

Structural and Surface Characteristics of $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ System as Being Influenced by Doping with CeO_2 and La_2O_3

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Abstract: Ferric chromic mixed oxides system having the nominal composition of $0.75 \text{Fe}_2\text{O}_3 \cdot 0.25 \text{Cr}_2\text{O}_3$ was prepared by co-precipitation from ferric and chromic sulphate solution using $1 \text{M NH}_4\text{OH}$ at pH 8 and 50°C . The obtained precipitate was carefully washed by distilled water, dried then calcined at 500°C . Pure uncalcined mixed solids sample was doped with different amounts of La_2O_3 or CeO_2 namely 0.75, 1.5 and 3 mol%. The dopant salts employed were $\text{La}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_2$ which were dissolved in a least amount of distilled water, dried then calcined at 500°C . Pure and variously doped mixed solids were characterized using XRD, TEM, EDX and N_2 adsorption carried out at -196°C . The results revealed that pure and variously doped $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solids calcined at 500°C consisted of a mixture of nanosized α - and γ - Fe_2O_3 phases. The doping process much decreased the crystallite size of the phases present. TEM examination showed that all investigated solids consisted of nano sized homogeneous particles. The surface and bulk compositions of pure mixed oxides are very close to each other. La_2O_3 -doping increased the surface concentration of Cr species to an extent proportional to the amount of dopant added. The maximum increase attained 49%. The presence of the smallest amount of CeO_2 (0.75 mol%) increased the surface concentration of Cr species which decreased progressively upon increasing the amount of ceria added falling to a value close to that measured for pure sample. Pure and doped solids are mesoporous adsorbents measuring specific surface area (S_{BET}) which decreased upon doping either with La_2O_3 or CeO_2 . The decrease was, however, more pronounced for the solids doped with CeO_2 . The decrease attained 43%.

Key words:

INTRODUCTION

Metal oxides play a very important role in many areas of chemistry, physics and materials science [1-5]. In technological applications, the oxides are used in fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion and as catalysts [6-8]. Nanophase metal and metal oxide catalysts, with controlled particle size and shape, exhibit high specific surface area and densely populated unsaturated surface coordination sites that can result in significant improvement catalytic performance over conventional catalysts [9-12]. The surface and catalytic properties of mixed metal oxides depend, mainly, on method of preparation, their chemical composition, the calcination conditions and doping. The doping process might alter the concentration and/or the nature of the catalytically active species leading thus to an effective change in their catalytic activities. The doping process might alter the

concentration and/or the nature of the catalytically active species leading thus to an effective change in their catalytic activities. The present investigation reports the results of a study on the effects of CeO_2 and La_2O_3 doping on structural and textural characteristics of $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system. The techniques employed were EDX, TEM, XRD, adsorption of N_2 at -196°C .

MATERIALS AND MATERIALS

Experimental: Iron (III) and chromium (III) mixed hydroxides having Fe/Cr ratio of 0.75/0.25 were prepared using an aqueous solution of ferric and chromic mixed sulphate solutions used of analytical grade and supplied by BDH company at 50°C and a pH 8 in presence of conc. NH_4OH solution subjected to bubbling by a current of dry air free from CO_2 flowing at a rate of 20 ml/min. The carefully washed mixed hydroxides were dried at 120°C then heated at 500°C for 4h. Three CeO_2 -doped and three La_2O_3 -doped samples were prepared by taking

calculated amounts of mixed hydroxides that having Fe/Cr ratio of 0.75/0.25 with calculated amounts of cerium or lanthanum nitrates dissolved in the least amount of distilled water sufficient to make pastes. The symbols of pure and doped samples are designated as follows: Fe Cr, Fe Cr Ce₁, Fe Cr Ce₂, Fe Cr Ce₃ and Fe Cr La₁, Fe Cr La₂ and Fe Cr La₃. These solids were doped with 0.75, 1.5 and 3 mol% CeO₂ or La₂O₃, respectively.

