

Effects of Ferric and Chromic Salts in Physicochemical, Surface and Catalytic Properties of Pure and Doped Fe₂O₃-Cr₂O₃ System

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FERRIC/CHROMIC mixed oxides having the formula 0.85 Fe₂O₃: 0.15 Cr₂O₃ were obtained by thermal decomposition of the mixed hydroxides prepared from mixed nitrate and sulphate solutions using NH₄OH. Pure mixed hydroxides were heated at 500°C. The doped solids were prepared by treating the precipitated hydroxides with different amounts of Li₂O and K₂O (0.5, 0.75 and 1.5 mol %) followed by calcination at 500°C. The techniques employed were XRD, N₂-adsorption and oxidation of CO by O₂ at 200-300°C. The results revealed that pure and doped systems consisted of nanocrystalline phases having crystallite size varying between 8-64 nm depending on the nature of ferric and chromic salts used and dopant concentration. Pure mixed solids consisted of a mixture of α and γ -Fe₂O₃ phase whose crystallite size decreases by increasing the dopant concentrations. K₂O-doping of the investigated systems resulted in the formation of K₂FeO₄ together with ferric oxide phases. Li₂O-doping (0.5 and 0.75 mol %) led to the formation of LiFe₅O₈ together with γ -Fe₂O₃ phase. However, the heavily Li₂O-doped samples consisted entirely of LiFe₅O₈. The S_{BET} of pure system prepared from ferric and chromic sulphates measured higher S_{BET} values as compared to those prepared from mixed nitrates, whereas K₂O-doping decreased the S_{BET}. On the other hand, Li₂O-doping exerted a measurable increase in the S_{BET}. The increase was however, more pronounced in case of the system prepared by using mixed sulphate solutions. The catalytic activity was higher in case of the catalysts prepared by using mixed nitrates as compared to the catalysts prepared by using mixed sulphate solutions. The doping process led to a progressive significant increase in the catalytic activity. The increase was, however, much more pronounced in case of the catalysts prepared from the mixed sulphates. The maximum increase in the k_{200°C} value due to doping with 1.5 mol % K₂O attained 30.8% and 285% for the solids prepared from mixed nitrates and mixed sulphates, respectively. These values measured 27% and 241% in case of the catalysts prepared by using mixed nitrate and mixed sulphate solutions, respectively. The doping process did not affect the mechanism of the catalyzed reaction but increased the concentrations of active sites involved in catalytic reaction without changing their energetic nature.

Keywords: Nanocrystalline, Fe₂O₃-Cr₂O₃, Doping and Catalytic behavior.

The catalytic oxidation of CO by O₂ is considered as an effective way to minimize air pollution and is being utilized in an increasing number of practical applications⁽¹⁻⁵⁾. A number of catalysts have been studied in the past decades. It was found that the

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nanoparticles are much more effective as carbon monoxide catalysts than the big-sized solids. Iron-based compounds are widely used in heterogeneous catalysis either pure or in mixtures with other elements to catalyze many reactions. Volatile organic compounds (VOCs) are the main source of air pollutants, emitted from many industrial processes and transportation activities ⁽⁶⁾. Iron oxide, α -Fe₂O₃, has drawn enormous attention due to a wide range of applications such as red pigments ⁽⁷⁾, catalysts ⁽⁸⁾, gas sensor ⁽⁹⁾ and can be used as a catalyst of carbon monoxide oxidation in the presence and absence of oxygen ⁽¹⁰⁾. These applications were focused on the particle size of order of nanometer. So, superfine Fe₂O₃ nanoparticles were evaluated as a catalyst for oxidation of carbon monoxide ⁽¹¹⁾.

The catalytic activity of a large variety of catalysts can be modified by various methods. The doping of different catalytic systems can be considered as an important parameter in modifying their catalytic activities. The doping with certain foreign oxides such as Li₂O, K₂O or ZnO hinders the metal oxide-support interactions thus increasing the stability of catalytically active constituents ⁽¹²⁻¹⁷⁾.

The present work reports the results of a study on the influence of effects of ferric and chromic salts in physicochemical, surface and catalytic properties of pure and doped Fe₂O₃-Cr₂O₃ system. The techniques employed were XRD, adsorption of N₂ at -196°C besides catalysis of CO oxidation by O₂ at different temperatures between 200-300°C.

Experimental

Materials

Iron (III) and chromium (III) mixed hydroxides samples were prepared by using co precipitation method. This process was carried out using an aqueous solution of ferric and chromic mixed nitrate or mixed sulphate solutions at 50°C and at a pH 8 in presence of conc. NH₄OH solution subjected to bubbling by a current of dry air free from CO₂ flowing at a rate of 20 ml/min. The salts used were of analytical grade and supplied by BDH Company and their amounts were calculated in a manner that Fe/Cr ratio was 0.85: 0.15. The molecular formula of the prepared calcined mixed solids was 0.85Fe₂O₃:0.15Cr₂O₃. The carefully washed mixed hydroxides were dried at 120°C then heated at 500 °C for 4hr.

Three Li₂O-doped and three K₂O-doped samples were prepared by taking calculated amounts of pure mixed hydroxides with calculated amounts of Li or K nitrates dissolved in the least amount of distilled water sufficient to make pastes. The pastes were dried at 120°C till constant weight then calcined in air 500°C for 4hr. The dopant concentrations were 0.5, 0.75 and 1.5 mol % Li₂O or K₂O.

Pure mixed solids were designated as Fe Cr and Fe Cr-S for the solids prepared by using mixed nitrate and mixed sulphate solutions, respectively. The solids prepared by using mixed nitrate solutions and doped with K₂O and Li₂O were designated as Fe Cr K₁, Fe Cr K₂, Fe Cr K₃ and Fe Cr Li₁, Fe Cr Li₂ and Fe Cr Li₃. These solids contained 0.5, 0.75 and 1.5 mol% K₂O or Li₂O, respectively. The solids prepared by using mixed sulphate solutions and doped with K₂O or Li₂O were designated as Fe Cr-S K₁, Fe Cr-S K₂, Fe Cr-S K₃ and Fe Cr-S Li₁, Fe Cr-S Li₂ and Fe Cr-S Li₃ containing 0.5, 0.75 and 1.5 mol%, respectively.

*Techniques**X-ray diffraction (XRD) analysis of different mixed oxides*

X-ray powder diffractograms of various investigated solids 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⁽¹⁸⁾.

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

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 in radian and θ is the diffraction angle.

Measurements of different surface characteristics

The different surface characteristics of various adsorbents were determined from analysis of nitrogen adsorption isotherms carried out at -196 °C over various solids. These characteristics include specific surface areas (S_{BET}), total pore volume (V_p), mean pore radius (\bar{r}) and pore volume distribution curves ($\Delta v/\Delta r$). 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_t -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 (\bar{r}) and pore volume distribution curves ($\Delta v/\Delta r$) 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 $V_p = 15.45 \times 10^{-4} \times V_{\text{st}}$ cm³/g, where V_{st} is the volume of nitrogen adsorbed at P/P° tends to unity. The values of \bar{r} were determined from the equation

$$\bar{r}(\text{Å}) = \frac{2V_p}{S_{\text{BET}}} \times 10^4 \text{ Å}$$

Apparatus for measuring the catalytic activity

Catalytic oxidation of CO by O₂ over the various catalysts was carried out at temperatures in the range of 200–300°C using a static method. A stoichiometric mixture of CO and O₂ (CO + 1/2 O₂) at a pressure of 2 Torr was used. A fresh catalyst sample (200 mg) was employed for each kinetic experiment and was activated by heating under a reduced pressure of 10⁻⁶ Torr for 1 hr at 250°C. The CO₂ produced was removed from the reaction system by freezing in a liquid nitrogen trap. The kinetics of the catalytic reaction was monitored by measuring the pressure of the reacting gases at different time intervals until no change in pressure was attained. The percentage decrease in pressure at a given time determines the percentage conversion

of the catalytic reaction at that time. The saturation vapour pressure of CO at -196°C being 160 Torr makes its liquefaction at that pressure improbable under the employed conditions (2 Torr) ⁽¹⁹⁾.

