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Ageing of fresh and used Ca–Sr–cuprate-based catalysts

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An ageing degeneration process was observed in a Ca–Sr–cuprate catalyst, both unused and after use in an NO decomposition reaction. The formation of strongly interacting dipoles (SIDs) by Cu^{2+} and oxygen ions perturbs the layerlike structure, which is typical of $Sr_3Cu_5O_8$ species and is also characteristic of the present catalyst when it is fresh. This phenomenon was observed with both unused and used aged samples. Furthermore, in the case of the used catalysts, the degeneration process lead to the disappearance of both the layerlike crystal structure and of the SID systems. However, the samples recover their properties when recalcined.

1. Introduction

In previous papers [1, 2] a few alkaline-earth copper oxides were compared as catalysts for NO decomposition. A sample of $(Ca_{0.55}Sr_{0.45})_3Cu_5O_8$ was the most active for this reaction. Its catalytic activity appeared to be connected with the presence of a layerlike crystal structure approximating a two-dimensional ferromagnet, which was stable over quite a wide range of temperatures. This was confirmed by the peculiar dependence on temperature of the line width of the electron paramagnetic resonance (EPR) signal generated by the solid. The line broadened linearly with increasing temperature, in line with the data in the literature for similar cases. A variation was also noticed in the EPR pattern after adsorption of NO. In fact, a new line appeared at about 0.2 T; this was attributed to the formation of strongly interacting dipoles (SIDs) composed of copper and oxygen ions.

Aiming to gain a deeper insight into this puzzling subject, we examined the same samples again, to see what changes occurred during their ageing process; that is, to see if they underwent a time-dependent evolution. In particular we were interested to see: (i) whether the unused catalyst is stable in time, (ii) whether the used catalyst, which was surely modified, preserves the previous physico-chemical characteristics, and (iii) whether the change of such characteristics affected the catalytic activity.

2. Experimental procedure

The instruments employed and the procedure followed for collecting the EPR spectra, the X-ray diffraction (XRD) patterns and for checking the catalytic activity for NO decomposition are described in detail elsewhere [1].

3. Results

3.1. Ageing of the unused catalyst

No appreciable difference was noticed when comparing the X-ray diffractograms (CuK_α radiation, Ni-filtered) of the one-year aged catalyst, stored in the usual screw-capped vials, with the pattern obtained with the same sample just as-prepared. Also, the EPR spectrum of this sample did not change significantly for about one year. A single Lorentzian-shaped line was observed at spectroscopic factor $g \approx 2$, accompanied by a $\Delta M_s = 2$ *half-field line*, where M_s is the total electron spin quantum number. However, a small difference in the broadening of the $g \approx 2$ line with increasing temperature was observed in the two (fresh and one-year aged) samples, as shown in Fig. 1. In fact, the slopes of the two curves are slightly different. Therefore, a further examination was made at a higher microwave power, with simultaneous extension of the temperature range (Fig. 2). No significant influence of the microwave power on the broadening of the line was noted and the temperature-dependent broadening effect acting on this line (Fig. 1b), as well as on the $\Delta M_s = 2$ line (Fig. 2), was confirmed up to 150 °C. However, very surprisingly, a new line was observed with the one-year aged catalyst at temperatures higher than about -70 °C. This line depended on the temperature in the opposite way to the other EPR transitions present in the experimental pattern. In fact, it

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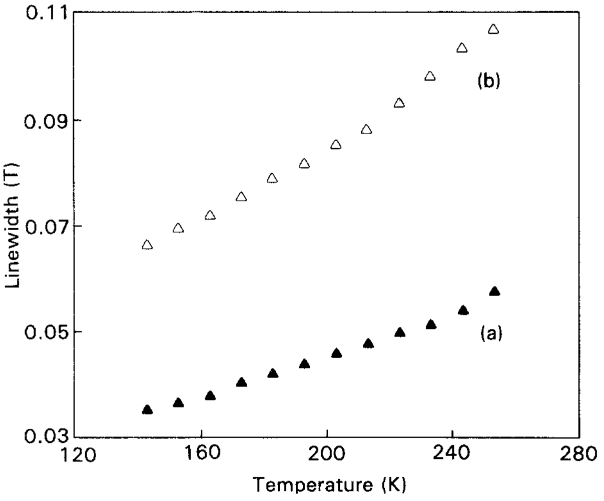

Figure 1 The $g \approx 2$ EPR line width plotted against temperature: (a) the fresh, unused catalyst, and (b) the one-year-aged, unused catalyst.

increased in intensity, narrowing at higher temperatures and moving from nearly 0.18 T (at – 70 °C) up to 0.25 T (at 150 °C). No line of this kind was observed, under the same experimental conditions, with the same sample when fresh.

