Title	FORMATION AND ACTIVITY OF CERTAIN CHROMITE CATALYSTS
Author(s)	FAHIM, R. B.; ZAKI, M. I.; EL-ROUDI, A. M.; HASSAAN, A. M. A.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 29(1), 25-36
Issue Date	1981-11
Doc URL	http://hdl.handle.net/2115/25112
Type	bulletin (article)
File Information	29(1)_P25-36.pdf

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 29, No. 1, pp. 25 to 36 (1981)

FORMATION AND ACTIVITY OF CERTAIN CHROMITE CATALYSTS

By

R. B. FAHIM,*) M. I. ZAKI,*) A. M. EL-ROUDI*)
and A. M. A. HASSAAN*)

(Received January 7, 1981; in revised form June 30, 1981)

Abstract

Atomic absorption spectrophotometry in conjunction with a conventional solvent technique was used to study the kinetics of interaction between MO and Cr_2O_3 in powder mixtures (where M stands for Zn^{2+}, Mg^{2+} or Ni^{2+}). The kinetics of interaction can best be described by a rate equation developed by the geometrical model of Ginstling-Brounshtein and/or Jander. Formation of MCr_2O_4 proceeds through an intermediate chromate. The step formation of the intermediate chromates is hindered in hydrogen atmosphere, while retarded when curing medium was nitrogen. Catalytic activity of the formed chromites was tested for the decomposition of H_2O_2. It was found to depend on the availability of an electron transfer cycle between two different valency states of M–Cr surface pairs. Data are presented for kinetic parameters of both solid state formation and catalyzed reactions.

§ 1. Introduction

Recently[1] it was shown that the electron transfer between two different valency states of copper as well as manganese in hopcalite catalysts is possible within the spinel lattice without a change of structure. Such a concept would indicate an activity of spinel catalysts for redox reactions.[2,3] Chromites seem to be a unique example for such a surface electron transfer cycle. The efficiency of this cycle is favoured by the easiness of establishing the known redox process $Cr^{3+} \rightarrow Cr^{6+} \rightarrow Cr^{3+}$.[4] Meanwhile, it is controlled by the extent to which the divalent cation (M) can exchange electrons with surface chromium ions.

The aim of the present article is to extend the applicability of the preceeding concept on chromites, thus correlating the pertaining formation structural changes of these catalysts and their activity towards the decomposition of H_2O_2 as an acceptor reaction.[1] Therefore the kinetics of chromites

---

*) Chemistry Department, Faculty of Science, University of El-Minia, El-Minia, A. R. E.

reaction formation were studied with elaboration on the effect of reactivity of MO (where M stands for Mg^{2+}, Zn^{2+} or Ni^{2+}) on the mechanism of the reaction.

§ 2. Experimental

(2-1) *Catalyst used*

The raw materials used in this investigation were NiO, ZnO, MgO and Cr_2O_3 obtained by thermal decomposition, at 700°C for 10 hr in air, of AR-grade nickel hydroxide, zinc hydroxide, magnesium hydroxide and chromia gel respectively. Chromia gel was prepared according to the method described by Burwell *et al.*[5] MCr_2O_4 was prepared by calcining for 10 hr a powder mixture of $M(OH)_2$ and chromia gel (providing an equimolar $MO : Cr_2O_3$ system) at 400°-1200°C in air and at 1000°C in purified nitrogen or hydrogen atmospheres, according to the procedure described by Hulbert *et al.*[6] Catalysts were characterized by differential thermal analysis (DTA), differential scanning calorimetry (DSC), infrared spectrophotometry (IRA) and x-ray diffractometry (XRD). Water extractable surface Cr^{6+} ions concentration was determined colorimetrically.[7]

(2-2) *Kinetics of catalysts formation*

Kinetics of the reaction between fine powders of MO and Cr_2O_3 to form MCr_2O_4 were studied isothermally between 400° and 1000°C in air. Atomic absorption spectrophotometry in conjunction with conventional solvent techniques was adopted to monitor the fraction reaction completed (the fraction of reaction completed is a quantity relating the amount of reaction product formed to the amount of complete reaction (calculated)) as a function of time.[6] The details of the analytical procedure are described elsewhere.[8] Kinetic analysis was performed using models adopted earlier.[9]

