

## Catalytic Behavior of Cr(III) and Fe(III) Spinels in the Oxidation of Propylene

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The catalytic oxidation of propylene in the temperature range 200–350°C has been investigated on various Cr(III) and Fe(III) spinels. The catalysts have been characterized by means of DTA, TGA, X-ray, and BET studies. Activity data have been obtained by means of the pulse technique. In all cases a nonselective oxidation to CO<sub>2</sub> has been observed. The kinetic analysis of conversion data indicates the occurrence of a zero order rate law. Normal spinels are more active than inverse spinels. The existence of a compensation effect between the kinetic parameters has been revealed. On the basis of the physicochemical properties of catalysts an interpretation of their behavior is offered.

### INTRODUCTION

The aim of the work is to examine closely the influence of the coordination degree and energetic state of a transition metal ion on its catalytic behavior (1). The following two sets of spinels have been considered: (i) NiCr<sub>2</sub>O<sub>4</sub>, CoCr<sub>2</sub>O<sub>4</sub>, and MnCr<sub>2</sub>O<sub>4</sub>; and (ii) NiFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, and MnFe<sub>2</sub>O<sub>4</sub>. These represent a series of oxides with the same structure and different coordination of metallic ions.

NiCr<sub>2</sub>O<sub>4</sub>, CoCr<sub>2</sub>O<sub>4</sub>, and MnCr<sub>2</sub>O<sub>4</sub> are normal spinels with the divalent ions in tetrahedral positions and Cr(III) in octahedral positions, and therefore allow the comparison of the behavior of the different divalent ions in tetrahedral positions. NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> have the inverse spinel structure with half the trivalent ions in tetrahedral positions and the other half together with the divalent ions in octahedral positions. MnFe<sub>2</sub>O<sub>4</sub> is closer to the normal structure, with about 80% of the divalent ions in tetrahedral positions.

### EXPERIMENTAL

**Materials.** All catalysts were prepared using C. Erba R.P. products. Cr(NO<sub>3</sub>)<sub>2</sub>

was a BDH product while the ammonia solution was a Merck product. Propylene (Phillips Petroleum Co., Pure grade), hydrogen (99.907% ex Sapiro) and Oxygen (99.50% ex Siad) were employed in the catalytic runs.

### Catalyst Preparation

The method suggested by Wickman (2) has been followed. This involves a stoichiometric mixture of divalent and trivalent oxalates which is decomposed in an oxidizing atmosphere by heating at 590°C for 72 hr. This offers a standardized procedure which guarantees a given oxidation state for the metals and allows highly pure compounds free from foreign ions to be obtained.

In the case of iron compounds the mixtures were obtained by coprecipitation of oxalates of both divalent ions. Iron is oxidized during calcination. In the case of chromium compounds the mixtures were obtained by evaporating a solution of oxalates.

The chemical analysis of the overall set of compounds is given in Table I.

TABLE 1  
 CHEMICAL ANALYSIS OF THE PREPARED SPINELS

Compound	Me <sup>3+</sup> (% wt)		Me <sup>2+</sup> (% wt)	
	Calculated	Experimental	Calculated	Experimental
NiFe <sub>2</sub> O <sub>4</sub>	47.65	47.77	25.05	25.35
CoFe <sub>2</sub> O <sub>4</sub>	47.60	48.30	25.12	24.99
MnFe <sub>2</sub> O <sub>4</sub>	48.43	47.37	23.82	22.88
NiCr <sub>2</sub> O <sub>4</sub>	45.88	47.20	25.89	26.09
CoCr <sub>2</sub> O <sub>4</sub>	45.83	45.76	25.97	25.50
MnCr <sub>2</sub> O <sub>4</sub>	46.65	46.59	24.64	24.61

### Physicochemical Properties

**X-ray diffractometry** was carried out using molybdenum radiation  $K_{\alpha}$  ( $\lambda = 0.711 \text{ \AA}$ ) with a Zr filter. Table 2 gives the comparison with literature data (3).

**Differential thermal analysis.** A programmed heating at a rate of  $10^{\circ}\text{C}/\text{min}$  between 25 and  $1000^{\circ}\text{C}$  was used. The absence of signals revealed that the spinels were thermally stable to  $1000^{\circ}\text{C}$ , confirming the high purity.