After longer ageing times (about 18 months) the $g \approx 2$ EPR line started to change into a different asymmetric pattern (Fig. 3a), indicating that some significant change occurred in the sample. In fact, at this stage, the catalytic performance of the catalyst also decreases as is shown in Fig. 4a, in which only a part of the first two pulses of NO is converted into O_2 (plus N_2, not shown in Fig. 4), the following five pulses remaining unconverted. Indeed the removal and not a formation of oxygen is shown in correspondence of these five NO pulses; and no formation of NO_2 (not reported for clarity) was observed for any of the seven NO pulses. The same sample, after reaction, had a different EPR spectrum. In particular, a new line appeared at about 0.2 T (Fig. 3b); it overlapped a broader band centred at a higher magnetic field. Both these bands also appeared in the EPR spectrum of the same sample (Fig. 3c) after it was submitted to recalcination in air at 870 °C for 2 h and before it was used for catalysing the NO decomposition. However, in the last case, the higher-field line was less intense (compare Fig. 3c and b). Furthermore, the recalcined sample recovered the same catalytic performance (Fig. 4b) as the original, fresh sample and, after the catalytic run, the lower-field line intensity increased considerably (Fig. 3d). The same effect seems to be produced by recalcination (Fig. 3c) and by pulse reaction with NO (Fig. 3b and d). In fact, in both cases an increase in the intensity of the EPR line at 0.2 T was noted. Indeed, this behaviour appears both when the sample has become a badly performing catalyst (Fig. 3b) due to ageing, and when, after recalcination, it recovers its initial catalytic activity (Fig. 3c).

3.2. Ageing of the catalyst after use for NO decomposition

A completely different ageing behaviour was observed after the use of the catalyst for NO decomposition. A

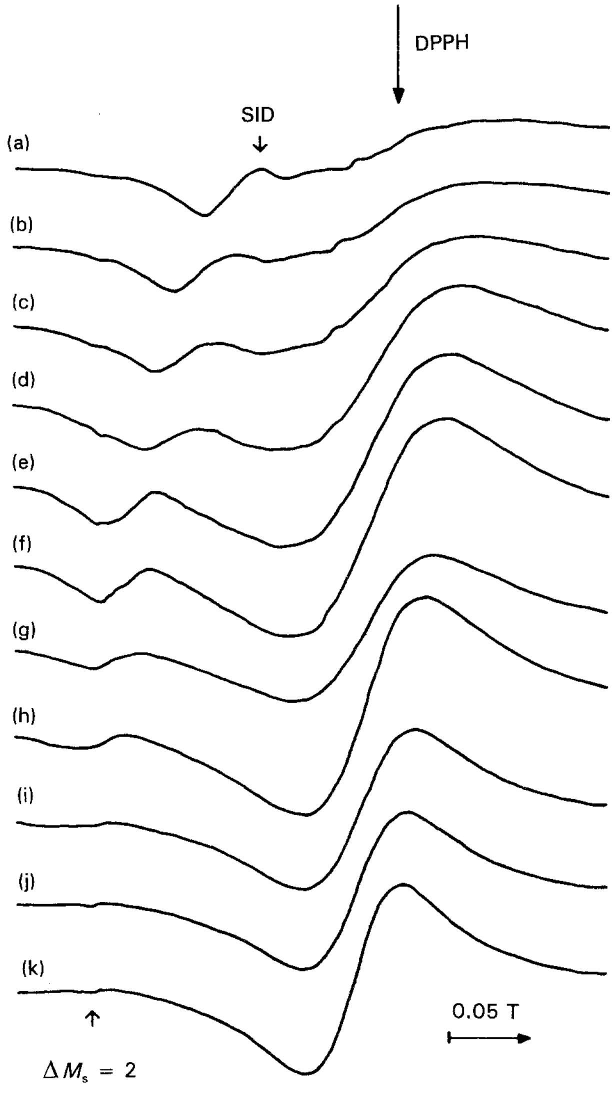

Figure 2 EPR spectra of the unused, one-year-aged catalyst (microwave power, 20 mW, modulation amplitude 8×10^{-5} T and receiver gain 10^4) for the following temperatures. (a) 150, (b) 110, (c) 70, (d) 30, (e) 0, (f) – 20, (g) – 40, (h) – 70, (i) – 100, (j) – 120, (k) – 140 °C.