(2-3) *Catalytic measurements*

Kinetics of catalytic decomposition of H_2O_2 in solution (35.5%) were followed gasometrically.[7] The analysis of experimental data has been carried out on the assumption[7] that the decomposition of H_2O_2 is a first order process. As the maximal conversion observed after 30 min never exceeded 0.05, it may be assumed in the first approximation that the reaction runs at the constant concentration of H_2O_2. At such conditions the integration of the first order equation gives that $v=v_0+kt$, where v represents the volume of oxygen evolved and v_0, the volume of oxygen evolved of the moment at which the time measurements started.

§ 3. Results and Discussion

(3-1) *Kinetics of solid state reaction formation*

Reaction rate curves (x, fraction reaction completed vs. t, time) were constructed (Fig. 1). Adjoining the kinetic analysis of solid state reaction in powder mixtures,[9] reaction rate data from each isothermal reaction were

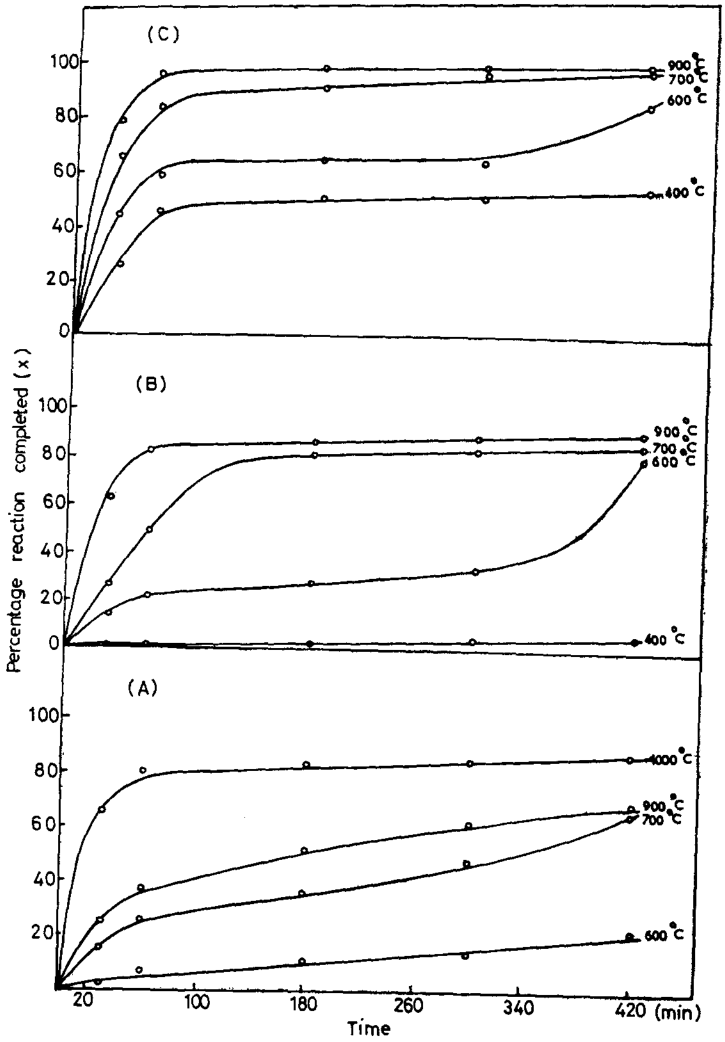

Fig. 1. Effect of temperature on the rate of the reaction in $ZnO+Cr_2O_3$ (A), $MgO+Cr_2O_3$ (B) or $NiO+Cr_2O_3$ (C) system.

analysed using equations corresponding to four reaction mechanism of basically different types and rate constants calculated. The calculated rate constants were then plotted vs. fraction reaction completed (Table 1 and Fig. 2). For a rate equation to represent a reaction, the rate constant should