**Surface areas and pore distribution.** Results obtained by B.E.T. and mercury porosimetry are summarized in Table 3.

**Thermogravimetric analysis.** TGA was performed by means of a Cahn microbalance, with programmed temperature increase, in streams of air, nitrogen, hydrogen, and propylene. With air and nitrogen there was no weight variation. The percentage weight changes in hydrogen as a function of temperature are illustrated in Figs. 1 and 2. The overall weight changes in hydrogen and in propylene, and the re-

sults of carbon analysis after heating in propylene, are shown in Table 4. The small weight increase observed in the runs with propylene is due to the formation of carbonaceous deposits.

### Catalytic Activity

The catalytic activities were measured by means of the pulse technique. The condensation of reaction products has been avoided by heating the exit line from the reactor. 0.3 g of Catalyst which has been employed in each run.

An analytical procedure suitable for the detection of the following products has been applied: HCHO, CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>CHO, CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>2</sub>=CH-CH<sub>2</sub>OH, CH<sub>3</sub>-CHOHCH<sub>3</sub>, CH<sub>3</sub>COCH<sub>3</sub>, HCOOH, CH<sub>3</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH, CO<sub>2</sub>, and H<sub>2</sub>O. The following operating conditions have been used: column-stainless steel, diam 2 mm, 2 m length, Porapak R 80-100 mesh; carrier gas-helium 30 c<sup>3</sup>/min.; temperature-isothermal conditions at  $50^{\circ}\text{C}$  for 9 min;

 TABLE 2  
 X-RAY ANALYSIS OF THE PREPARED SPINELS

Compound	$R^a$
NiFe <sub>2</sub> O <sub>4</sub>	0.757
CoFe <sub>2</sub> O <sub>4</sub>	0.65
MnFe <sub>2</sub> O <sub>4</sub>	9.72
NiCr <sub>2</sub> O <sub>4</sub>	8.8
CoCr <sub>2</sub> O <sub>4</sub>	2.74
MnCr <sub>2</sub> O <sub>4</sub>	—

<sup>a</sup>  $R = (2|d_c - d_e|/\Sigma d_e)100$ .  $d_c$ , tabulated value of diffractogram;  $d_e$ , experimental value of diffractogram.

 TABLE 3  
 SURFACE AREA AND POROSITY OF THE CATALYSTS

Compound	Surface area m <sup>2</sup> /g	Specific pore volume
		$10 \text{ \AA} < r < 4$ $\times 10^5 \text{ \AA}$
NiFe <sub>2</sub> O <sub>4</sub>	10.8	0.41
CoFe <sub>2</sub> O <sub>4</sub>	6.1	0.39
MnFe <sub>2</sub> O <sub>4</sub>	11.3	0.52
NiCr <sub>2</sub> O <sub>4</sub>	17.5	0.46
CoCr <sub>2</sub> O <sub>4</sub>	16.6	0.45
MnCr <sub>2</sub> O <sub>4</sub>	15.0	0.40

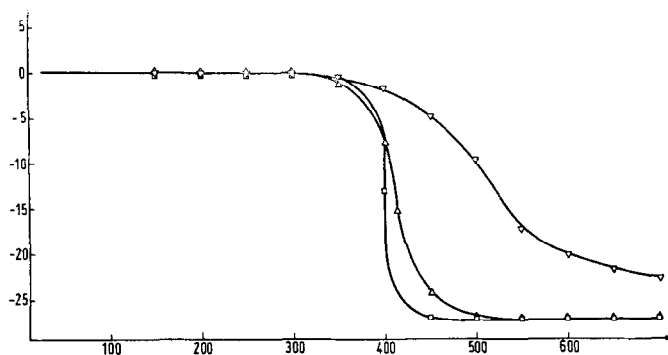


FIG. 1. Thermogravimetric analysis with hydrogen for iron compounds.  $\nabla$ , Mn;  $\Delta$ , Ni;  $\square$ , Co.

TABLE 4  
THERMOGRAVIMETRIC ANALYSIS WITH HYDROGEN  
OR PROPYLENE STREAMS<sup>a</sup>

	A	B	C
NiFe <sub>2</sub> O <sub>4</sub>	27.15	1.392	1.44
CoFe <sub>2</sub> O <sub>4</sub>	27.17	0.888	0.65
MnFe <sub>2</sub> O <sub>4</sub>	23.54	-0.900	0.97
NiCr <sub>2</sub> O <sub>4</sub>	7.16	1.38	1.21
CoCr <sub>2</sub> O <sub>4</sub>	4.93	0.897	1.35 + 0.1 hydrogen
MnCr <sub>2</sub> O <sub>4</sub>	1.73	1.02	1.59 + 0.2 hydrogen

<sup>a</sup> All data are corrected for the effect of gas stream. (A), Percentage of weight decrease in hydrogen atmosphere; (B) percentage of weight increase in propylene atmosphere; (C) percentage of carbon found by chemical analysis.

followed by programmed temperature rise at 4°C/min to 180°C, and then isothermal at 180°C for 10 min. The entire analysis required 45 min.