Techniques

X-Ray Diffraction (XRD) Analysis of Different Mixed Oxides: X-ray powder diffractograms of various investigated samples calcined at 500°C were determined using a Bruker diffractometer (Bruker D8 advance target) the scanning rate was fixed at 8° in 2θ/min for phase identification and 0.8° in 2θ/min for line broadening profile analysis, respectively. The patterns were run with Cu Kα1 with secondly monochromator ($\lambda = 0.1545$ nm) at 40 kV and 40 mA. The crystallite size of crystalline phases present in different solids investigated was calculated from the line broadening profile analysis of the main diffraction lines of the phases present using the Scherrer equation [13]:

$$D = \frac{K\lambda}{\beta_{1/2} \cos \theta}$$

Where D is the mean crystallite diameter in Å, λ the wave length of X-ray beam, K the Scherrer constant (0.89), $\beta_{1/2}$ the full-width at half-maximum (FWHM) of the main diffraction peak of crystalline phases expressed in radian and θ is the diffraction angle.

(EDX) Analysis of Different Mixed Oxides: EDX measurements were carried out on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The parameters were as follows: - 15 kV accelerating voltage,

100 s accumulation time, 8 mm window width. The surface molar composition was determined by the Asa method (Zaf-correction, Gaussian approximation).

Measurements of Different Surface Characteristics:

The different surface characteristics of various solids were determined from analysis of nitrogen adsorption isotherms carried out at -196°C over various adsorbents. These characteristics include specific surface areas (S_{BET}), total pore volume (V_p), mean pore radius (r) and pore volume distribution ($\Delta v/\Delta r$). The S_{BET} values were determined from linear portion of the BET equation. Another series of specific surface area (S_t) was determined from V_{1-t} plots constructed using suitable standard t-curves depending on the values of the BET- C constant. The specific surface area (S_{BET}), total pore volume (V_p), mean pore radius (r) and pore volume distribution ($\Delta v/\Delta r$) of the various adsorbents were determined from nitrogen adsorption isotherms measured at -196°C using Quantachrome NOVA Automated Gas sorbometer. The values of V_p were computed from the relation $V_p = 15.45 \times 10^{-4} \times V_{\text{at}}$ cm³/g, where V_{at} is the volume of nitrogen adsorbed at P/P° tends to unity. The values of r were determined from the equation

$$\bar{r} \left(\text{\AA} \right) = \frac{2V_p}{S_{\text{BET}} \times 10^4 \text{ A}}$$

RESULTS AND DISCUSSION

XRD Investigation of Different Solids: The XRD diffractograms of pure and doped solids calcined at 500°C were determined in Figs. 1 and 2. Figs. 1 and 2 show the following. (i) No single diffraction peak of Cr₂O₃ phase was detected in the diffractograms of different

Table 1: XRD data of pure and variously doped Fe Cr solids calcined at 500°C

Solid	Phases present	Crystallite Size (nm)	Degree of Crystallinity (a.u.)*
Fe Cr	γ -Fe ₂ O ₃	33	16
	α -Fe ₂ O ₃	20	6
Fe Cr La ₁	γ -Fe ₂ O ₃	51	9
	α -Fe ₂ O ₃	33	2
Fe Cr La ₁	γ -Fe ₂ O ₃	36	13
	α -Fe ₂ O ₃	24	4
Fe Cr La ₁	γ -Fe ₂ O ₃	8	21
	α -Fe ₂ O ₃	4	9
Fe Cr Ce ₁	γ -Fe ₂ O ₃	11	30
	α -Fe ₂ O ₃	5	19
Fe Cr Ce ₁	γ -Fe ₂ O ₃	9	37
	α -Fe ₂ O ₃	4	20
Fe Cr Ce ₁	γ -Fe ₂ O ₃	24	26
	α -Fe ₂ O ₃	8	56

* The peak area of the main diffraction peaks of crystalline phases present was taken as a measure of degree of crystallinity of this phase.

