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Determination of the Active Center in Calcium–Nickel Phosphate Dehydrogenation Catalyst

Calcium–nickel phosphate $Ca_8Ni(PO_4)_6$ was first prepared by Britton *et al.* (*1*), and its activity as a dehydrogenating catalyst is used industrially to obtain butadiene from butenes. $Ca_8Ni(PO_4)_6$ is prepared by substituting Ni for Ca in the β-$Ca_3(PO_4)_2$ host lattice. Only about 10% nickel atoms can be substituted (*2*). X-Ray Debye–Scherrer patterns of $Ca_8Ni(PO_4)_6$ and β-$Ca_3(PO_4)_2$ are quite similar. As the β-$Ca_3(PO_4)_2$ structure is known to be analogous to that of whitlockite (*3*), which has a formula close to $6[Ca_3(PO_4)_2, 2MHPO_4]$, where M is a small cation such as Mn, Fe, or Mg which substitutes Ca^{2+} ions in certain chains of the lattice, it seems likely that $Ca_8Ni(PO_4)_6$ has the whitlockite structure. The maximum nickel solubility corresponds to the maximum catalytic activity in the dehydrogenation of isopropanol (*4*). The dehydrogenating activity is not observed for amorphous mixtures of calcium and nickel phosphates, showing that the activity results from substitution of Ni for Ca within a crystalline host lattice. The purpose of this note is to determine the Ni oxidation states involved, and to propose a mechanism. Conclusions are drawn from comparing catalytic activity with electron spin resonance (ESR) spectra.

Amorphous calcium–nickel phosphate was obtained by the method of Britton *et al.* (*1*), starting from dilute solutions of $CaCl_2$, $NiCl_2$, and $(NH_4)_2HPO_4$. Mixing the solutions at pH 8 leads to coprecipitation. The cake resulting from filtration was dried at 120°C for 2 hr. Three amorphous compounds have been prepared corresponding respectively to 0, 0.05, and 0.1 values of the Ni/Ca ratio. The catalyst is obtained by calcining the amorphous compound at temperatures ranging from 400 to 900°C. The heating has been carried out under different atmospheres (O_2, air, N_2, CO, and H_2); the compound was placed in a crucible inside a quartz tube heated by a tubular furnace and flushed by the chosen gas. The products obtained under air, O_2, and N_2 have a light yellow color, whereas CO and H_2 give gray and black products, respectively.

The catalytic activity has been characterized by studying isopropanol decomposition. The conversion and the selectivity to acetone (dehydrogenation) and propylene (dehydration) have been measured using an apparatus of the type described by Durand *et al.* (*5*). The catalyst (1 g), deposited on a sintered glass inside the reactor, was flushed by a stream of N_2 saturated with isopropanol. The conversion percentage C and the selectivity S were deduced from (i) the amount of catalyst used, (ii) the partial pressure of isopropanol in the nitrogen flow, and (iii) gas chromatographic analysis of the mixture after reaction. The catalysis experiments were performed at 250°C. S is given by the ratio: amount of acetone (or propylene)/amount of alcohol converted.

The ESR spectra have been obtained with modulation spectrometer, a detailed description of which is given elsewhere (*6*). It differs from conventional spectrometers by the fact that the microwave field is amplitude modulated; a pickup coil, close to the sample and with its axis along the static field, receives an induction signal proportional to the time derivative of the longitudinal magnetization. The apparatus gives an absorption line directly and is more suitable for observing wide lines because it does not involve modulation of the static field.

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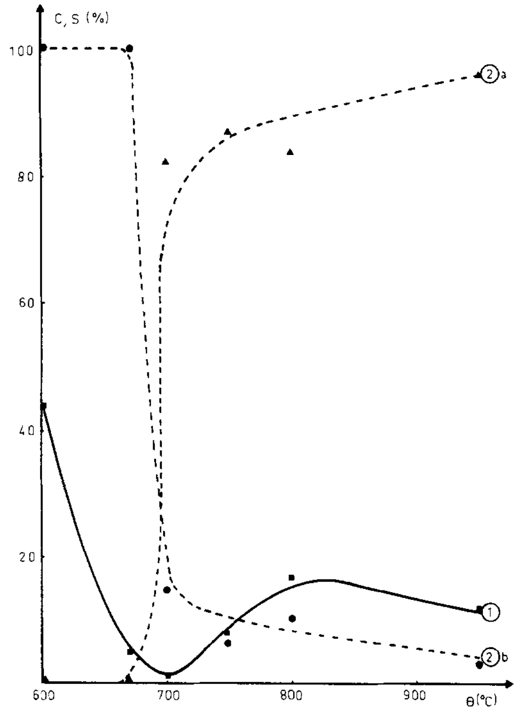

FIG. 1. Influence of the calcination temperature (in air) θ of amorphous calcium phosphate on the catalytic decomposition of isopropanol at 250°C: (1) conversion *C*; (2) selectivity *S* (*a*, acetone; *b*, propylene).