Before each catalytic run the solids were introduced into the thermostated reactor and conditioned for 13–14 hr at 400°C in

an inert atmosphere. After cooling to 150°C a standardized amount (1 cm<sup>3</sup>) of reacting mixture (one-fifth propylene/oxygen corresponding to almost the stoichiometric ratio) was injected for complete oxidation. This operation was repeated at intervals of 50° to 350°C. The runs were also repeated on cooling in order to examine the reproducibility of the data and the stability of the catalyst. An example is shown in Fig. 3.

In any run the only products revealed by gas chromatography were carbon dioxide and water.

At the lowest temperature (150°C) there was negligible reaction in some cases; a material balance of the exit gas revealed a small decrease of the amount of propylene, probably due to its polymerization.

## RESULTS

The pulse technique for obtaining kinetic data has been often criticized, particularly

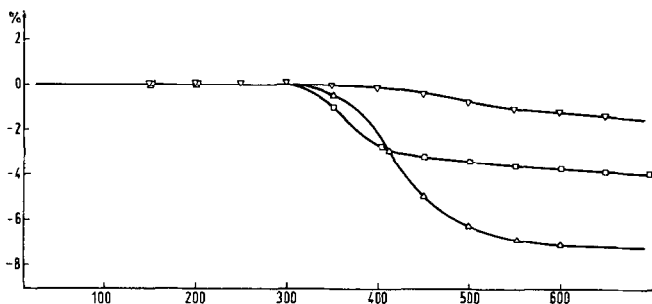


FIG. 2. Thermogravimetric analysis with hydrogen for chromium compounds.  $\nabla$ , Mn;  $\Delta$ , Ni;  $\square$ , Co.

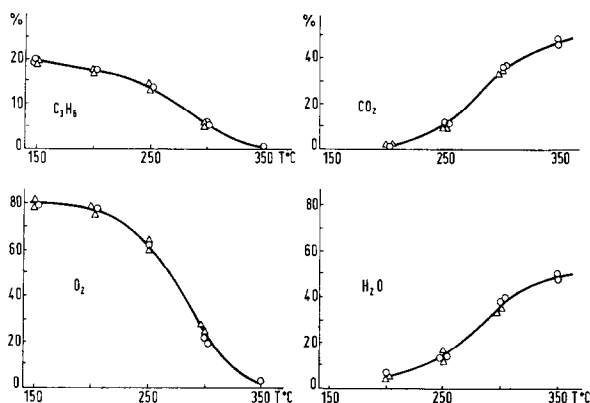


Fig. 3. Examples of results of catalytic runs at different temperatures. Catalyst  $\text{NiCr}_2\text{O}_4$ ;  $\Delta$ , runs performed by heating the catalyst,  $\circ$ , runs performed by cooling the catalyst.

with regard to the difficulties encountered in the integration of the continuity equation (4). However, the aim of the present work is essentially a comparison of the activities of different catalysts and for such a purpose the pulse technique can be considered reliable.

The balance equation has been written in the following simplified form in accordance with the assumption of a square top peak (5, 6);

$$-(dc/dt) = r, \quad (1)$$

$r$  being the reaction rate. If zero order kinetics are assumed, it follows that

$$\ln X = \ln(k/C^0) + \ln t, \quad (2)$$

where  $t$  is the contact time and  $C^0$  the initial concentration of propylene. Thus, for the same values of  $C^0$  and  $t$ , as in all our runs, the preceding relation can be written as follows:

$$\ln X = -(E^\ddagger/RT) + \text{const}, \quad (3)$$

where  $E^\ddagger$  is the activation energy,  $X$  the conversion of propylene and  $\text{const} = \ln$