TABLE 1. Rate constants (*k*) of solid state reaction formation of MCr_2O_4 at different temperatures and the corresponding activation energies (ΔE_a)

$MgCr_2O_4$	$k_{400°C}$	$k_{600°C}$	$k_{700°C}$	$k_{900°C}$	ΔE_a kcal/mole
Jander	6.2×10^{-7}	6.4×10^{-5}	5.7×10^{-4}	1.7×10^{-3}	35.8
Ginstling-Brounshtein	6.1×10^{-7}	6.0×10^{-5}	4.3×10^{-4}	1.2×10^{-3}	30.6
$ZnCr_2O_4$	$k_{600°C}$	$k_{700°C}$	$k_{900°C}$	$k_{1000°C}$	ΔE_a kcal/mole
Jander	7.7×10^{-6}	11.8×10^{-5}	2.5×10^{-4}	13.5×10^{-4}	47.6
Ginstling-Brounshtein	7.5×10^{-6}	10.5×10^{-5}	2.2×10^{-4}	10.1×10^{-4}	44.3
$NiCr_2O_4$	$k_{400°C}$	$k_{600°C}$	$k_{700°C}$	$k_{900°C}$	ΔE_a kcal/mole
Jander	3.1×10^{-4}	7.8×10^{-4}	2.3×10^{-3}	3.9×10^{-3}	25.8
Ginstling-Brounshtein	2.8×10^{-4}	6.4×10^{-4}	1.6×10^{-3}	2.4×10^{-3}	25.3

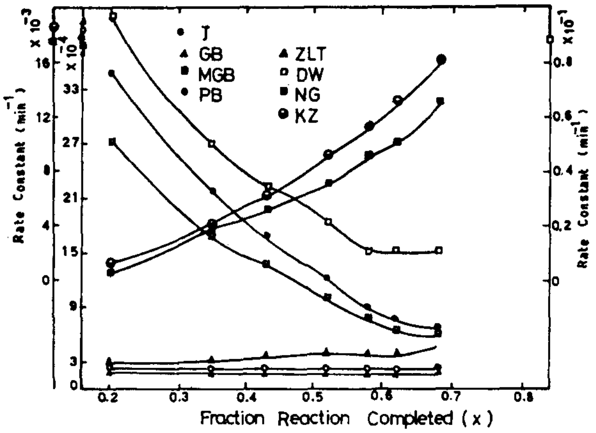

Fig. 2. Analysis of rate constants for 900°C isothermal reaction of ZnO with chromia calculated from: Jander (○), Ginstling-Brounshtein (▲), modified Ginstling-Brounshtein (■), Phase Boundary controlled (●), Zhuravlev-Lesokhin-Tempel (△), Dünwald-Wagner (□), Kröger-Ziegler (◒) or Nuclei growth controlled (▄) kinetic equation.

be independent of the amount of reaction completed under isothermal conditions. All of the rate constants calculated by the reviewed models[9] drift over several orders of magnitude for the three reaction systems. This is with the exception of:

Jander, $k_J t = [1-(1-x)^{1/3}]^2$ and/or

Ginstling-Brounshtein, $k_{BG} t = 1-2/3x-(1-x)^{2/3}$

equations which assign a product growth controlled by diffusion of reactants through a continuous product layer. This finding copes with ideas of Greskovich[10] who suggested that the reaction formation of nickel and magnesium chromites should follow the same kinetics.