Results and Discussion

XRD investigation of pure and variously K₂O and Li₂O-doped solids prepared from mixed nitrates and calcined at 500°C

The XRD diffractograms of pure and variously doped solids calcined at 500°C were determined. The obtained diffractograms of pure solids and those doped with 0.5, 0.75 and 1.5 mol% K_2O are illustrated in Fig. 1-a. Examination of Fig 1-a shows the following: (i) Pure and variously K_2O -doped samples consisted of nanosized phases measuring crystallite size varying between 9-48 nm for ferric oxide phases. (ii) Doping the investigated system with K_2O followed by calcination at 500°C led to the formation of nanosized K_2FeO_4 measuring a crystallite size that increases by increasing the dopant concentration and varies between 8 and 64 nm. (iii) Pure and doped solids consisted of a mixture of α and γ - Fe_2O_3 phases together with the potassium ferrite phase. Figure 1-b shows the diffractograms of pure and variously Li_2O -doped solids calcined at 500°C . Inspection of Fig. 1-b shows the following: (i) Similarly as the case of K_2O -doped solids, the 0.5 and 0.75mol% Li_2O -doped samples consisted of a mixture of nanocrystalline α and γ - Fe_2O_3 phases together with nanocrystalline LiFe_5O_8 whose crystallite size increases slightly by increasing the amount of Li_2O present. (ii) The heavily Li_2O -doped samples consisted entirely of LiFe_5O_8 phase. However, one can not exclude the presence of ferric oxides in a very poorly crystalline state that could not be detected by XRD investigation.

XRD investigation of pure and variously K₂O and Li₂O-doped solids prepared from mixed sulphates and calcined at 500°C

The XRD diffractograms of pure and variously doped solids calcined at 500°C were determined. The obtained diffractograms are illustrated in Fig. 2-a. Examination of Fig 2-a shows the following: (i) Pure and variously K_2O -doped samples consisted of nanocrystalline phases measuring crystallite size varying between 15-42 nm for ferric oxide phase. (ii) K_2O -doping (0.5- 1.5mol %) conducted at 500°C led to the appearance of γ - Fe_2O_3 as a major phase. It is known that the crystallite of γ - Fe_2O_3 generally possess an imperfect cubic spinel structure, which is different from that of α - Fe_2O_3 , hexagonal structure. The imperfect γ - Fe_2O_3 spinel allows promoter such as Cr to be incorporated into vacant sites in the γ - Fe_2O_3 resulting in less sintering of active phase in the catalysts consisting of γ - Fe_2O_3 than those consisting of α - Fe_2O_3 employed under identical operating conditions ⁽²⁰⁾. (iii) Doping the system investigated with 0.5- 1.5 mol% K_2O followed by calcination at 500°C led to the appearance of new diffraction lines at $d= 2.97\text{\AA}$ and 2.94\AA corresponding to K_2FeO_4 , JCPDS-ICDD 25-652.

Figure 2-b shows the diffractograms of pure and variously Li_2O doped solids calcined at 500°C . Inspection of Fig. 2-b shows the following: (i) Pure and variously Li_2O -doped samples consisted of nanocrystalline phases measuring crystallite size varying between 9-48 nm for ferric oxide phase. (ii) Similarly, as the case of K_2O -doped

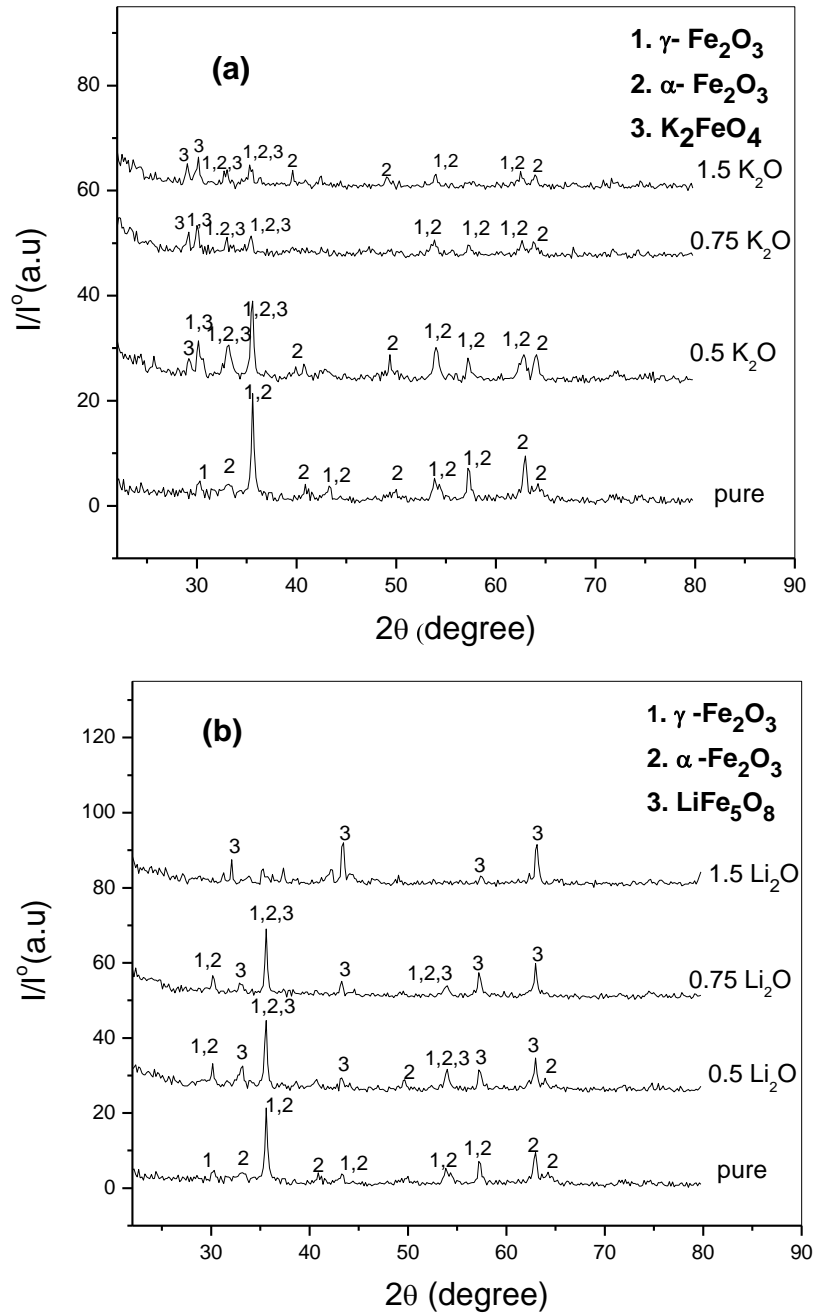


Fig. 1. X-ray diffractograms of pure and 0.5, 0.75 and 1.5 mol%: (a) K_2O and (b) Li_2O -doped samples prepared by using mixed nitrates and calcined at 500°C .

solids, the 0.5 and 0.75 mol% Li_2O -doped system consisted of a mixture of nanocrystalline α and γ - Fe_2O_3 phases together with nanocrystalline LiFe_5O_8 whose crystallite size increases slightly by increasing the amount of Li_2O present. (ii) However doping the mixed solid samples with 1.5 mole % Li_2O followed by calcination at 500°C led to the disappearance of both α - and γ - Fe_2O_3 phases and LiFe_5O_8 was the only phase present. However, one can not exclude the presence of ferric oxides in a very poorly crystalline state that could not be detected by XRD investigation.