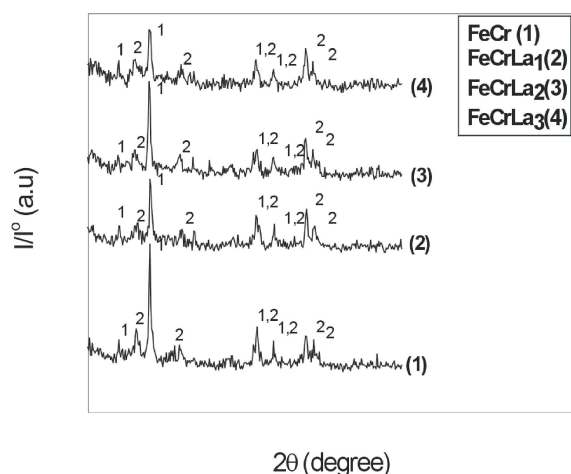


Fig. 1: X-ray diffractograms of (1) Fe Cr, (2) Fe Cr La, (3) Fe Cr La₂ and (4) Fe Cr La₃ calcined 500°C, lines 1 denote to γ Fe₂O₃, lines 2 correspond to α Fe₂O₃.

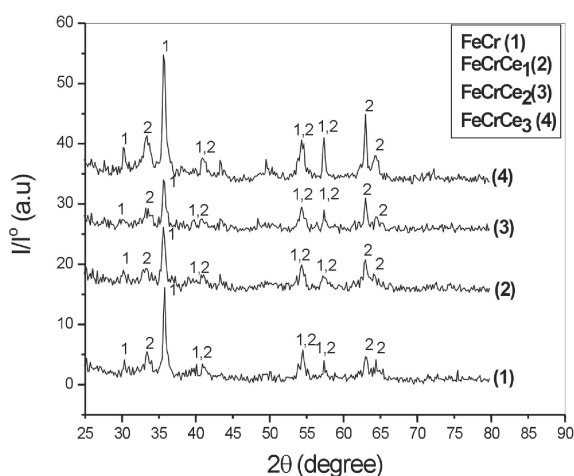


Fig. 2: X-ray diffractograms of (1) Fe Cr, (2) Fe Cr Ce, (3) Fe Cr Ce₂ and (4) Fe Cr Ce₃ calcined 500°C, lines 1 denote to γ Fe₂O₃, lines 2 correspond to α Fe₂O₃.

investigated solids. This finding might suggest the possible existence of chromic oxide as a very poorly crystalline phase and/or its dissolution in Fe₂O₃ lattice forming solid solution [14]. (ii) Pure and variously doped Fe₂O₃-Cr₂O₃ solids calcined at 500°C consisted of a mixture nanosized α and γ Fe₂O₃.

The crystallite size and degree of crystallinity of α -Fe₂O₃ phase present in different solids calcined at various temperatures are given in Table 1. It is clearly shown from this Table that: (i) α - and γ -Fe₂O₃ present in different mixed solids existed as nanosized solids measuring a crystallite size varying between 8 and 33 nm. (ii) Doping the system investigated with 0.75 or 1.5 mol% La₂O₃