It was indicated[6] that the rate of the reaction between MgO and Cr_2O_3 is controlled by the rate of the unidirectional lattice diffusion of chromium ions with vapour transport of oxygen. On the other hand, it was reported[11] that the mechanism of nickel chromite formation from its component oxides follows a counter-current diffusion of Ni^{2+} and Cr^{3+} through the spinel layer. In case of $ZnO:Cr_2O_3$ system, one can suggest that the mass transport is most likely unidirectional lattice diffusion of zinc ions with vapour transport of oxygen, since the vaporization rate of zinc oxide is greater than that of chromium oxide.[12] Branson,[13] working on $ZnO:Al_2O_3$ solid reaction, concluded that diffusing Zn^{2+} ions would recombine with atmospheric oxygen at the spinel/Al_2O_3 interface to form the spinel. Consequently one can ascribe the low activation energy (Table 1) obtained for $ZnO:Cr_2O_3$ reaction (47.6 kcal/mole) compared to that for $ZnO:Al_2O_3$ reaction system (57.3 kcal/mole),[13] to the presence of excess oxygen in Cr_2O_3 lattice which would accelerate the diffusion of the zinc ions through the spinel layer.

(3-2) *Catalyst characterization*

Table 2 presents structural information obtained by correlating the results of DTA, DSC, XRD and IRA. Magnesium chromite formation proceeds through an intermediate chromate which decomposes to the initial oxides that then would react giving eventually the spinel. This finding copes with that of Charcosset,[14] thus contradicting the ideas of Hulbert.[6] At the stage of decomposition of the intermediate chromate giving the initial oxides, magnesium oxide is not detected (Fig. 3). This phenomenon was observed by Haber[15] who claimed that chromia shields the MgO grains through the vapour-transport mechanism. This formation mechanism is applicable in case of $NiCr_2O_4$ (Fig. 3). On the other hand, the mechanism of the solid state reaction formation of $ZnCr_2O_4$ is temperature dependent. Thus at relatively low temperature ($\leqslant 400°C$), the intermediate hydroxy zinc chromate[16]

TABLE 2. Some structural information of calcined $MO:Cr_2O_3$ mixtures

Calcination Temperature °C	Calcination Media	Crystalline phase present			Extractable concentration surface $CrO_4^=$ (mg/gm catalyst)			C/a*		
		$NiO:Cr_2O_3$	$ZnO:Cr_2O_3$	$MgO:Cr_2O_3$	$NiO:Cr_2O_3$	$ZnO:Cr_2O_3$	$MgO:Cr_2O_3$	$NiO:Cr_2O_3$	$ZnO:Cr_2O_3$	$MgO:Cr_2O_3$
400	Air	Cr_2O_3(J), NiO(m), $NiO.CrO_3$(m).	Cr_2O_3(J), ZnO(J), $ZnO.CrO_3$(m), $ZnCr_2O_4$(m).	Cr_2O_3(J), MgO(m), $MgO.CrO_3$(m), $MgCr_2O_4$(m).	133.1	180.6	250.2	—	1.00	1.00
600	Air	Cr_2O_3(m), $NiO.CrO_3$(m), $NiCr_2O_4$(J).	Cr_2O_3(m), ZnO(m), $ZnO.CrO_3$(m), $ZnCr_2O_4$(J).	Cr_2O_3(m), $MgO.CrO_3$(m), $MgCr_2O_4$(J).	90.9	60.6	120.3	1.00	1.00	1.00
800	Air	Cr_2O_3(m), $NiO.CrO_3$(m), $NiCr_2O_4$(J).	$ZnO.CrO_3$(m), $ZnCr_2O_4$(J).	Cr_2O_3(m), $MgCr_2O_4$(J).	50.1	15.8	20.6	1.00	1.00	1.00
1000	Air	Cr_2O_3(m), $NiCr_2O_4$(J), $NiCrO_3$(m), $Ni_2O_3.3CrO_3$(m).	$ZnCr_2O_4$(J), $ZnO.CrO_3$(m),	Cr_2O_3(m), $MgCr_2O_4$(J).	142.7	5.5	10.8	1.00	1.00	1.00
	Nitrogen	Cr_2O_3(m), $NiCr_2O_4$(J), $NiCr_2O_4$(tr), $Ni_2O_3.3CrO_3$(tr).	$ZnCr_2O_4$(J), $ZnO.CrO_3$(m).	Cr_2O_3(m), $MgCr_2O_4$(J).	63.3	15.9	8.9	1.04	1.03	1.04
	Hydrogen	Cr_2O_3(J), NiO(m), $NiCr_2O_4$(m).	Cr_2O_3(J), ZnO(J), $ZnCr_2O_4$(m), $ZnO.CrO_3$(m).	Cr_2O_3(m), MgO(m), $MgCr_2O_4$(J).	10.5	4.3	2.5	1.03	1.03	1.04
1200	Air	$NiCr_2O_4$(m), $NiCrO_3$(m), $Ni_2O_3.3CrO_3$(m).	$ZnCr_2O_4$(J)	$MgCr_2O_4$(J)	171.3	2.00	—	1.00	1.02	1.00