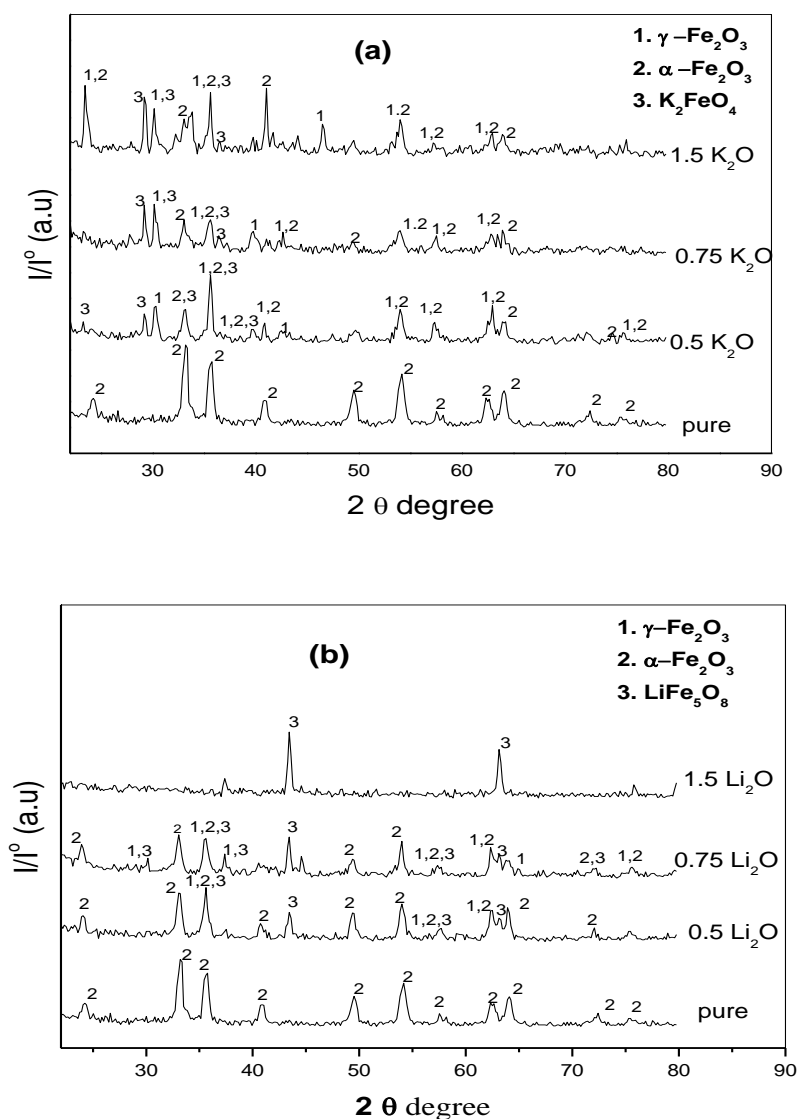


Fig. 2. X-ray diffractograms of pure and 0.5, 0.75 and 1.5 mol%: (a) K_2O and (b) Li_2O -doped samples prepared by using mixed sulphates solution and calcined at 500°C .

The crystallite size and degree of crystallinity of different crystalline phases in K_2O and Li_2O -doped solids calcined at $500^\circ C$ for the solids prepared from mixed nitrates and sulphates, respectively, are given in Tables 1 & 2. It is clearly shown from these tables that K_2O and Li_2O -doping (0.5- 1.5 mol%) conducted at $500^\circ C$ increased the degree of crystallinity and crystallite size of phases present which consisted of a mixture of alpha and gamma ferric oxides together with K_2FeO_4 and $LiFe_5O_8$ phases.

TABLE 1. XRD data of Fe Cr, Fe Cr K_1 , Fe Cr K_2 , Fe Cr K_3 and Fe Cr Li_1 , Fe Cr Li_2 , Fe Cr Li_3 solids prepared by thermal decomposition at $500^\circ C$ of their mixed hydroxides prepared from ferric and chromic mixed nitrates.

Catalyst	Phases present	Crystallite size (nm)	Degree of crystallinity (a.u.)*
Fe Cr	γ - Fe_2O_3	38	22
	α - Fe_2O_3	9	5
Fe Cr K_1	γ - Fe_2O_3	43	18
	α - Fe_2O_3	19	9
	K_2FeO_4	22	8
Fe Cr K_2	K_2FeO_4	43	7
	α - Fe_2O_3	48	4
	γ - Fe_2O_3	39	4
Fe Cr K_3	γ - Fe_2O_3	40	13
	K_2FeO_4	64	12
	α - Fe_2O_3	15	8
Fe Cr Li_1	γ - Fe_2O_3	39	13
	α - Fe_2O_3	31	12
	$LiFe_5O_8$	50	6
Fe Cr Li_2	γ - Fe_2O_3	29	12
	$LiFe_5O_8$	63	11
	α - Fe_2O_3	24	10
Fe Cr Li_3	$LiFe_5O_8$	53	16

* The peak area of the main diffraction lines of α - and γ - Fe_2O_3 was taken as a measure of degree of crystallinity of these phases.

Detection of potassium and lithium ferrite phases in variously doped solids in spite of the very small amounts of the dopant added (0.88 and 0.87 wt% Li_2O and K_2O in the heavily doped samples). These values are far below the detection limit of the X-ray diffractometer employed. This finding suggested clearly the enriched presence of the dopant substrate in the top surface layers of the dopant solids ⁽²¹⁾. The enriched presence of the dopant substrate might be tentatively attributed to the fact that the doped solids were prepared by wet impregnation method and not by co-precipitation method. The disappearance of ferric oxide phases could be tentatively attributed to the solid-solid interaction between K_2O and-or Li_2O and all surface ferric oxides leading to the formation of potassium and lithium ferrite phases.

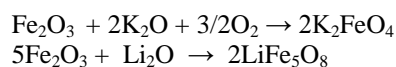


TABLE 2. XRD data of Fe Cr, Fe Cr K₁, Fe Cr K₂, Fe Cr K₃ and Fe Cr Li₁, Fe Cr Li₂, Fe Cr Li₃ solids prepared by thermal decomposition at 500°C of their mixed hydroxides prepared from ferric and chromic mixed sulphates.

Catalyst	Phases present	Crystallite Size (nm)	Degree of Crystallinity (a.u.)*
Fe Cr-S	α -Fe ₂ O ₃	22	12
Fe Cr-S K ₁	γ -Fe ₂ O ₃	37	16
	K ₂ FeO ₄	34	8
	α -Fe ₂ O ₃	25	7
Fe Cr-S K ₂	K ₂ FeO ₄	69	11
	γ -Fe ₂ O ₃	39	7
	α -Fe ₂ O ₃	42	8
Fe Cr-S K ₃	γ -Fe ₂ O ₃	40	13
	K ₂ FeO ₄	64	12
	α -Fe ₂ O ₃	15	8
Fe Cr-S Li ₁	γ -Fe ₂ O ₃	39	13
	α -Fe ₂ O ₃	31	12
	LiFe ₅ O ₈	50	6
Fe Cr-S Li ₂	γ -Fe ₂ O ₃	29	12
	LiFe ₅ O ₈	63	11
	α -Fe ₂ O ₃	24	10
Fe Cr-S Li ₃	LiFe ₅ O ₈	53	16

*The peak area of the main diffraction lines of α - and γ -Fe₂O₃ was taken as a measure of degree of crystallinity of these phases.

Surface properties of pure and doped solids prepared from ferric and chromic mixed nitrates

The different surface characteristics of pure and variously doped adsorbents 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 (\bar{r}) and pore volume distribution curves ($\Delta v/\Delta r$). 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 of de Boer⁽²²⁾.