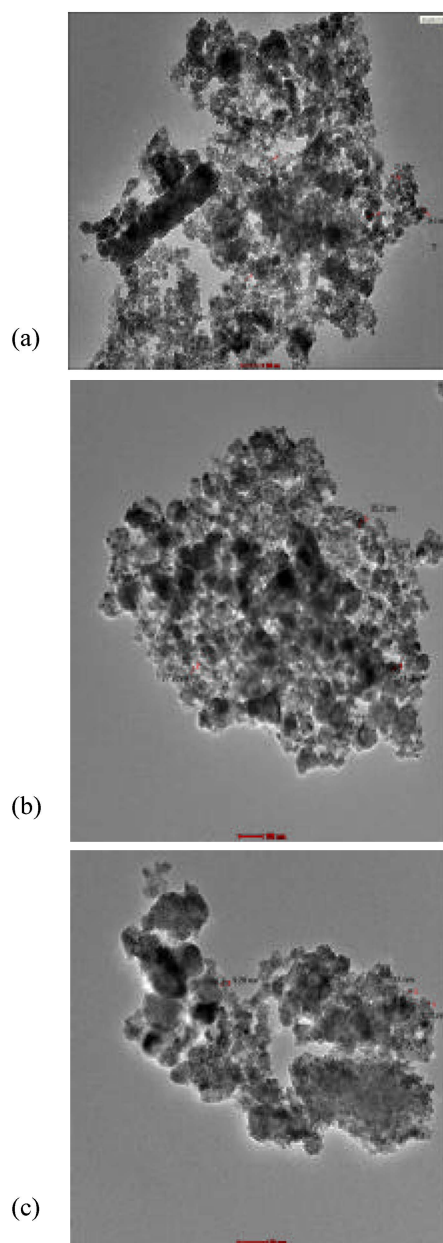


Fig. 3: TEM images of (a) FeCr, (b) Fe Cr La₃ and (c) Fe Cr Ce₃ calcined at 500°C

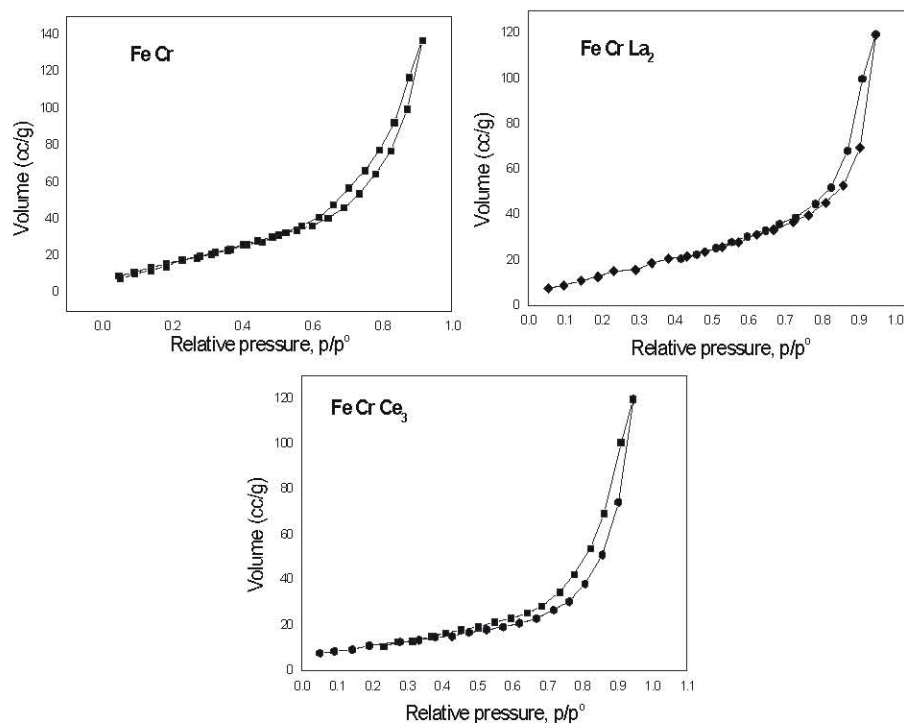
increased the crystallite size. (iii) Doping the system investigated with CeO₂ and the highest concentration of La₂O₃ decreased the crystallite size and increases the degree of crystallinity of the solids.

Transmission Electron Micrographs Analysis (TEM):

The TEM images of pure and doped solids calcined at 500°C were determined and given in Fig. 3. Data revealed that the particle size measured with TEM (transmission electron micrograph), ranged from 4-36 nm,

Table 2: Surface and bulk molar composition of pure and doped Fe Cr system calcined at 500°C.