m = minor, J = major, tr = trace, *calculated from X-ray diffraction patterns.

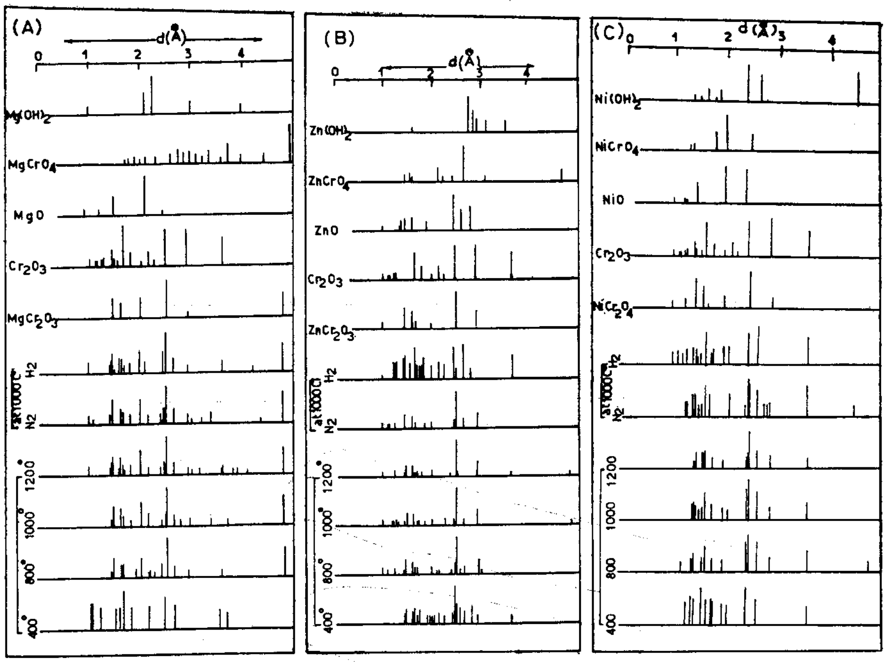

Fig. 3. X-ray diffraction patterns of the calcination products of the mixtures of chromia gel with $Mg(OH)_2$ (A) or $Zn(OH)_2$ (B) or $Ni(OH)_2$ (C) at different temperatures in air, nitrogen or hydrogen atmosphere.

decomposes giving the parent oxides that would then react giving the chromite. While at temperature $\geqslant$800°C, the formed hydroxy chromates give directly the chromite (Table 2).

The step formation of the intermediate chromates is hindered in hydrogen atmosphere, while retarded when curing medium is nitrogen (Table 2). This indicates that oxygen is necessary for this intermediate formation and hence for the spinel itself. However, curing in N_2 atmosphere (1000°C) did not hinder formation of spinel crystallites as a minor component. Hence it is plausible to suggest that the limited supply of oxygen resulting from lateral hydroxyl group condensation of chromia gel partner,[4] taking place during heating up the solid mixture, contributes to oxidation.