The results obtained are given in Table 3. Examination of Table 3 shows the following: (i) The values of S_{BET} and S_t of 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 ultra micro pores. (ii) Doping the system investigated with the smallest amount of K₂O led to a measurable decrease in the S_{BET} values which remained almost unchanged by increasing the dopant concentration. (ii) K₂O-doping resulted in a progressive significant decrease in \bar{r} (an effective progressive pore narrowing) which decreased from 83 to 20 Å in presence of 1.5 mol% K₂O. This decrease might be expected to increase the S_{BET}. This expectation has not been verified experimentally. So, the observed decrease in S_{BET} due to doping with K₂O might be

tentatively attributed to the considerable drop in the V_p value due to this process. In fact, V_p decreases from 0.217 to 0.036 up on doping with 1.5 mol% K_2O .

TABLE 3. Surface characteristics of pure and variously K_2O and Li_2O -doped Fe_2O_3 - Cr_2O_3 solids prepared by thermal decomposition at $500^\circ C$ of their mixed hydroxides prepared from ferric and chromic mixed nitrates.

Adsorbent	S_{BET} m^2/g	S_t m^2/g	Total pore volume V_p , cc/g	Mean pore radius r Å	BET-C constant
Fe Cr	52	54	0.21658	83	152
Fe Cr K_1	37	35	0.0555	30	3
Fe Cr K_2	35	32	0.03697	21	3
Fe Cr K_3	37	33	0.03635	20	3
Fe Cr Li_1	61	58	0.1106	36	5
Fe Cr Li_2	103	99	0.16243	32	4
Fe Cr Li_3	7.4	7.2	0.0242	65	-9

Examination of surface characteristics of Li_2O -doped solids (*c.f.* Table 3) shows the following: (i) The values of S_{BET} and S_t 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 ultra micro pores. (ii) Opposite to K_2O -doping Li_2O -doping of the system investigated (0.5 and 0.75 mol% Li_2O) resulted in a measurable significant increase in the S_{BET} ; the increase attained 98% for the sample doped with 0.75 mol% Li_2O . (iii) The increase in the dopant concentration up to 1.5 mol% led to a sudden drop in the S_{BET} . This significant decrease in the S_{BET} value in the heavily Li_2O doped sample could be discussed in terms of the considerable drop in the numbers of pores present. In fact, the V_p value decreases from 0.217 to 0.024cc/g. This dropping in the S_{BET} could be also attributed to the complete conversion of ferric oxide phases into $LiFe_5O_8$ phase.

The pore volume distribution curves ($\Delta v/\Delta r$) for pure and heavily doped adsorbents calcined at $500^\circ C$ were determined. The curves obtained are illustrated in Fig 3. These curves show multimodal distribution for pores present in pure and Li_2O -doped adsorbents. The maxima of the most probable pore radius are located at 18, 29 and 46Å for pure solid calcined at $500^\circ C$ and at 15, 18 and 54Å for 1.5 mol%-doped solid calcined at the same temperature. However, the majority of pores present in the doped adsorbent measured pore radius between 15 and 18Å . On the other hand, ($\Delta v/\Delta r$) curve of adsorbent doped with 1.5 mol% K_2O shows unimodal distribution of pores present at a value of 36Å . These findings might suggest that K_2O -doping led to the widening

of pores present. K₂O-doping shifted the value of most probable pore radius from 18, 29 Å to 36 Å. The comparison between the areas of ($\Delta v/\Delta r$) curves shows that the doping process conducted at 500°C decreased the volume of pores present. The decrease was, however, more pronounced in case of Li₂O-doping. These results agree well with the V_p values measured for pure and doped solids calcined at 500°C (*c.f.* Table 3).

Surface properties of pure and doped solids prepared from ferric and chromic mixed sulphates

The results obtained are given in Table 4. Examination of Table 4 shows the following: (i) The values of S_{BET} and S_t 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 ultra micro pores. (ii) Doping the system investigated with the smallest amount of K₂O led to a progressive measurable decrease in the S_{BET} values. This decrease reaches to about 29% , 39% and 48% for 0.5 , 0.75 and 1.5 mol% K₂O-doped samples, respectively (iii) K₂O doping resulted in a progressive significant decrease in r^- (an effective progressive pore narrowing) which decreased from 44 to 19 Å in presence of 1.5 mol% K₂O. This decrease might be expected to increase the S_{BET}. This expectation has not been verified experimentally. So, the observed decrease in S_{BET} due to doping with K₂O might be tentatively attributed to the considerable drop in the V_p value due to this process. In fact, V_p decreased from 0.193 to 0.043 cc/g upon doping with 1.5 mol% K₂O. The decrease in S_{BET} values might be also attributed to a possible location of some of K₂O in the pores of the system investigated leading to their blocking. Furthermore, the decrease in specific surface area might be also attributed to the formation of potassium ferrite. The formation of this compound might be accompanied by a significant loss in their porosity followed by a corresponding decrease in their S_{BET} values.

The surface characteristics of variously Li₂O-doped adsorbents subjected to heating at 500°C were determined. Examination of surface characteristics of Li₂O-doped solids (*c.f.* Table.4) shows the following: (i) The values of S_{BET} and S_t 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 ultra micro pores. (ii) Treatment of the investigated system with 0.5 mol% of Li₂O followed by calcination at 500°C led to an increase in its S_{BET} of about 26%. The observed increase in the S_{BET} of Fe₂O₃/Cr₂O₃ system due to doping with the smallest amount of Li₂O (0.5 mol%) could be attributed to the creation of new pores during the thermal treatment of the doped solids via liberation nitrogen oxides gases during thermal decomposition of LiNO₃ dopant added. Similar results have been reported in the case of CuO/Al₂O₃ ⁽²³⁾, CuO-ZnO/Al₂O₃ ⁽²⁴⁾ Cr₂O₃/Al₂O₃ ⁽²⁵⁾ and NiO/Al₂O₃ systems ⁽²⁶⁾. (iii) On the other hand, Li₂O-doping decreased the S_{BET} to an extent proportional to the amount of dopant added. The decrease attained 22% for the heavily doped samples. This significant decrease in the S_{BET} value in the heavily Li₂O doped sample could be discussed in terms of the considerable drop in the numbers of pores present. In fact, the V_p value decreases from 0.194 to 0.084 cc/g and could be also attributed to the complete conversion of ferric oxide phases into LiFe₅O₈ phase.