The catalytic activity of the precipitated amorphous phosphate depends on the treatment temperature. For the 10% nickel compound, the activity for heat treatments below 700°C is mainly dehydrating (Fig. 1), but above 700°C the catalyst becomes dehydrogenating. This change corresponds to a crystallization observed at about 670°C by differential thermal analysis. For the catalyst calcined at 800°C, the activity depends nonlinearly on nickel concentration (Table 1). When the phosphates are heated at 800°C under inert (N_2) or oxidizing (air, O_2) atmosphere, they give a practically constant conversion ratio ($C \simeq 15\%$). A slightly reducing atmosphere (CO) decreases the activity ($C \simeq 2\%$). H_2 atmosphere reduces the nickel ion sites giving zero-valent nickel species: a high activity develops ($C \simeq 98\%$) but this is irrelevant to the mechanism investigated here.

ESR spectra have been measured at 77 K and show two lines: (i) R_1 (peak amplitude r_1) centered at $H_0 \simeq 1380$ Oe, and (ii) R_2 (peak amplitude r_2) centered at $H_0 \simeq 3070$ Oe (Fig. 2). The r_1 and r_2 intensities are given in Table 1 as functions of the nickel concentration. The accuracy of these intensities is about 20%. For zero Ni concentration (i.e., for $Ca_3(PO_4)_2$) there is a spectrum ($r_1 = 25$, $r_2 = 60$) which seems to be due to impurities. The same spectrum with the same intensity is also obtained from the amorphous calcium–nickel phosphate calcined at temperatures below 670°C. When the calcination temperature is raised above 670°C, the ESR spectra become more intense (Table 1). Such an influence of the crystallization on the ESR intensity has already been reported by Andrushkevich *et al.* (*7*) for calcium–nickel–chromium phosphate, a similar catalyst. After calcination at 800°C, the r_2 value remains approximately constant when the nickel concentration is increased from 5 to 10%. In contrast, the r_1 value strongly increases following a nonlinear law, in accordance with the catalytic activity. Thus, the line R_1 can be considered as describing satisfactorily the activity.

Both the R_1 and R_2 lines can be attributed to nickel because an isomorphous compound, prepared with cadmium instead of nickel in the β-$Ca_3(PO_4)_2$ lattice, provides after calcination in air at 800°C a spectrum

TABLE 1

Conversion in the Catalytic Decomposition of Isopropanol at 250°C and ESR Line Intensities for Calcium–Nickel Phosphates Crystallized in Air at 800°C

	Ni/Ca (%)		
	0	5	10
Conversion (%)	0	1.5	17
ESR intensities (arb. units)			
r_1	25	100	630
r_2	60	760	780

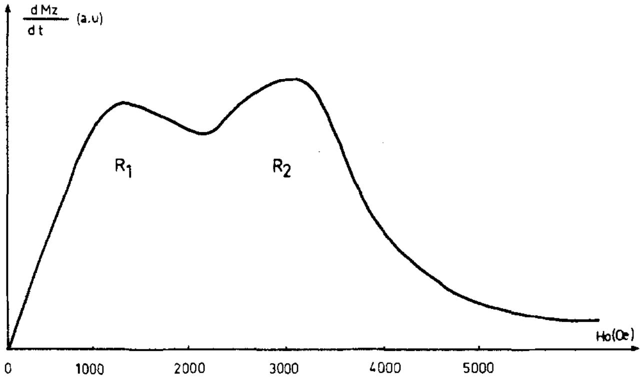

FIG. 2. ESR spectrum of calcium-nickel phosphate at 77 K and 8600 MHz (catalyst calcined at 800°C in air, with Ni/Ca $\simeq$ 10%).

with r_1 and r_2 intensities equal to those obtained with zero nickel concentration. Moreover, $(r_1 + r_2)$ is roughly proportional to Ni concentration (Table 1): the value passes from 775 to 1325 with a twofold increase in the Ni concentration. The linewidth ΔH equals 1600 and 1300 Oe for R_1 and R_2, respectively. It remains the same for both R_1 and R_2 when passing from 5 to 10% nickel concentrations. This indicates that the exchange narrowing is either negligible or the same for both concentrations. This enables us to use r_1 and r_2 as definitions of the line intensities, whereas the areas should have been used if ΔH had not been proved independent of the Ni concentration.