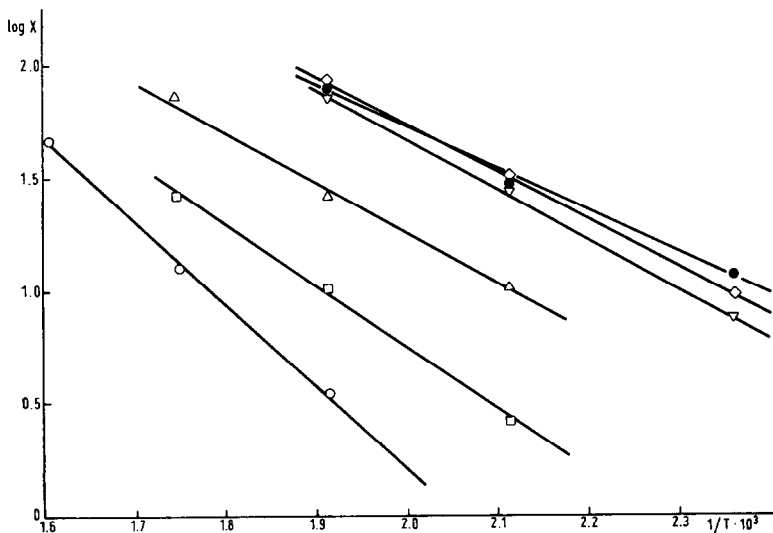


Fig. 4. Plots corresponding to Eq. (3).  $\bullet$ ,  $\text{MnFe}_2\text{O}_4$ ;  $\blacklozenge$ ,  $\text{MnCr}_2\text{O}_4$ ;  $\blacktriangledown$ ,  $\text{CoCr}_2\text{O}_4$ ;  $\Delta$ ,  $\text{NiCr}_2\text{O}_4$ ;  $\square$ ,  $\text{NiFe}_2\text{O}_4$ ;  $\circ$ ,  $\text{CoFe}_2\text{O}_4$ .

TABLE 5  
 KINETIC PARAMETERS

	$E^\ddagger$ (kcal/mole)	$\ln A + \text{const}$
NiFe <sub>2</sub> O <sub>4</sub>	12.58	3.22
CoFe <sub>2</sub> O <sub>4</sub>	16.93	4.81
MnFe <sub>2</sub> O <sub>4</sub>	8.00	2.12
NiCr <sub>2</sub> O <sub>4</sub>	10.29	2.51
CoCr <sub>2</sub> O <sub>4</sub>	10.06	2.82
MnCr <sub>2</sub> O <sub>4</sub>	9.15	2.55

( $At/C^0$ ),  $A$  being the frequency factor. Such a relation implies a linearity between  $\ln X$  and the reciprocal temperature.

A plot of the experimental data is given in Fig. 4. The good linearity seems to confirm a low value of the order of reaction with respect to propylene; this finding is in accordance with a strong influence on the kinetics of reactant adsorption.

The activation energies obtained are summarized in Table 5. The values of pre-exponential factors, given in the same table, were referred to unit surface area; they all contain the same arbitrary constant ( $t/C^0$ ).

Figure 5 shows a plot of the logarithm of the preexponential factors versus the activation energies, and reveals the existence of a compensation effect.

#### DISCUSSION

Despite attempts to detect traces of partial oxidation products of propylene, our work revealed that CO<sub>2</sub> and H<sub>2</sub>O were the only reaction products.

This finding confirms that over strongly ionic oxides a completely nonselective hydrocarbon oxidation takes place (7, 8), consistent with the low mobility of the oxygen ions in the lattice. This is confirmed by the thermogravimetric results obtained in propylene atmosphere, where no evidence was obtained for oxygen depletion of the catalysts.

It follows that the oxidation mechanism implies the intervention of chemisorbed oxygen on the catalyst surface. It is known

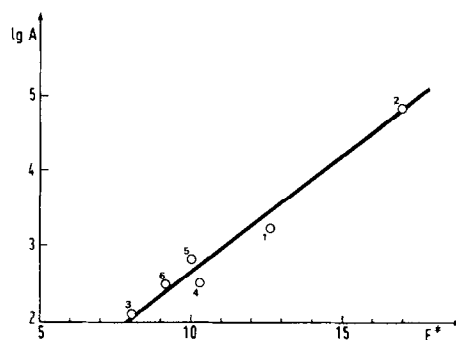
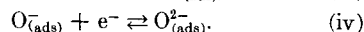
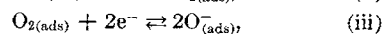
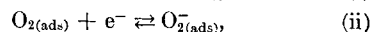
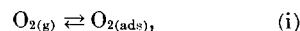