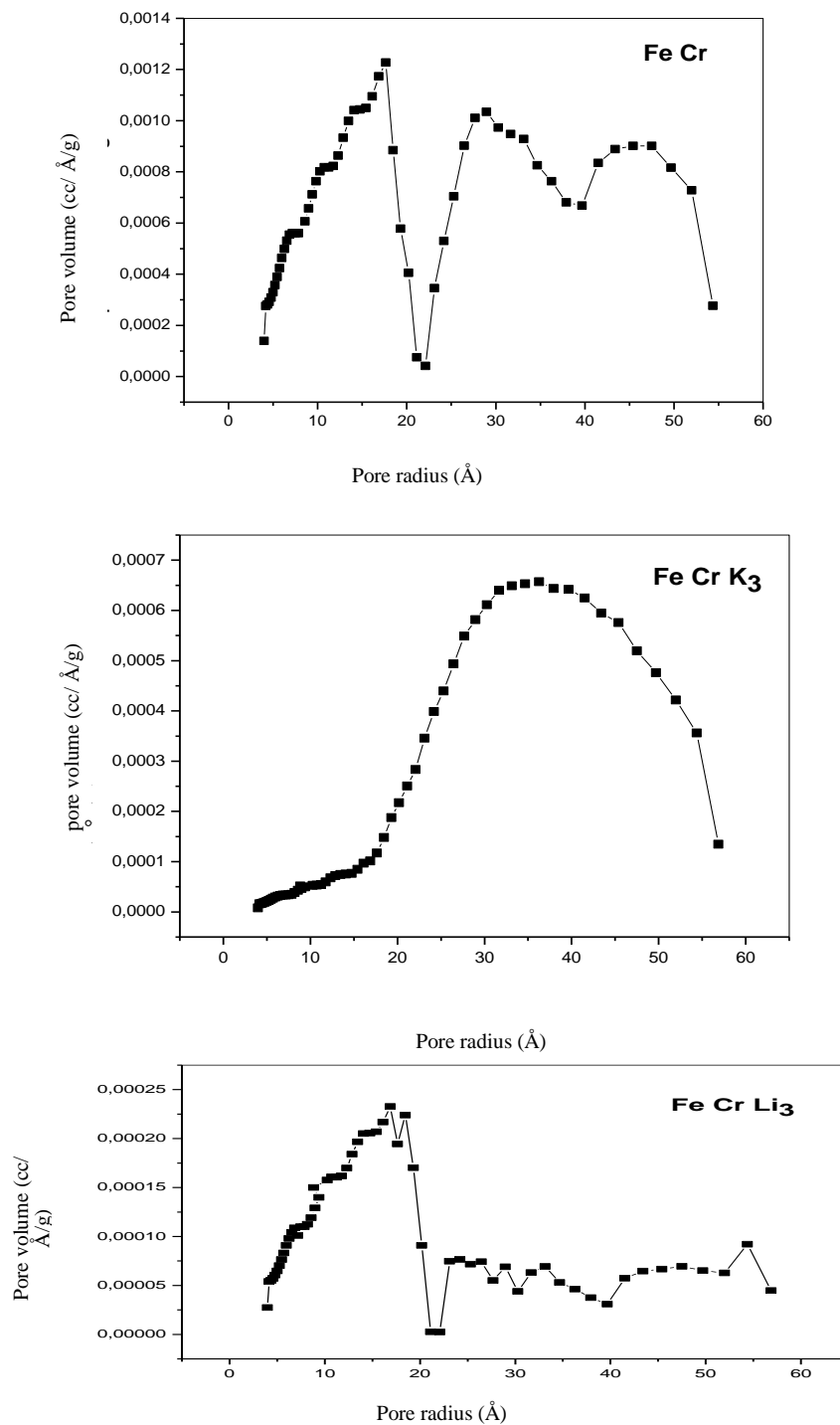


Fig. 3. Pore volume distribution curves of Fe Cr, Fe Cr K₃ and Fe Cr Li₃ samples calcined at 500°C.

TABLE 4. Surface characteristics of pure and K₂O-or Li₂O-doped Fe₂O₃- Cr₂O₃ solids prepared using thermal decomposition of their mixed hydroxides at 500°C using ferric and chromic mixed sulphates

Adsorbent	S _{BET} m ² /g	S _t m ² /g	Total pore volume V _p , cc/g	Mean pore radius r̄, Å	BET-C constant
Fe Cr	87	85	0.19352	44	1
Fe Cr-S K ₁	62	60	0.07967	26	3
Fe Cr-S K ₂	53	52	0.0881	33	2
Fe Cr-S K ₃	45	46	0.0433	19	2
Fe Cr-S Li ₁	110	112	0.25307	46	4
Fe Cr-S Li ₂	78	77	0.1067	27	3
Fe Cr-S Li ₃	68	70	0.0835	25	3

TABLE 5. Reaction rate constant per unit mass ($k \times 10^{-3} \text{ min}^{-1} \text{ g}^{-1}$) for the catalytic reaction carried out at 200-300°C over pure and Li₂O or K₂O-doped Fe₂O₃-Cr₂O₃ solids calcined at 500°C and prepared using ferric and chromic mixed nitrates.

Catalyst	Reaction temperature °C	$k \times 10^{-3}$ $\text{min}^{-1} \text{ g}^{-1}$
Fe Cr	200	7.8
	250	8.1
	300	8.9
Fe Cr K ₁	200	9
	250	10
	300	11
Fe Cr K ₂	200	9.6
	250	11.1
	300	11.2
Fe Cr K ₃	200	10.2
	250	10.8
	300	11.5
Fe Cr Li ₁	200	8.8
	250	9.3
	300	10.1
Fe Cr Li ₂	200	9.1
	250	9.7
	300	10.9
Fe Cr Li ₃	200	9.9
	250	10.1
	300	10.4

The pore volume distribution curves ($\Delta v/\Delta r$) for pure and heavily doped adsorbents calcined at 500°C were determined. The curves obtained are illustrated in Fig 4. These curves show multimodal distribution for pores present in pure and adsorbent. The maxima of the most probable pore radius are located at 18, 28 and 40 Å for pure solid calcined at 500°C. On the other hand, ($\Delta v/\Delta r$) curve of adsorbent doped with 1.5 mol% K₂O and 1.5 mol% Li₂O shows unimodal distribution of pores present at a value of 36 Å. These findings might suggest that K₂O and Li₂O-doping led to the widening of pores present. K₂O and Li₂O-doping shifted the value of most probable pore radius from 18, 28 Å to 36 Å. The comparison between the areas of ($\Delta v/\Delta r$) curves shows that the doping process conducted at 500°C decreased the volume of pores present. The decrease was, however, more pronounced in case of K₂O-doping. These results agree well with the V_p values measured for pure and doped solids calcined at 500°C (*c.f.* Table 3).

Catalytic activity of pure and variously doped solids prepared from mixed nitrates

The oxidation of CO by O₂ at 200-300°C was carried out over pure and variously doped solids calcined at 500°C. First order kinetics was observed in all cases; the slopes of the first order plots determine the values of reaction rate constant (k) measured at a given temperature over a given catalyst sample. Figure 5 shows representative first order-plots of CO oxidation by O₂ carried out at 200, 250, and 300°C over Fe Cr, Fe Cr K₃ and Fe Cr Li₃ samples calcined at 500°C. The computed k values are given in Table 5. Examination of Table 5 shows the following: k increases progressively upon increasing the amounts of Li₂O or K₂O added in the doped solids. The maximum increase in the k value due to doping with 1.5 mol% Li₂O or 1.5 mol% K₂O for the reaction carried out at 200°C attained 26.9% and 30.8%, respectively. These results clearly indicate the role of the nature of dopant in modifying the catalytic activity in CO oxidation by O₂.

The parameters which determine the catalytic activity of Fe₂O₃/Cr₂O₃ system include the concentration of catalytically active constituents on the top surface layers of treated solids and their possible interactions. The doping process might affect the number of active sites on the catalyst's surface contributing in chemisorption and catalysis of CO-oxidation by O₂. The energetic nature of these sites could be also influenced by doping. Furthermore, the mechanism of the catalytic reaction could be altered by doping.