Solid		Featom %	Cratom %	Oatom %	Laatom %	Ceatom %
Fe Cr	Surface	29.49	9.19	61.32	--	--
	bulk	30	10	60	--	--
Fe Cr La ₁	Surface	29	12.03	58.7	0.27	--
	bulk	29.8	9.93	60	--	--
Fe Cr La ₂	Surface	29.1	12.51	57.91	0.46	--
	bulk	29.6	9.85	60	0.59	--
Fe Cr La ₃	Surface	31.07	13.73	54.41	0.79	--
	bulk	29.31	9.71	60	1.17	--
Fe Cr Ce ₁	Surface	28.12	13.30	58.42	--	0.17
	bulk	29.9	9.96	60.02	--	0.15
Fe Cr Ce ₂	Surface	22.19	9.40	68.09	--	0.32
	bulk	29.7	9.9	60.06	--	0.29
Fe Cr Ce ₃	Surface	29.83	11.4	58.14	--	0.63
	bulk	29.5	9.82	60	--	0.59

Fig 4: N₂- adsorption-desorption isotherms of (a) Fe Cr₁, (b) Fe Cr La₁ and Fe Cr Ce₃ calcined at 500°C

is in a reasonable agreement with that determined through the use of the Scherrer equation using x-ray line broadening profile analysis as given in Table 1. In fact, the calculated crystallite size of α - and γ - Fe₂O₃ varied between 4 and 51 nm.

Energy Dispersive X-Ray (EDX) Analysis of Various Solids: EDX investigation of pure and doped Fe₂O₃-Cr₂O₃ system calcined at 500°C was carried out. The relative atomic abundance of Fe, Cr, La, Ce and oxygen species

present in the uppermost surface layers of different solids investigated is given in Table 2. It is well known that EDX technique supplies the effective atomic concentration of different constituents of the solids investigated present on their top surface layers. Also, enclosed in Table 1 are the values of atomic abundance of Fe, Cr, La, Ce and oxygen present in the bulk (calculated) of various solids. Examination of Table 1 shows that (i) the surface atomic Fe/Cr ratio in pure and doped solids calcined at 500°C is strongly dependent on dopant concentrations.