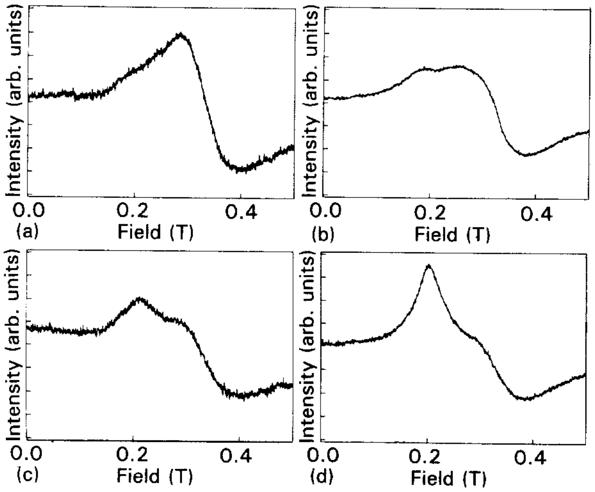

Figure 3 EPR spectra of the unused, 18-month-aged sample: (a) before the reaction, (b) after the reaction, (c) unused, recalcined, and (d) used after recalcination.

remarkable decrease in crystallinity was shown by XRD analysis one year after the reaction. An EPR spectrum which is typical of magnetically diluted Cu^{2+}-ions was detected (Fig. 5a). The optimized parameters are $g_1 = 2.2476$, $g_2 = 2.1168$ and $g_3 = 2.0500$. The simulation was made [3] with the line-width depending on the orientation within the 6.2–10.2 $\times 10^{-3}$ T, range, to account for the unresolved copper hyperfine coupling, which was assumed to be coaxial with the g tensor. This sample is no more active for the reaction mentioned above (Fig. 6a). After the reaction, the sample had a completely new EPR pattern, composed of a broad band centred at about 0.32 T and of a second band appearing at about 0.04 T (Fig. 5b). However, the same sample, if recalcined before use, had an EPR spectrum (Fig. 5c) rather similar to that reported in Fig. 3c for the aged but unused recalcined sample. Furthermore, after recalcining, the catalytic activity (Fig. 6b) became as good as that of the unused aged and recalcined sample (Fig. 4b). At last, after the reaction the intensity of the EPR line at 0.2 T (Fig. 5d) increased as mentioned above for the cases in Fig. 3b and d. An attempt to ascertain the origin of the increase of the EPR line intensity at 0.2 T was made by X-ray photoelectron spectroscopy (XPS) analysis. Although limited to the external surface layer, this showed that (during the reaction) the increase in the intensity of this EPR line was accompanied by a decrease in the relative oxygen abundancy from about 12.5% to about 8.0%.