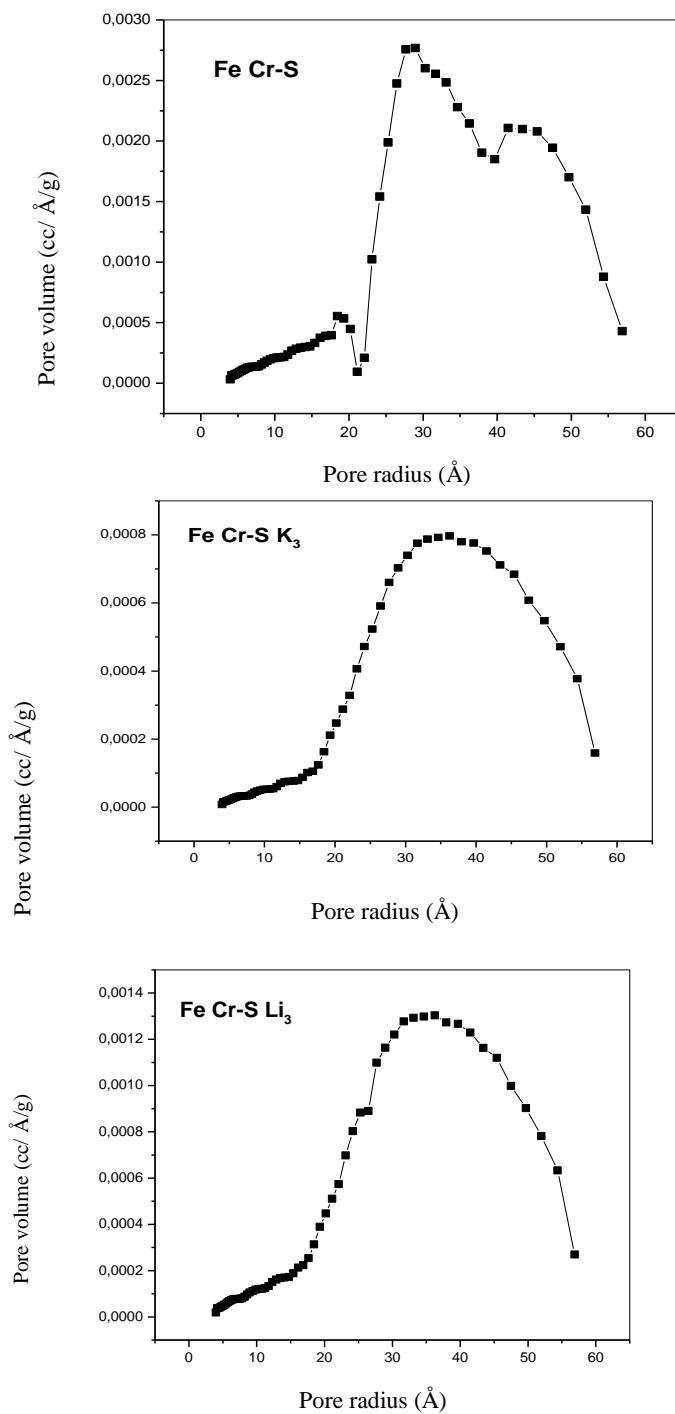


Fig. 4. Pore volume distribution curves of Fe Cr-S, Fe Cr-S K₃ and Fe Cr-S Li₃ samples calcined at 500°C.

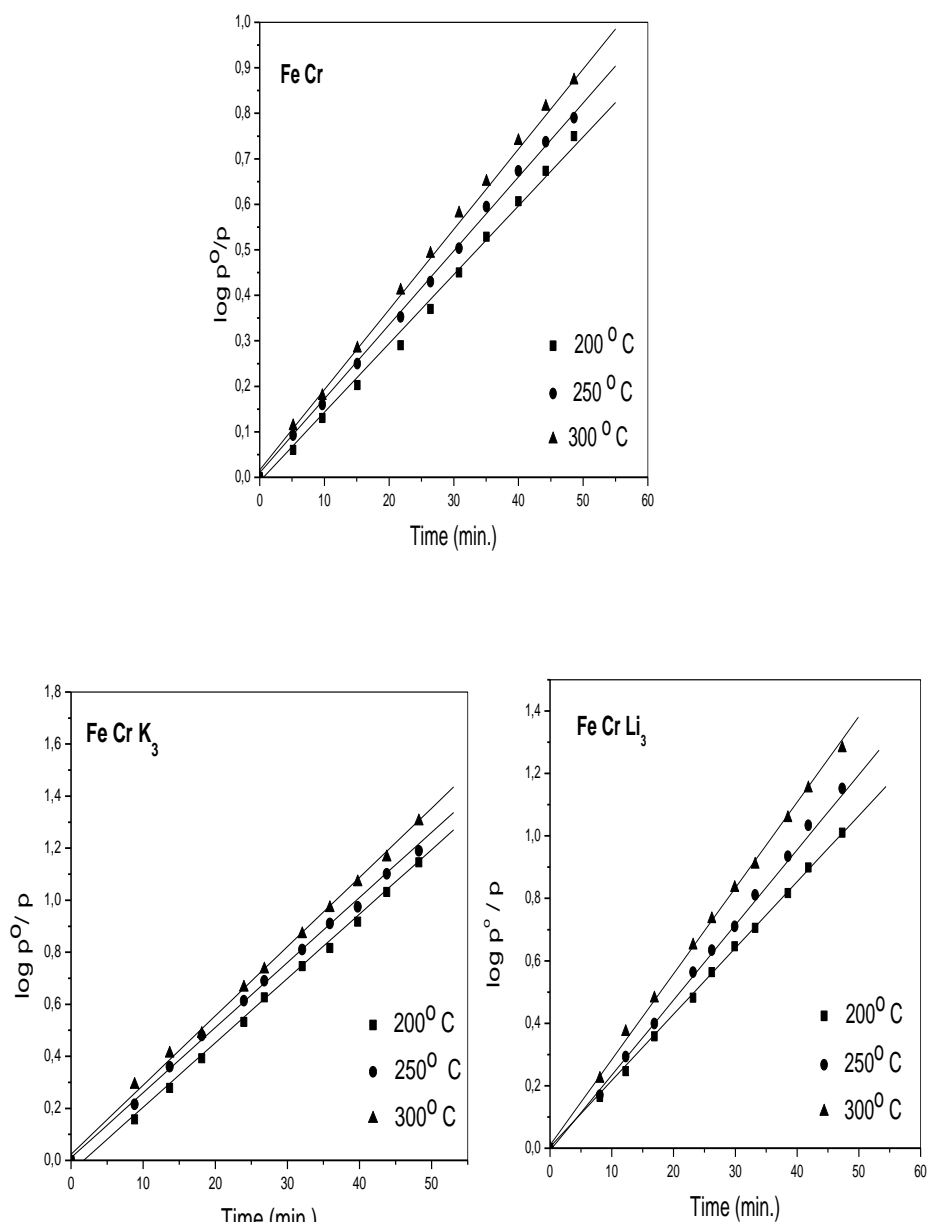


Fig. 5. First order-plots of CO oxidation by O₂ carried out at different temperatures over Fe Cr, Fe Cr K₃ and Fe Cr Li₃ systems calcined at 500°C.

The change in the catalytic activity of the system investigated due to doping either with K_2O or Li_2O could be discussed in terms of the following parameters: (i) The change in S_{BET} , (ii) The change in the crystallite size of the catalytically active constituents (some of surface Fe_2O_3), (iii) Conversion of some of α - Fe_2O_3 into γ - Fe_2O_3 , (iv) Conversion of some of Fe_2O_3 into lithium or potassium ferrites. The increase in the S_{BET} is normally accompanied by an increase in the activity. The decrease in the crystallite size of Fe_2O_3 might be also followed by an increase in the catalytic activity and vice versa. The formation of lithium or potassium ferrites (devoted with smaller activity compared to Fe_2O_3) might decrease the catalytic activity of the doped solids. In order to account for the induced change in the S_{BET} , the reaction rate constant per unit surface area (k^-) was calculated and the computed values for the reaction carried out at $200^\circ C$ were 15×10^{-5} , 24.3×10^{-5} , 27.4×10^{-5} and $27.6 \times 10^{-5} \text{ min}^{-1} \text{ m}^{-2}$ for pure sample and those doped with 0.5, 0.75 and 1.5 mol% K_2O , respectively. The maximum increase in the $k^-_{200^\circ C}$ value due to doping with 1.5 mol% K_2O reached 84%. The $k^-_{200^\circ C}$ values for the variously Li_2O -doped samples are 14.4×10^{-5} , 8.8×10^{-5} and $133.8 \times 10^{-5} \text{ min}^{-1} \text{ m}^{-2}$ for 0.5, 0.75 and 1.5 Li_2O -doped solids, respectively. So, the maximum increase in the $k^-_{200^\circ C}$ due to doping with 1.5 mol % Li_2O reached a considerable value (892%). This value might be attributed to an effective sintering of the heavily doped catalyst (the S_{BET} decreased from 52 to $4.7 \text{ m}^2/\text{g}$).