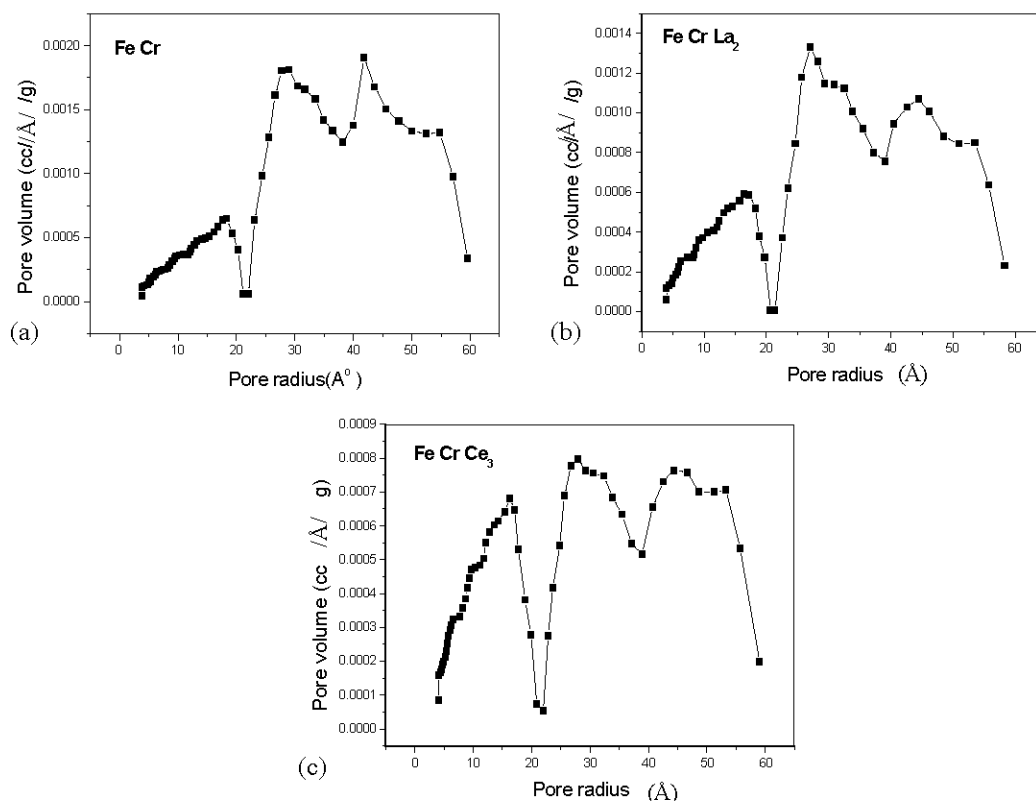


Fig 5: Pore volume distribution curves of (a) Fe Cr, (b) Fe Cr₂ La₂ and (c) Fe Cr Ce₃ adsorbents calcined at 500°C

Table 3: Surface characteristics of 0.75Fe₂O₃-0.025Cr₂O₃ solids and solids doped with different amounts of La₂O₃-or CeO₂-doped calcined at 500°C

Adsorbent	SBETm ² /g	Stm ² /g	Total pore volume V _p , ml/g	Mean pore radius r- Å	BET-C constant
Fe Cr	67	65	0.215	64	19
+ Fe Cr La ₁	54	50	0.236	86	38
+ Fe Cr La ₂	79	80	0.294	74	12
+ Fe Cr La ₃	57	57	0.183	64	18
+ Fe Cr Ce ₁	49	50	0.172	60	11
+ Fe Cr Ce ₂	46	45	0.363	89	25
+ Fe Cr Ce ₃	38	41	0.192	99	71

(ii) The surface and bulk compositions of pure mixed oxides are very closed to each other. (iii) La₂O₃ doping increased the surface concentration of Cr species to an extent proportional to the amount of dopant added. The maximum increase attained to 49%. (iv) The presence of smallest amount of CeO₂ (0.75mol%) increased the surface concentration of Cr species which decreased progressively upon increasing the amount of ceria added falling to a value close to that measured for pure sample.

Surface Properties of Different Prepared Solids:

The surface characteristics system calcined at 500°C were determined by analysis of N₂ adsorption isotherms measured at -196°C over various adsorbents. These

isotherms, not given, belong to type II of BDDT classification. These characteristics include specific surface area (S_{BET}), total pore volume (V_p), mean pore radius (r̄) and pore volume distribution curves (Δv/Δr). The S_{BET} values were determined from linear portion of the BET equation. Another series of specific surface area (S_t) was determined from V_{t-1} plots constructed using suitable standard t-curves depending on the values of the BET- C constant. The t- curve of deBoer was used in constructing the different V_{t-1} plots. Fig. 4 depicts nitrogen adsorption-desorption isotherms of (Fe Cr, Fe Cr La₂ and Fe Cr Ce₃) calcined at 500°C. These isotherms belong to type II of Brunauer classification and having hysteresis loops of different areas closing at p/p° of about 0.2. The hysteresis

loops of different investigated adsorbents indicate clearly the porous nature of the different solids. The pore volume distribution curves ($\Delta v/\Delta r$) of (Fe Cr, Fe Cr La₂ and Fe Cr Ce₃) preheated at 500°C were determined and illustrated in Fig. 5. These curves show, in most cases multimodal distribution of pores present. The values of most probable hydraulic pore radius lies between 18 and 55 Å depending on nature of dopant and its concentration.