Detection of extractable Cr^{6+} ions from reaction products indicates that rise of calcination temperature is accompanied by a drastic drop in its concentration as well as that of chromate intermediate (Table 2). This picture is not applicable for nickel chromite formation. Thus in latter case, there is a mild drop in concentration of Cr^{6+} starting from 400°C to 600°C, followed by a marked increase with temperature rise. The persistence of stable Cr^{6+} ions above 600°C (which should be unstable at such temperature range[4]) taking into consideration of possible existence of Ni^{3+} ions,[10] would suggest the formation of $Ni_2O_3 \cdot 3\,CrO_3$ chromate intermediate. Such an intermediate when formed in minor amounts would decompose to form $NiCrO_3$ spinal as referred to in IRA by strong absorption below 500 cm^{-1} (Fig. 4). Such absorption was used to assign the formation of $SmCrO_3$, $LaCrO_3$ and $NdCrO_3$ in similar systems.[17]

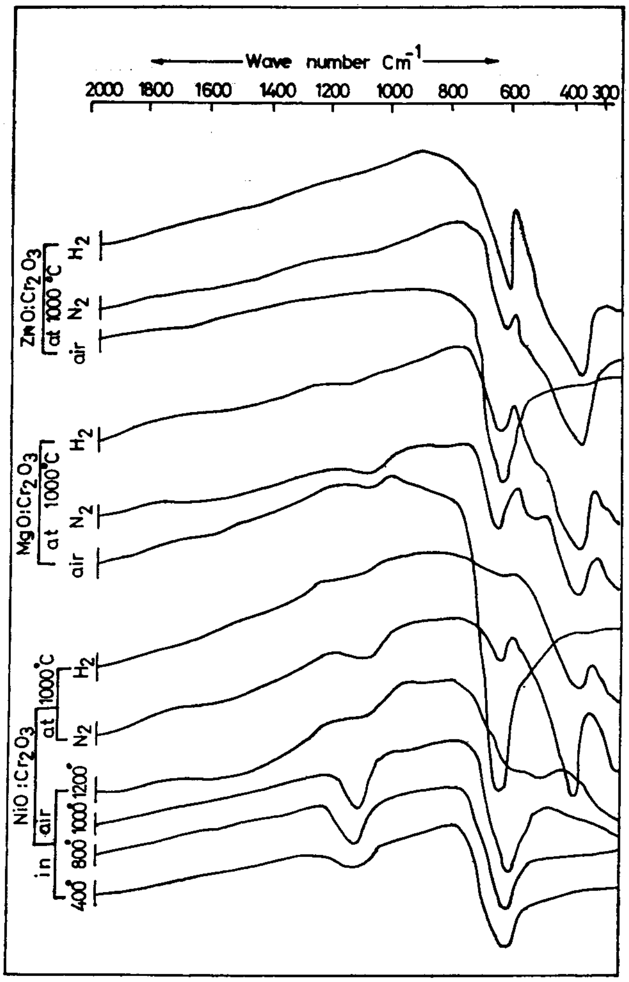

Fig. 4. IR-spectra for the calcination products of chromia gel mixtures with $Mg(OH)_2$, $Zn(OH)_2$ or $Ni(OH)_2$ at different calcination temperatures in air, nitrogen or hydrogen atmosphere.

The observed ν_4-ir absorption splitting in spectrum of $MgO:Cr_2O_3$ sample cured at 1000°C in nitrogen or hydrogen atmospheres (Fig. 4) as well as the elongation of the unit cell (Table 2) of the corresponding chromite lattice along c-axes (viz., $c/a > 1$) would indicate a tetragonal distortion. Greskovich and Stubican[18] showed that a new spinel-type crystalline solution with cell formula $(Mg_{8-x}\,Cr_x^{2+})^{IV}\,Cr_{16}^{3+VI}O_{32}$ was obtained on heating a mixture of MgO and Cr_2O_3 in a reducing atmosphere. They observed such a distortion when a critical value of $\simeq 1$ Cr^{2+} $(3d^4)$ ion per unit cell formula in the tetrahedral sites was reached. This interpretation can be safely adopted to the observed distortion in case of both $NiO:Cr_2O_3$ (Fig. 4) and $ZnO:Cr_2O_3$ mixtures.