The fact that the computed k^- values for the catalytic reaction carried out at $200^\circ C$ are different from each other and indicated that the doping process increased the catalytic activity of the investigated system. The increase was, however, more pronounced in case of K_2O -doping. Furthermore, the induced changes in the specific surface area due to doping are not a dominant parameter determining the catalytic activity of the system investigated. The formation of lithium and potassium ferrites in the doped solids might decrease their catalytic activity. This expectation was not verified experimentally since an increase and not decrease in the activity was found. So, one might expect that the doping process might increase the portion of Fe_2O_3 phases involved directly in the catalytic reaction.

Effects of Li_2O and K_2O -doping on ΔE of the catalyzed reaction prepared from mixed nitrates

Determination of the apparent activation energy (ΔE) for the catalysis of CO oxidation by O_2 over pure and variously doped solids precalcined at $500^\circ C$ may shed some light on the possible change in the mechanism of the catalyzed reaction and hence gives useful information about the possible alteration in the concentration and nature of catalytically active constituents.

The values of k measured at temperatures varying between 200 and $300^\circ C$ over the variously doped solids enable ΔE to be calculated by direct application of the Arrhenius equation. The calculated values of ΔE are listed in Table 6 which also includes the values of the pre-exponential factor A of the Arrhenius equation. Table 6 shows that A changes with doping, which may be an indication of the heterogeneity of the catalyst's surface. It can be seen from the results in Table 6 that, fluctuation in ΔE and $\ln A$ values for the investigated solids were observed (*i.e.* both increase and decrease in their values).

TABLE 6 Computed activation energies (ΔE , ΔE^*) and logarithm of pre-exponential factor of the Arrhenius equation for the catalytic reaction carried out at 200-300°C over pure and Li₂O or K₂O-doped Fe₂O₃/Cr₂O₃ solids calcined at 500°C and prepared using ferric and chromic mixed nitrates.

Catalyst	ΔE (kJ/mol)	ln A	ΔE_1^* (kJ/mol)
Fe Cr	2.7	-1.88	2.7
Fe Cr K ₁	3.34	-1.54	2.8
Fe Cr K ₂	3.7	-1.43	2.9
Fe Cr K ₃	2.7	-1.58	2.9
Fe Cr Li ₁	3.0	-1.67	3.0
Fe Cr Li ₂	4.0	-1.38	2.7
Fe Cr Li ₃	1.0	-2.04	2.7

The fact that ΔE and ln A values for all solids investigated fluctuate in almost the same manner might suggest that the observed changes in ΔE values might come from corresponding change in lnA values. This speculation could be confirmed from recalculation of ΔE values for the reaction conducted over pure and variously doped solids calcined at 500°C adopting the lnA value for pure sample to all doped solids calcined at the same temperature (500°C). The recalculated values of the activation energies (ΔE^*) are given in the last column of Table 6. It is clearly shown from the data given that ΔE^* values of pure and doped solids showed almost the same values ($2.85 \pm 0.15 \text{ kJmol}^{-1}$) for the solids doped with K₂O and Li₂O. This finding suggested clearly that doping Fe₂O₃/Cr₂O₃ system either with Li₂O or K₂O followed by heating at 500°C did not much modify the activation energy of CO oxidation by O₂ over different solids but changed the concentration of active sites involved in the catalyzed reaction. This conclusion leads to an additional evidence from the plot of the equation: $A = a \exp h \Delta E$, derived on the basis of the dissipation function of active sites by their energy as a consequence of surface heterogeneity⁽²⁷⁾. $F(E_i) = a \exp h E_i$ where E_i is the energy of interaction of site 'i' with the substrate⁽²⁷⁾. The constants "h" and "a", indicate that the doping process followed by precalcination at 500°C did not change the energetic nature of the active sites but changed their concentration on the top surface layers of the treated catalysts.

Catalytic activity of pure and doped solids prepared by using mixed sulphate solutions

Figure 6 shows representative first order-plots of CO oxidation by O₂ carried out at 200, 250, and 300°C over Fe Cr-S, Fe Cr-S K₃ and Fe Cr-S Li₃ samples calcined at 500°C. The computed *k* values were calculated for different solids measured at 200, 250 and 300°C are given in Table 7. Examination of Table 7 shows the following: *k* increases progressively upon increasing the Li₂O or K₂O contents in the doped solids. The increase was, however, more pronounced in case of K₂O-doping. In fact, the maximum increase in the *k* value due to doping with 1.5 mol% K₂O or 1.5 mol% Li₂O for the reaction carried out at 200°C attained 285% and 241%, respectively. These results clearly indicate the role of the nature of dopant in modifying the catalytic activity in CO oxidation by O₂.

TABLE 7. Reaction rate constant per unit mass ($k \times 10^{-3} \text{ min}^{-1} \text{ g}^{-1}$) for the catalytic reaction carried out at 200-300°C over pure and Li₂O or K₂O-doped Fe₂O₃-Cr₂O₃ solids calcined at 500°C and prepared using ferric and chromic mixed sulphates.

Catalyst	Reaction temperature oC	$k \times 10^{-3}$ $\text{min}^{-1} \text{g}^{-1}$
Fe Cr-S	200	3.4
	250	6.5
	300	7.5
Fe Cr-S K ₁	200	11
	250	12
	300	12.9
Fe Cr-S K ₂	200	12.2
	250	13
	300	13.9
Fe Cr-S K ₃	200	13.1
	250	14.3
	300	15.1
Fe Cr-S Li ₁	200	10.4
	250	11.2
	300	12.4
Fe Cr-S Li ₂	200	10.6
	250	11
	300	12.4
Fe Cr-S Li ₃	200	11.6
	250	13
	300	14.4