Examination of Table 3 reveals the following (i) The values of S_{BET} and St for all adsorbents investigated are close to each other which justifies the correct choice of standard t-curve used in pore analysis and indicates the absence of the ultramicro pores. (ii) Pure and doped solids were measured specific surface area (S_{BET}) which decreased upon doping either with La₂O₃ or CeO₂. The decreased was however more pronounced for the solids doped with CeO₂. The decrease attained 43%. This drop could be tentatively attributed to location of some of La₂O₃ or CeO₂ added in the pores of the heavily doped sample leading to an effective blocking of some of their pores decreasing thus its specific surface area which is attributed to that most of the active compositions enter into the micro-pore of the support and stock into some tiny pores [15]. Also this decreased can be attributed to La₂O₃ preventing sintering of Fe₂O₃ particles [16]. (v) All adsorbents investigated are mesoporous solids.

CONCLUSIONS

The Following Are the Main Conclusions That May Be Drawn from the Obtained Results:

- Nanosized Fe₂O₃ and Cr₂O₃ mixed oxides were prepared by heating their co-precipitated mixed hydroxides at 500°C.
- Ferric oxide present in different solids existed as nanosized α - and γ - Fe₂O₃ phases.
- The effects of CeO₂ and La₂O₃ doping on surface compositions, morphology and surface characteristics of ferric chromic mixed oxides were investigated.
- La₂O₃ and CeO₂-doping increased the surface concentration of chromium species.
- Doping either with CeO₂ or La₂O₃ decreased the S_{BET} of the system investigated.

REFERENCES

1. Noguera, C., 1996. Physics and Chemistry at Oxide Surface Cambridge University Press: Cambridge, UK.,
2. Kung, H.H., 1989. Transition Metal Oxides Surface Chemistry and Catalysis. Elsevier: Amsterdam.,
3. Henrich, V.E. and P.A. Cox, 1994. The surface Chemistry of Metal Oxides, Cambridge University Press: Cambridge, UK.
4. Wells, A.F., 1987. Structural Inorganic Chemistry. 6th Ed.; Oxford University Press: New York,
5. Harrison, W.A., 1989. Electronic Structure and the Properties of Solids. Dover: New York,
6. Wyckoff, R.W.G., 1964. Crystal Structures. 2nd Ed. Wiley, New York,
7. Fernandez-Garcia, M., A. Martinez-Arias, J.C. Hanson and J.A. Rodriguez, 2004. Chem. Rev., 104: 1044.
8. Ozkan, U.S. and R.B. Watson, 2005. The structure-function relationships in selective oxidation reactions over metal oxides. Catalysis Today, 100(1-2): 101-114
9. Moser, W.R., 1996. Advanced Catalysts and Nanostructure Materials. Academic Press, New York,
10. Vatden, M., X. Lai and D.W. Goodman, 1998. Sci., 281: 1647.
11. McCrea, K.R., J.S. Parker and G.A. Somorjai, 2002 J. Phys. Chem. B., 106: 10854.
12. Ahmadi, I.S., Z.L. Wang, T.C. Green, A. Henglein and M.A. El-Sayed, 1996. Sci., 272: 1924.
13. Cullity, B.D., 1978. Elements of X-ray Diffraction, Addison-wesely Publishing Cos, Second edition, Addison-Wesley, Reading, MA., pp: 102.
14. Gamil, A., El-Shobaky, A.I Ahmed, Hassan M.A. Hassan and S.H.E. El-Shafey, 2010. Egypt. J. Chem., 53(1): 37-59.
15. Gamil A., El-Shobaky, A.I Ahmed, Hassan M.A. Hassan and S.H.E. El-Shafey, 2011. Effects of K₂O-Li₂O doping on surface and catalytic properties of Fe₂O₃/Cr₂O₃ system J. Alloys and Compounds, 509: 1314-1321.
16. Nanping Hua, Haitao Wang, Yukou Du, Ming Shen and Ping Yang, 2005. Catalysis Communications, 6: 491-496.