Combining the foregoing results with conclusions cited for kinetic treatments on solid state reactions, the mechanism of magnesium chromite formation can be postulated as follows: the first step is the formation of a thin layer of spinel on MgO grains ($\leqslant 600$°C). This step takes place through two consecutive stages, a rapid surface reaction then a slower growth of product layer. At temperature >600°C, these two consecutive stages would overlap kinetically. The foregoing picture can also be applied in case of $NiO:Cr_2O_3$ system (Fig. 1). The only difference which could be observed is that NiO is more reactive than MgO. Such a phenomenon can tentatively be ascribed to the difference in the mode of diffusion during chromite formation.

Due to similar reaction kinetics as well as diffusion models for both reactions of ZnO with Cr_2O_3 or Al_2O_3, one can suggest a three steps reaction sequence for $ZnCr_2O_4$ formation (Fig. 1): i) the formation of a solid solution of ZnO in Cr_2O_3 (between 600° to 700°C); ii) the formation of disordered spinel structure between 700° and 900°C; and iii) the formation of an ordered spinel when mixtures are heated at 900°C and above.

(3-3) *Catalytic activity*

Checking on the results of catalytic data (Table 3), it can be noticed that nickel chromite has exceptionally high activity as compared to that of both $MgCr_2O_4$ and $ZnCr_2O_4$. This fact may be attributed to the presence of both Cr and Ni ions co-existence, each with different valency, at the surface (viz., Ni^{2+}, Ni^{3+}, Cr^{3+}, Cr^{6+}). One would then expect a possible existence of various redox systems that can contribute in the surface electron transfer cycle. If we take the system Ni^{2+}/Cr^{6+} as being the most active redox centres, one can present the following mechanism[1]:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$HO_2^- \longrightarrow HO_2 + e$$

$$e + Cr^{6+} \longrightarrow Cr^{5+}$$

$$H^+ + Ni^{2+} \longrightarrow Ni^{3+} + H$$

$$Ni^{3+} + Cr^{5+} \longrightarrow Ni^{2+} + Cr^{6+}$$

$$H \text{ and } HO_2 \longrightarrow \text{chain} \longrightarrow H_2O + 1/2\ O_2$$

Such a mechanism can also be applicable as well to Cr^{3+}/Cr^{6+} redox centres.[16] In case of $MgCr_2O_4$ and $ZnCr_2O_4$, the Cr^{3+}/Cr^{6+} system would be the only available active sites for the decomposition of H_2O_2. Hence, one would expect the relatively low activity of these catalysts.

TABLE 3. Rate constants (k), pre-exponential factors (k_0) and activation energies (ΔE_a) of H_2O_2 decomposition on MCr_2O_4 catalysts

Calcination temperature	Calcination medium	$k_{25°C}$	$k_{30°C}$	$k_{35°C}$	$k_{40°C}$	ΔE_a kcal/mole	k
$NiCr_2O_4$							
400°C	Air	16.250	21.430	35.290	58.040	16.30	591.10
600	Air	2.950	5.860	9.890	13.280	20.40	246.60
800	Air	11.540	16.670	30.770	83.330	17.50	591.10
1000	Air	38.880	87.880	133.590	173.330	18.30	3102.70
1000	Nitrogen	40.260	95.260	150.630	210.620	16.20	3232.50
1000	Hydrogen	1.210	1.300	2.210	3.410	31.30	22.50
1200	Air	45.830	106.250	233.330	383.330	9.40	3318.20
$ZnCr_2O_4$							
400°C	Air	11.590	17.640	26.660	39.390	15.20	364.50
600	Air	3.330	6.250	10.000	15.620	15.70	159.10
800	Air	1.510	1.190	2.080	5.160	27.60	182.70
1000	Air	0.568	0.800	0.454	1.570	12.10	11.52
1000	Nitrogen	2.110	1.000	1.900	3.570	22.60	60.50
1000	Hydrogen	—	—	0.080	1.470	—	—
1200	Air	—	0.250	1.250	1.428	18.30	20.60
$MgCr_2O_4$							
400°C	Air	450.000	633.330	1600.000	2900.00	28.10	91563.00
600	Air	16.000	29.230	43.330	75.000	18.40	1100.70
800	Air	3.330	4.170	7.570	16.700	14.70	91.56
1000	Air	0.779	1.482	4.176	4.722	25.80	120.70
1000	Nitrogen	3.125	6.347	11.100	26.920	31.50	1100.70
1000	Hydrogen	2.499	4.443	9.256	18.050	29.40	694.60
1200	Air	—	0.769	1.071	1.785	14.70	19.13