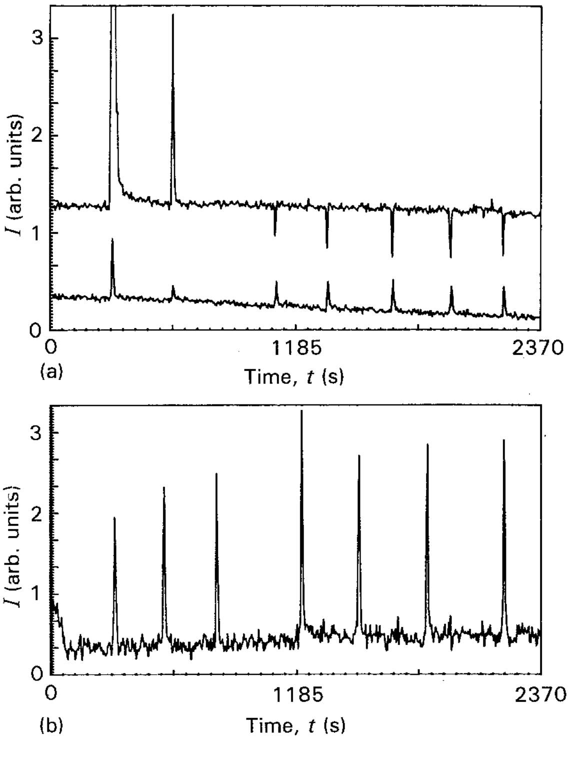

Figure 4 Results of a NO decomposition pulse reaction at 150 °C. (a) Unused, 18-months-aged catalyst: upper trace, mass spectrometric monitoring of oxygen formation (a.m.u. = 32), and lower trace, NO pulses (a.m.u. = 30). Notice that oxygen is consumed instead of being formed after the second NO pulse. (b) The same catalyst after recalcination using mass-spectrometric monitoring of oxygen formation.

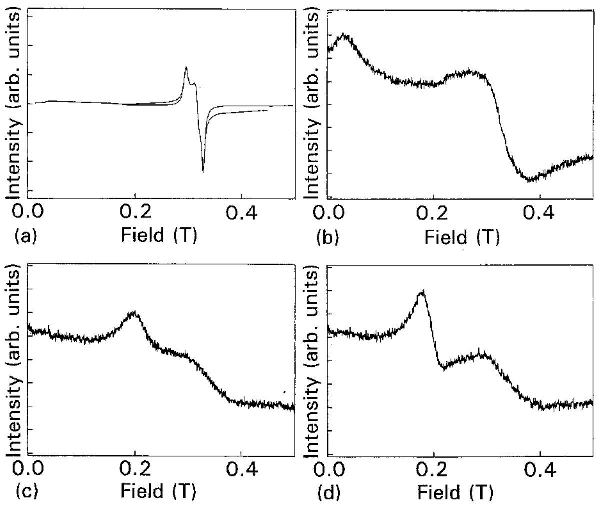

Figure 5 EPR spectra of the 18-months-aged-after-first-use sample: (a) before the second use (the lighter line is the computer simulation), (b) after the second use, (c) recalcined before the second use, and (d) used a second time after recalcination.

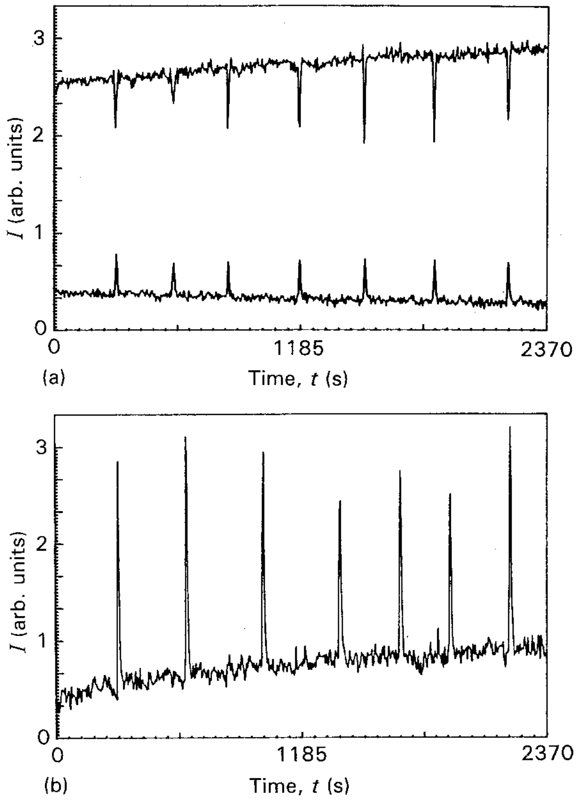

Figure 6 The results of the NO decomposition pulse reaction at 150 °C. Key as for Fig. 4, but for the 18-months-aged-after-first-use catalyst.

4. Discussion

4.1. Aged unused catalyst

The unused catalyst preserved its essential physicochemical properties for a long time. In fact, its crystal structure, as revealed by XRD analysis, was still the same one year after the sample preparation, and the EPR Lorentzian line-shape did not change during this rather long delay. Only a slightly different temperature-induced broadening was observed, indicating that some change had started to occur in the sample.

