decomposition products of CdFCN solid calcined at 600–800 °C consists of K₂CdO₂, K₂Cd₂O₃, K₂FeO₄, and Fe₂O₃ (Maghemite phase). The S_{BET} of CdFCN and ZnFCN compounds is small and decreases with increasing the calcination temperature. CdFCN and ZnFCN are ion exchangers for ¹³⁷Cs⁺-removal. The exchange capacity remained almost unaffected by changing the concentration of HNO₃ within 0.05-0.5M. CdFCN and its thermal products have higher extraction efficiencies more than ZnFCN complex and its thermal products. The catalytic activity of CdFCN and ZnFCN being calcined at 100 and 600 °C in H₂O₂ decomposition is very small. The catalytic activity is much increased for the solids calcined at 800 °C. The maximum increase in the catalytic activity expressed as reaction rate constant, k (min⁻¹) at reaction temperature 30 °C due to increasing the calcination temperature from 100 to 800 °C attained 40 and 4-fold for cadmium and zinc ferrocyanide, respectively. The catalytic activities for various investigated solids have been also determined by following up the conversion of isopropyl alcohol under certain conditions. This catalytic reaction yielded mainly acetone (above 90%) via dehydrogenation mechanism. The catalytic activity CdFCN being calcined at 800 towards both of H₂O₂ decomposition and isopropyl alcohol conversion is bigger than that of ZnFCN calcined at the same temperature.

References

1. **Tewari, B. B., Kamaluddin, J.** *Colloid Interface Sci.* **193**, 167-171 (1997).
 2. **Tewari, B. B., Mohan, D., Kamaluddin,** *Colloids Surf. A:* **131**, 89-93 (1998).
 3. **Balmaseda, J., Reguera, E., Rodriguez-Hernandez, J., Reguera, L. and Autie, M.,** *Microporous Mesoporous Mater.* **96**, 222-236 (2006).
 4. **Reguera, E., Fernandez -Bertran, J., Diaz, C, and Molerio, J.,** *Hyperfine Interact...* **73**, 285-294 (1992).
- Egypt. J. Chem.* **59**, No. 5 (2016)

5. Roberts, L, *Science* ,**238**, 1028-1031 (1987).
6. Rodríguez-Hernández, J, Reguera, E., Lima, E., Balmaseda, J., Martínez-García, R. and Yee-Madeira, H., *J. Phys. Chem. Solids*, **68**, 1630-1640 (2007).
7. Srivastava, S. K., Jain, C.K., Oberoi, C.K. and Sharma, A.K., *Can. J. Chem.* **60**, 1681 (1982).
8. Gómez, A. and Reguera, E., *Inter. J. Inorg. Mater.* **3 1**, 045-1051 (2001).
9. Balmaseda, J., Reguera, E., Gómez, A., Díaz, B. and Autie, M., *Microporous Mesoporous Mater.* **54**, 285-292 (2002).
10. Tewari, B.B. and Boodhoo, M., *J. Colloid Interface Sci.* **289**, 328-332 (2005).
11. Tewari, B.B. and Hamid, N., *Colloids Surf. A:* **296**, 264-269 (2007).
12. Ng, C. W., Ding, J., Shi, Y. and Gan, L.M., *J. Phys. Chem. Solids*, **62**, 767 (2001).
13. Frost, R.L., Musumeci, A.W., Bouzaid, J., Adebajo, M.O., Martens, W.N. and J. Theo Klopogge, *J. Solid State Chem.* **178**, 1940-1948 (2005).
14. Sreekumar, K., Sugunan, S., *Appl. Catal. A* **230**, 245-251 (2002).
15. Lee, D.Y., Kim, D., Kim, K.H., J. S. Choi, *Bull. Korean Chem. Soc.* **9**, 333-420 (1988).
16. Rana, M.U, Ul-Islam, M. and Abbas, T, *Mater. Lett.* **41**, 52-56 (1999).
17. Nakamoto, K, "*Infrared Spectra of Inorganic and Coordination Compounds*", Wiley, New York, 166 (1963).
18. Ratnasamy, P. and Leonard, A.J., *J. Phys. Chem.* **76**, 1838-1843 (1972).
19. Ali, A.M.I. and Nowier, H.G., *Radiochim. Acta*, **90**, 285-288 (2015).
20. El-Molla, S.A., Fagal, G.A., Hassan, N.A. and Mohamed, G.A., *Research on Chem. Intermed.* **41**, 679-689 (2015)
21. Hassan, N.A., El-Molla, S.A., Mohamed, G.A. and Fagal, G.A., *Mater. Res. Bull.* **47**, 2655– 2661 (2012).
22. El-Molla, S.A. and Mahmoud, H.R., *Matter. Powder Technol.*, **253**, 695– 702 (2014)
23. El-Molla, S.A., Ebrahim, S. M. and Ibrahim, M.M., *Int. J. Indust. Chem.* (In press) (2016).

تحضير و توصيف فيزيوكيميائي ل فروسيانيدات الكاديوم و الزنك كحفازات ومستبدلات ايونية

سحر الملا¹، امال على² ، غادة محمد³

¹قسم الكيمياء كلية التربية جامعة عين شمس، ²هيئة الطاقة الذرية مركز المعامل الحارة، ³قسم الكيمياء - المركز القومي للبحوث- الجيزة - مصر.
اليحت مقدم اهداء الى روح استاذنا الراحل ا.د. جميل على الشويكى

مترابكات فيروسيانيدات الكاديوم و الزنك تم تحضيرها وتحميصها عند درجات حرارة 100, 400, 600 و 800 درجة مئوية. تم توصيف المواد المحضرة باستخدام طيف الاشعة تحت الحمراء- الاشعة السينية- قياسات امتزاز النيتروجين- تكسير فوق اكسيد الهيدروجين- تحول الايزوبروبانول. اوضحت النتائج ان طيف الشعة السينية لمركب ZnFCN المحمص عند 600- 800 درجة مئوية يتالف من اطوار ZnO , K_2FeO_4 , $K_2O-Fe_2O_3$, $ZnFe_2O_4$ و بينما مركب CdFCN و المحمص عند 600- 800 درجة مئوية يتالف من اطوار K_2CdO_2 , $K_2Cd_2O_3$, $K_2O-Fe_2O_3$ و Fe_2O_3 و K_2FeO_4 . المساحة السطحية لمركبات CdFCN و ZnFCN صغيرة ووجد انها تقل برفع درجة التحميص. مركبات CdFCN و ZnFCN استخدمت كمستبدلات ايونية لغرض ازالة ايون $^{137}Cs^+$. كفاءة عملية الاستبدال لم تتأثر بالتغير الحادث في تركيز حمض النيتريك المستخدم من 0.05 الى 0.5 مولار. زيادة تركيز الحمض اكبر من ذلك قللت كفاءة عملية الاستبدال. وكان النقص واضحا في حالة مترابك ZnFCN. النشاط الحفزى لمترابكات فيروسيانيدات الكاديوم و الزنك المحمص عند 100 و 600 درجة مئوية كانت ضعيفة للغاية. بينما المترابكات المحمص عند 800 درجة مئوية اظهرت نشاطا حفزيا جيدا في اتجاه تكسير فوق اكسيد الهيدروجين. مركبات فيروسيانيدات الكاديوم و الزنك كانت ضعيفة تجاه تحول الكحول حفزيا وازداد هذا النشاط برفع درجة التحميص من 100 والى 800 درجة مئوية. الزيادة في النشاط الحفزى كان واضحا في حالة مركبات CdFCN.