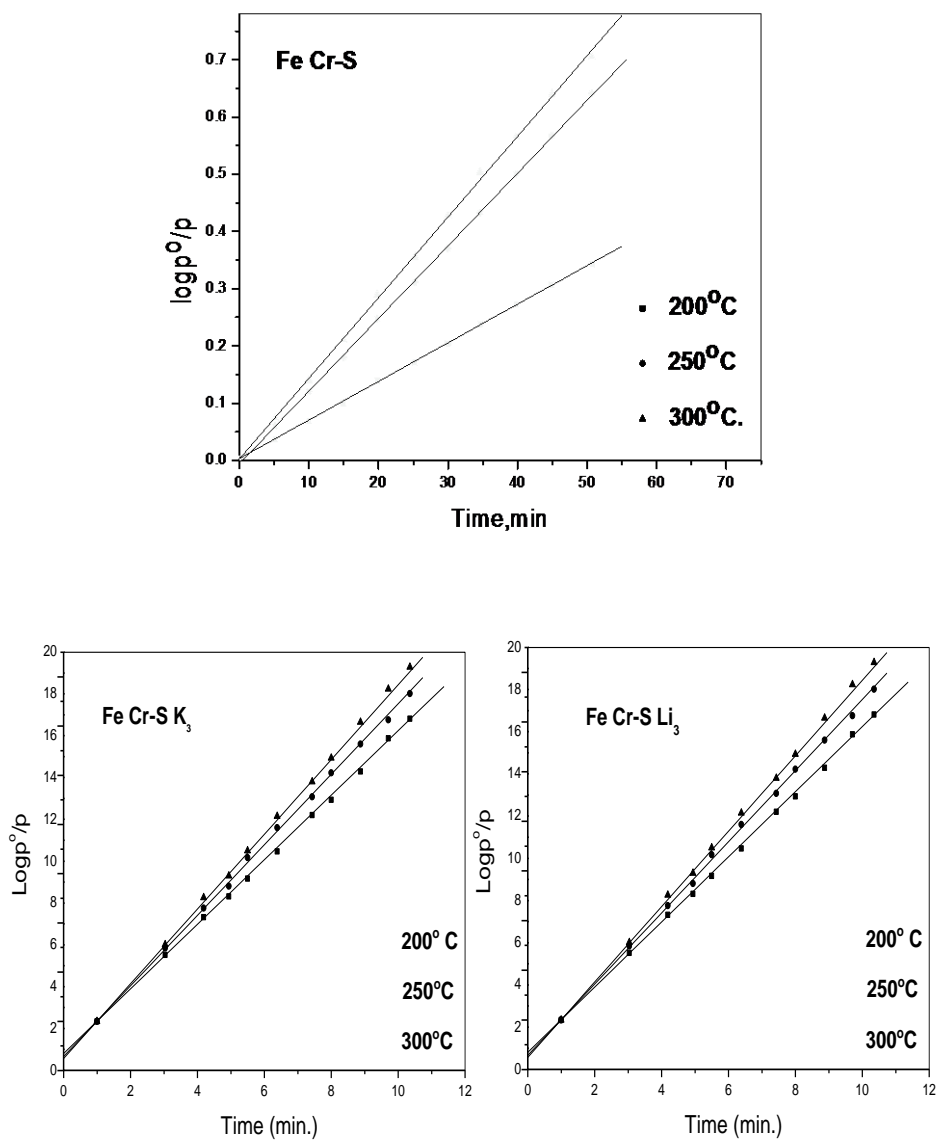


Fig. 6. First order-plots of CO oxidation by O_2 carried out at different temperatures over Fe Cr-S, Fe Cr-S K_3 and Fe Cr-S Li_3 systems calcined at $500^\circ C$.

The change in the catalytic activity of the system investigated due to doping either with K_2O or Li_2O could be discussed in terms of the parameters previously given in the preceding section of the present work. The observed increase due to the doping process could not be attributed to induce changes in the S_{BET} of the doped solids. So, the conversion of some of $\alpha\text{-Fe}_2O_3$ into $\gamma\text{-Fe}_2O_3$, devoted with higher catalytic activity, might account for the observed increase in the catalytic activity of doped solids. It is

well known that γ -Fe₂O₃ is more active than α -Fe₂O₃⁽²⁸⁾. So, the formation of γ -Fe₂O₃ in the doped solids overcomes the possible decrease in the activity due to the formation of potassium and lithium ferrites.

Effects of Li₂O and K₂O doping on ΔE of the catalyzed reaction prepared from mixed sulphates

The values of (ΔE) and recalculated values of the activation energies (ΔE^*) are given in Table 8. It is clearly shown from the data given in Table 8 that ΔE^* values of pure and doped solids showed almost the same values (17 ± 2 kJmol⁻¹) for solids doped with K₂O and (18 ± 2 kJmol⁻¹) for the solids doped with Li₂O. This finding suggested clearly that doping Fe₂O₃/Cr₂O₃ system either with Li₂O or K₂O followed by heating at 500°C did not much modify the activation energy of CO oxidation by O₂ over different solids but changed the concentration of active sites involved in the catalyzed reaction.

TABLE 8. Computed activation energies (ΔE , ΔE^*) and logarithm of pre-exponential factor of the Arrhenius equation for the catalytic reaction carried out at 200-300°C over pure and Li₂O or K₂O-doped Fe₂O₃/Cr₂O₃ solids calcined at 500°C and prepared using ferric and chromic mixed sulphates.

Catalyst	ΔE (kJ/mol)	ln A	ΔE_1^* (kJ/mol)
Fe Cr-S	19.2	1.68	19.2
Fe Cr-S K ₁	3.6	-1.28	16.5
Fe Cr-S K ₂	3.3	-1.28	16.2
Fe Cr-S K ₃	7.9	-0.125	15.7
Fe Cr-S Li ₁	4.1	-1.25	16.8
Fe Cr-S Li ₂	3.7	-1.35	16.9
Fe Cr-S Li ₃	2.6	-1.44	16.2

Conclusions

The results obtained permitted to draw the following main conclusions: Physicochemical, surface and catalytic properties of pure and variously K₂O and Li₂O-doped Fe₂O₃/Cr₂O₃ solids were much influenced by the nature of ferric and chromic salts used in the preparation of the mixed hydroxides. However, all prepared solids consisted of nanocrystalline phases having crystallite size between 8-64 nm.

- Pure mixed solids calcined at 500°C and prepared by using ferric and chromic mixed nitrates were entirely composed of nanocrystalline α -Fe₂O₃ phase and a mixture of α and γ -Fe₂O₃ phases in case of the solids prepared by mixed sulphates. Various K₂O and Li₂O-doped solids consisted of nanocrystalline potassium and lithium ferrites together with ferric oxide phases. However, heavily Li₂O-doped solids consisted only of LiFe₅O₈ phase.

- Pure and variously doped solids prepared from mixed sulphates measured specific surface areas bigger than those determined for the other solids. The doping process modified the surface characteristics of the treated adsorbents in a different manner depending on the nature of dopant and its concentration besides the salts used in preparation process.

- Pure mixed solids prepared from ferric and chromic mixed nitrates are more catalytically active than those prepared from mixed sulphates. Doping either with K₂O or Li₂O much increased the catalytic activity to an extent proportional to the dopant concentration. However, the increase was pronounced in case of the doped solids prepared from mixed sulphates.

- The doping process did not change the mechanism of the catalytic reaction but increased the concentration of active sites involved in chemisorption and catalysis of CO oxidation reaction without modifying their energetic nature.

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الخواص الفيزيوكيميائية والسطحية والحفزية لأكاسيد الحديد والكروم النقيه والمشابهه بأكاسيد البوتاسيوم والليثيوم ومدى تأثيرهم بأملاح الحديد والكروم المستخدمه فى عملية التحضير

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تم فى هذا البحث تحضير عينات من حفازات مكونه من أكاسيد الحديد والكروم بنسب جزيئيه 0.85 : 0.15: تم تحضيرهم بالتفكك الحرارى لهيدروكسيداتهم عند درجة 500 مؤبوه وتم تحضير مخاليط الهيدروكسيدات بالترسيب المتزامن لمخاليط من نترات وكبريتات الحديد والكروم باستخدام هيدروكسيد الأمونيوم المركز. هذا وقد تم تحضير 6 عينات من الحفازات المشابه بنسب مختلفه من أكاسيد البوتاسيوم والليثيوم (0.5، 0.75، 1.5 مول %).

أوضحت أهم النتائج أن جميع الحفازات النقيه والمشابه تتكون من أطوار بللوريه ذات حجم حبيبي متناهى الصغر يتراوح حجمها بين 8-64 نانومتر والحفازات المشابه تتكون من فيريتات البوتاسيوم والليثيوم بجانب أكاسيد الحديد (α ، γ).

المساحة السطحيه النوعيه للحفازات النقيه والمشابه والمحضرة باستخدام كبريتات الحديد والكروم تتمتع بمساحة سطحيه نوعيه أكبر من الحفازات الأخرى المحضره بنتراتها. تتأثر الخواص السطحيه بالاشابه بشكل يعتمد على نوع وتركيز ماده المستخدمه فى الاشابه.

الكفاءه الحفزيه للعينات النقيه المحضره من النترات أكبر من الكفاءه الحفزيه للعينات النقيه المحضره من الكبريتات. تودى عملية الاشابه بأكاسيد البوتاسيوم والليثيوم الى زياده كبيره فى الكفاءه الحفزيه تتناسب طرديا مع تركيز هذه الأكاسيد مع ملاحظه أن الزيادة فى الكفاءه الحفزيه تكون أكبر بكثير فى حالة الاشابه بأكاسيد البوتاسيوم للعينات المحضره باستخدام الكبريتات اذا ما قورنت بالعينات المحضره بالنترات. لذا تتمتع العينات المشابه والمحضره بكبريتات الحديد والكروم بكفاءه حفزيه أكبر من كفاءه الحفازات المشابه والمحضره من النترات. لا تؤثر عملية الاشابه فى آلية التفاعل المحفز ولكنها تودى الى زياده فى تركيز المواقع النشطه المشتركه فى التفاعل المحفز.