This $g \approx 2$ Lorentzian-shaped line can be attributed to dipolar interactions which are small enough for the long-time spin diffusion mechanisms to dominate the relaxation process [4]. This is typical [5] of crystals having large superexchange interactions (antiferromagnets) as well as sufficiently low symmetries. Such a situation occurs in many bidimensional antiferromagnetic Cu^{2+} layerlike crystals with very weak exchange between the ions in different layers (in which, in contrast, the copper ions belonging to the same layer are coupled by a strong superexchange). These systems may be characterized by an appreciable deviation of the g-value with respect to that of free electrons, as well as by a sufficiently strong value of the isotropic exchange constant, J. In these cases the antisymmetric exchange

$$\sum_{jk} d_{jk} S_j \times S_k \qquad (1)$$

overcomes the dipole–dipole interaction, and the temperature dependence

$$\Delta H(T) = \alpha + \beta T + \gamma/(T - T_N)^p \qquad (2)$$

of the exchange-narrowed EPR line-width, $\Delta H(T)$, becomes observable [5]. In Equation 2, p is an experimental parameter and the third term is important only in proximity to the Néel temperature, T_N. A linear trend of ΔH with temperature is thus commonly observed in these systems not too far from room temperature.

The broadening effect described by Equation 2 is attributed [4–7] to absorption and emission of phonons of frequency $\nu_{ph} = J/h$, which mix triplet and singlet states. In Equation 2 [5]

$$K \equiv \beta/\alpha = \frac{24(\lambda R)^2 J^3}{9\pi\rho c_{eff}^5 \hbar^3} k \qquad (3)$$

where R is the distance between nearest-neighbour copper ions, ρ is the crystal density, c_{eff} is the sound velocity in the crystal and

$$\partial J/\partial R \approx \lambda J \qquad (4)$$

In our case, a straight line can correctly fit the trend of ΔH with temperatures, below 213 K, with $K = (2.2 \pm 0.2)10^{-2}$ and $K' = (1.46 \pm 0.06)10^{-2}$ for the fresh and for the one-year aged sample, respectively.

The physical quantities which can change during the ageing process of the catalyst are R and J. Since the latter decreases exponentially, while the former increases linearly,

$$\begin{aligned} K'/K &= (R'/R)^2 (J'/J)^3 \approx (J'/J)^3 \\ &= 0.7 \pm 0.1 \qquad (5) \end{aligned}$$

or

$$J' \approx (0.89 \pm 0.06) J \qquad (6)$$

This means that, for the unused catalyst, the long-time spin diffusion mechanism is a relaxation process which is a little less effective for the aged than for the fresh sample. This seems very likely to be connected with the local lower degree of crystallinity of the former and it is perfectly in line with the appearance of the second EPR line observed at magnetic fields in the range 0.18–0.23 T. In fact, local defects are characterized by a dipolar interaction overcoming even spin-exchange and Zeeman interactions, as reported [8] for $SrCuO_2$. An EPR line at the same magnetic field-values was also detected by us with Ca_2CuO_3 and accurate line-shape measurements were made with that sample at different temperatures [9]. The line narrowed and moved towards higher fields with increasing temperature exactly as in the present case with $(Ca_{0.55}Sr_{0.45})_3Cu_5O_8$. This line can be attributed to the same phenomenon of SIDs, due to the formation of local canted defects (LCDs) presumably caused by the occurrence of oxygen-deficient states. In fact it is well-known [10] that a "normal" EPR triplet pattern can no longer be detected when the strength D of the electron–electron dipolar coupling overcomes the electron Zeeman energy possessed by the single unpaired electron in the external magnetic field set by the spectrometer. This energy, when operating with the usual X-microwave band (≈ 9 GHz), is of the order of 0.3 cm^{-1}. For $D > 0.3$ cm^{-1}, the EPR triplet pattern is expected to exhibit severe distortion. The low-field z_1 line would disappear, being replaced, in a low-field region, by a strong new z_2' line, due to a transition between the same levels characteristic of the z_2 line at higher field. So, an EPR line at about 0.2 T can be attributed to a z_2' line due to a dipolar coupling D of about 0.5 cm^{-1}; this is larger than the electron Zeeman energy. The z_2 line should be still detectable at about 0.8 T, but with a very low intensity, and so it is not surprising that it has not been observed in all of the above reported cases. Furthermore, when a SID system forms, the $\Delta M_s = 2$ line, typical of triplet state, must be less intense. This has been observed in the present case, in which the appearance of the SID line at about 0.2 T in the aged unused sample corresponds to a decrease (Fig. 2) of the intensity of the $\Delta M_s = 2$ transition.