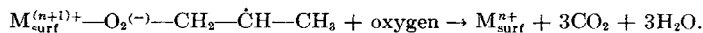
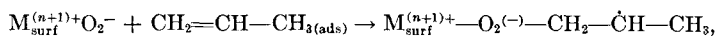
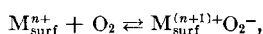
FIG. 5. Log  $A$  versus  $E^\ddagger$ . NiFe<sub>2</sub>O<sub>4</sub> (1), CoFe<sub>2</sub>O<sub>4</sub> (2), MnFe<sub>2</sub>O<sub>4</sub> (3), NiCr<sub>2</sub>O<sub>4</sub> (4), CoCr<sub>2</sub>O<sub>4</sub> (5), MnCr<sub>2</sub>O<sub>4</sub> (6).

that over metallic oxides, depending on the system under investigation, the formation of O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, and O<sup>2-</sup> ions has been postulated according to the following reactions (9):



The O<sub>2(ads)</sub><sup>-</sup> ions can be considered to be the precursors in the incorporation of oxygen into the lattice. The presence of O<sub>2</sub><sup>-</sup> and O<sup>-</sup> on surfaces of oxides has been revealed by E.S.R. spectroscopy (10). In ionic oxides such as NiO, CaO, and MnO, their presence has been confirmed also by chemical methods (9).

In strongly ionic oxides, with low mobility of oxygen in the lattice, at temperatures which are not too high, the rate of the last reaction is low and therefore O<sub>2</sub><sup>-</sup> and O<sup>-</sup> can be considered the most abundant surface intermediates (*masi*). Due to the high reactivity of such ion-radical species, the oxidation of a hydrocarbon can take place through a direct radical attack of the hydrocarbon, followed by its rapid complete destruction. It might be suggested that the overall process takes place through a set of free radical reactions in which the activation of oxygen, through a charge transfer, can play an important role:



On the basis of the foregoing scheme, resembling the autoxidation of hydrocarbons (11), the absence of intermediate oxidation products is justified.

If the rate limiting step is given by the latter reaction the Langmuir-Hinshelwood scheme leads to a rate  $r$ , where

$$r = k \frac{b_0 b_P P_{O_2} P_P}{(1 + b_0 P_{O_2} + b_P P_P)^2} \quad (4)$$

with  $b_0$  and  $b_P$ , respectively, the adsorption equilibrium constants of oxygen and propylene, and  $P_{O_2}$ ,  $P_P$  their partial pressures. For a strong chemisorption of oxygen, unity can be neglected in the denominator of the preceding equation, so that:

$$r \simeq k[zR/(1 + zR)^2], \quad (5)$$

where  $z = b_0/b_P$  is the relative adsorption coefficient of oxygen with respect to propylene and  $R = P_{O_2}/P_P$  the ratio of the partial pressures of reactants. Since in our runs an approximately stoichiometric ratio (oxygen/propylene) for the complete oxidation has been employed, the value of  $R$  is not affected by the reaction degree. Therefore the previous equation can be written as

$$r \simeq kz \text{ const} = k_e, \quad (6)$$

and the observed value of zero of the reaction order, even up to very high reaction degrees, is justified.

From the data summarized in Table 5 the behavior of chromium spinels is very consistent. This finding seems to indicate that in this case only the trivalent ions play an important role in propylene oxidation. In the chromium compounds  $Cr^{3+}$  ions are all in octahedral positions, and the most important factor in the behavior of the solids as catalysts seems to be the coordination of the ions.

Turning to the iron compounds, an inversion of structure occurs which implies a different coordination and different energy levels for the metallic ions, due to the electrostatic interactions with the other ions of the lattice. In this set of spinels a more pronounced difference in reactivity is observed. This difference cannot be justified on the basis of the coordination effects in

chemisorption since, as far as a  $d^5$  ion ( $Fe^{3+}$ ) is concerned, the crystal field stabilization energy is zero.

It seems reasonable therefore to attribute the observed difference in reactivity to the differences in the electrostatic energy of the levels of the iron ions. In fact such differences can affect the energy of the charge transfer processes (ii) and (iii). For instance, the energy variation of reaction (ii) can be expressed as follows:

$$E_{O^-} = \phi - (A + W) \quad (7)$$

where  $A$  is the electron affinity of the oxygen molecule,  $\phi$  is the electron work function of the solid, and  $W$  the interaction energy of the ion formed with the catalyst (12). The latter value includes both coulomb and exchange terms and it has a complex dependence on the electronic structure of the catalyst.