The influence on the ESR lines of the oxidation–reduction properties of the atmosphere present during crystallization has been studied for the 10% Ni catalyst treated at 800°C (Table 2). r_1 is approximately the same for samples prepared in oxidizing (O_2, air) or neutral (N_2) atmospheres. It decreases and becomes equal to zero when a CO or a more reducing atmosphere (H_2) is used, respectively. The line R_2 shows a more complex behavior, except in the case of H_2. A third line, with amplitude r_3 and centered at $H_0 \simeq$ Oe, is observed on CO or H_2 treatment. Heating under CO, r_3 is very low as compared to r_1 and r_2, but r_3 is quite strong after heating in H_2. In this case, a zero-field ESR signal is detected which could be due to zero-valent nickel species, considered as responsible for the high catalytic activity of hydrogen-reduced phosphates.

Let us now discuss the results. The most stable oxidation state for nickel is Ni^{2+}. The ESR spectrum of Ni^{2+} (d^8) in an octahedral crystal field generally shows a g value between 2.00 and 2.35 (*8*). We accordingly attribute our R_2 line at $g \simeq 2.0$ to Ni^{2+}.

The R_1 line has been shown to be linked with the catalytic activity. Moreover, both the r_1 amplitude and the activity are increased for samples prepared under an oxidizing atmosphere. These observations lead us to conclude that the R_1 line corresponds to a high nickel oxidation state, possibly Ni^{3+}. One may ask if this conclu-

TABLE 2

Conversion in Isopropanol Decomposition at 250°C and ESR Line Intensities for Calcium–Nickel Phosphate (Ni/Ca $\simeq$ 10%), Crystallized at 800°C under Various Atmospheres

	Atmosphere				
	O_2	Air	N_2	CO	H_2
Conversion (%)	15	15	15	2	98
ESR intensities (arb. units)					
r_1	560	700	650	300	0
r_2	460	720	410	820	0
R_3	0	0	0	70	620

sion is compatible with the observed ESR spectrum centered at $g \simeq 4.5$. Abragam and Bleaney (*8*) have computed the g value for the $3d^7$ configuration (Ni^{3+}) in octahedral symmetry. For a weak ligand field,, they obtain $g = 4.33$ which is close to our $g \simeq 4.5$ value. In contrast, for a strong ligand field the experimental g values for d^7 are generally between 2.1 and 2.3. Unfortunately, the lack of information about the crystal field strength of $Ca_3(PO_4)_2$ does not allow a definite answer. Other interpretations remain possible for the R_1 line, such as $\Delta m = 2$ transitions in the triplet state of Ni^{2+}. We can simply state that our ESR results are compatible with the appearance of Ni^{3+} ions. However, we may note that this idea is supported by (i) the correlation between the increase of r_1 and the oxidizing nature of the calcination atmosphere, and (ii) the basic character of the phosphate lattice well known to stabilize high oxidation states (*9*). Moreover, we shall see below how the existence of Ni^{3+} ions allows an interpretation of the catalytic phenomenon.

Figure 1 shows that the activity changes from dehydrating to dehydrogenating when increasing the calcination temperature, i.e., when passing from the amorphous to the crystalline compound. The dehydrating process can be related to the surface acidity, ascribable probably to HPO_4^{2-} ions which exist at low calcination temperature. In this case, Ni^{2+} does not play any role and the active sites are analogous to those present in $Ca_3(PO_4)_2$ (*10*) or hydroxyapatites (*11*). These sites would produce protonation of isopropanol following the mechanism of Kibby and Hall (*12*). When the coprecipitate is calcined at temperatures above 700°C, the activity becomes dehydrogenating, an effect due to nickel. An attempt to explain the role played by nickel leads us to use Kibby and Hall's assumptions for dehydrogenation of secondary alcohols over apatites. The first step consists of alcohol oxidation ($R_2CHOH \rightarrow R_2CO + 2H^+ + 2e$) and is followed by a second one in which the electrons are eliminated by reducing a cation. In contrast with apatites where such a reaction is impossible, in our case it can occur if we assume the existence of Ni^{3+} ions. The following overall mechanism can then be proposed:

$$\begin{array}{ll} R_2CHOH & \rightarrow R_2CO + 2H^+ + 2e \\ 2Ni^{3+} + 2e & \leftrightarrows 2Ni^{2+} \\ 2H^+ + 2Ni^{2+} & \rightarrow 2Ni^{3+} + H_2 \\ \hline R_2CHOH & \rightarrow R_2CO + H_2 \end{array}$$

The formation of Ni^{3+} ions during the thermal activation of the amorphous phosphate remains as yet unexplained. Ni^{3+} ions are probably created during the crystallization, and stabilized by the lattice. Such an example of the stabilization of high oxidation states of transition metals has already been reported in phosphates and arsenates (*9*).

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