After longer ageing times (ca. 18 months) more evident changes occur in the still unused sample. The EPR line (Fig. 3a) is no longer Lorentzian shaped, indicating that the previous layer-like structure is no longer preserved. At this stage, the catalytic activity also decreases (see Fig 4a), and it completely disappears after just two NO pulses. A parallel increase of the oxygen-deficient defects can be argued from the change shown by the EPR pattern, with enhancement of the SID line (Fig. 3b). Recalcination is the only way to recover good activity from the unused 18-months-aged sample (Fig. 4b). Recalcination produces an enhancement of the SID line (Fig. 3c), which increases further during the reaction (Fig. 3d). This leads to the conclusion that the formation of the SID line is triggered by a reaction as well as by calcination, but it is not directly related to the sample's catalytic activity.

4.2. Aged used catalyst

A faster degeneration process must be hypothesized for the used sample, with respect to the unused sample. Indeed, after one year of ageing, the single Lorentzian-shaped line due to antisymmetric exchange (see Equation 1) is still present, together with the SID line, whilst both these patterns disappear in used samples, being substituted by a spectrum typical of isolated Cu^{2+}-ions (Fig. 5a). The formation of a disordered system must be at the origin of this spectrum. Pairs of copper ions would couple directly with each other in this new system, forming chemical bonds and leaving just a small amount of isolated uncoupled copper ions in a non-cubic environment. The measured g-values of these spectra are very close to those reported for samples prepared from powdered $BaCO_3$ and CuO, or attributed to the so-called green phase (Y_2BaCuO_5) which is sometimes present as impurity in "1–2–3" superconducting oxide mixtures [11–14]. The formation of this new situation is accompanied by total loss of catalytic activity (Fig. 6a). The completely new EPR pattern observed after reaction (Fig. 5b) can be explained on the basis of the formation of still-interacting paramagnetic species. Some of these species strongly interact in SID states (the line at about 0.04 T) characterized [10] by a dipolar constant, D, just a bit higher than the Zeeman energy (about $0.3\ cm^{-1}$). It is well-known that the dipolar constant, D, decreases with the third power of the distance between the interacting spins. It can be argued that in the case of the sample in Fig. 5b (that is, a sample used a second time after the one-year-ageing following the first use) the interacting paramagnetic particles are farther from each other than in all other SID-line-showing samples ($D \approx 0.5\ cm^{-1}$) examined here. However, this sample also recovers its catalytic activity after recalcination (compare Figs 6b and 4b). Also, in this case, the isolated Cu^{2+} ions disappear, but the EPR spectrum (Fig. 5c) shows that the new situation matches perfectly the situation attained after recalcining of the 18-months-aged unused sample (Fig. 3c). Furthermore, in both cases the SID band enhances after reaction, due to formation of local oxygen-deficient defects (at least on the sample surface). Furthermore, when moving the sample in the EPR cavity, it was observed that the SID band disappears sometimes, suggesting that the sample is not completely homogeneous.

5. Conclusions

EPR spectroscopy proved to be a very sensitive tool for monitoring the ageing degeneration process of the Ca–Sr-cuprate-based catalysts, both as unused and after use for promoting NO decomposition. The freshly prepared catalyst shows a layerlike structure, typical of the $Sr_3Cu_5O_8$ species [1, 2], which proved to be rather stable in the unused catalyst, in which long-time spin diffusion mechanisms dominate the relaxation process. The formation of SIDs can perturb the previous situation, but it seems not to be directly connected with the catalytic properties of the sample. The unused catalyst loses its activity in about 18 months. A faster degeneration process affects the used catalyst, accompanied by a loss of the layerlike crystal structure and of the SID systems, while copper ions directly couple, leaving just a small amount of isolated Cu^{2+} ions. However, both unused and used catalysts recover their original catalytic activity, as well as their paramagnetic properties, when recalcined.

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