The path of the oxidation reaction can be described by means of the energetic diagram given in Fig. 6 in which the progress of oxygen from the adsorbed to the reaction products is illustrated. The transfer of oxygen on the solid surface to hydrocarbon is illustrated for three different solids in which the adsorbed oxygen is at different energetic levels corresponding to different values of  $W$ . It appears that, consistent with the Polanyi rule (13), the following proportionality relation can be applied:

$$E^\ddagger = E_O - \alpha \Delta H, \quad (8)$$

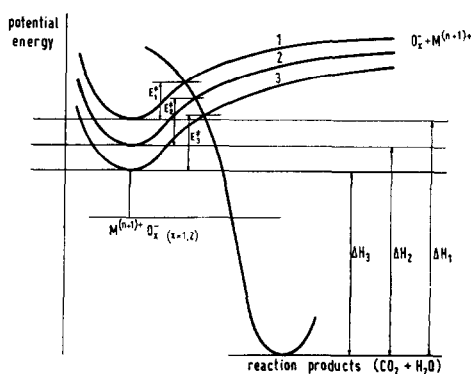


Fig. 6. Reaction paths of the oxidation process.

where  $E_0$  and  $\alpha$  are constants. In addition

$$\Delta H = E_{\text{products}} - (E_{\text{MO}_x} + E_{\text{ol(ads)}}), \quad (9)$$

and since the first term of the previous equation is the same for all the considered catalysts, it follows that the activation energy must be proportional to the sum of the adsorption heats of both reactants:

$$E^\ddagger \simeq E_1 + \alpha(\Delta H_{\text{ads(O}_1)} + \Delta H_{\text{ads(O}_2)}) \\ = E_1 + (1 + \xi)\gamma, \quad (10)$$

where  $\xi = \Delta H_{\text{ads(O}_2)}/\Delta H_{\text{ads(O}_1)}$  and  $\gamma = \alpha \Delta H_{\text{ads(O}_1)}$ .

On the basis of Eq. (6), the effective rate constant  $k_e$  can be written as follows:

$$k_e \simeq e^\xi e^{-[E_1 + \gamma(1 + \xi)]/RT}. \quad (11)$$

Inasmuch as the adsorption heat of the olefin is not significantly affected by the nature of the different oxides, and therefore the value of  $\gamma$  can be assumed constant, the preceding relation justifies the observed compensation effect.

#### ACKNOWLEDGMENT

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#### REFERENCES

1. DOWDEN, D. A., *Catal. Rev.* **5**, 1 (1971).
2. WICKHAM, D. G., in "Inorganic Synthesis" (S. Y. Tyree, Ed.), Vol. 9, p. 152. McGraw-Hill, New York, 1967.
3. PARRISH, M., EKSTEIN, M. G., AND IRVIN, B. W., "Data for X-Ray Analysis," Vols. I, II. Philips' Technical Library, Irvington on Hudson, NY, 1953.
4. BASSETT, D. W., AND HABGOOD, H. W., *J. Phys. Chem.* **64**, 769 (1960).
5. GAZIEV, G. A., FILINOVSKII, V. Y., AND YANOVSKII, M. I., *Kinet. Katal.* **4**, 500 (1963).
6. BLANTON, W. A., BYERS, C. H., AND MERRILL, R. P., *Ind. Eng. Chem. Fundam.* **7**, 611 (1968).
7. TRIFIRÒ, F., AND PASQUON, I., *J. Catal.* **12**, 412 (1968).
8. CARRÀ, S., UGO, R., AND ZANDERIGHI, L., *Inorg. Chim. Acta* **3**, 55 (1969).
9. BIELANSKI, A., AND NAJBAR, M., *J. Catal.* **25**, 398 (1972).
10. VAN HOOFF, J. H. C., *J. Catal.* **11**, 277 (1968).
11. KAMIYA, Y., *J. Catal.* **24**, 69 (1972).
12. BORESKOV, G. K., "On Fundamentals of Gas-Surface Interactions" (H. Saltsburg, J. N. Smith, Jr., and M. Rogers, Eds.), p. 216. Academic Press, New York, 1967.
13. BOUDART, M., "Kinetics of Chemical Processes." Prentice-Hall, Englewood Cliffs, NJ, 1968.