Similar trend of variation between either k, k_0 or concentration of surface $CrO_4^=$ and catalyst calcination temperature (Table 2 and 3) would indicate that i) each of k or k_0 can be used as a base for activity classification of nickel chromite catalysts towards H_2O_2 decomposition and ii) surface Cr (VI)-intermediates are the active sites for this reaction. Similar conclusion was given using chromia catalysts.[16)]

The non-linear dependence of k values on concentration of extractable surface $CrO_4^=$ ions (Table 2 and 3), considering calcination products of NiO: Cr_2O_3 system, can be ascribed to a compensation effect.[19)] Such an effect can be due to the coexistence of different surface, Cr (VI)-intermediates, viz. $NiO \cdot CrO_3$ (major low temperature intermediate) and $Ni_2O_3 \cdot 3CrO_3$ (major high temperature intermediate).

From Table 3, it can be seen that the activity of a catalyst depends on the curing medium, thus being in the order $N_2 > \mathrm{Air} \gg H_2$. Such an order may be interpreted in terms of the contribution of tetragonal distortion, being responsible for creation of additional surface energetic domains. However, the poor activity of tetragonally distorted H_2-cured catalyst is due to the disappearence of surface Cr^{6+} ions, being effectively the dominant co-sharing active acceptor centres.

References

1) G.-M. Schwab and S. B. Kanungo, Z. phys. Chem. NF, **107**, 109 (1977).
2) D. E. R. Bennet and R. A. Ross, J. Catalysis, **18**, 122 (1970).
3) R. J. Rennard, Jr. and W. L. Kehl, J. Catalysis, **21**, 282 (1971).
4) R. B. Fahim, R. M. Gabr, M. I. Zaki and S. A. A. Mansour, J. Collid Inter. Sci., **81**, 468 (1981).
5) R. L. Burwell, Jr., G. L. Haller, K. C. Taylor and J. F. Read, *Adv. in Catalysis*, 20, Academic Press, New York, 1969, p. 2.
6) S. F. Hulbert, D. A. Brosman and R. H. Smoak, *Reactivity of Solids*, John Wiley & Sons, New York, 1969, p. 573.
7) R. B. Fahim, M. I. Zaki and R. M. Gabr, J. Surface Technology, in press, 1980.
8) A. M. A. Hassaan, M. Sc. thesis, Minia Univ., Egypt, 1980.
9) S. F. Hulbert and J. J. Klawitter, J. Am. Ceram. Soc., **50**, 484 (1967).
10) C. Greskovich, J. Am. Ceram. Soc., **53**, 498 (1970).
11) J. S. Armijo, D. L. Douglass and R. A. Huggins, J. Electrochem. Soc., **120**, 825 (1973).
12) G. V. Samsonov, *The Oxide Handbook*, Plenum Press, London, 1973, p. 194.
13) D. L. Branson, J. Am. Ceram. Soc., **48**, 591 (1964).
14) H. Charcosset, P. Turlier and Y. Trambouze, J. de Chimie Physique, **61**, 1249 (1964).
15) J. Burzyk and J. Haber, Bull. Acad. Polon. Sci., **9**, 531 (1969).

16) R. B. Fahim, R. M. Gabr and M. I. Zaki, J. Surface Technology, **11**, 215 (1980).
17) R. G. Darrie, W. P. Doyle and I. Kirkpatrick, J. Inorg. Nucl. Chem., **29**, 979 (1967).
18) C. Greskovich and V. S. Stubican, J. Phys. Chem. Solids, **27**, 1379 (1966).
19) E. Cremer, *Adv. in Catalysis*, **7**, Academic Press, New York, 1955, p. 75.