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A Method for Separation of X-Ray Diffraction Patterns from Co–ZSM-5 Catalysts

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A Fourier method to unfold an X-ray diffraction pattern from a mixture to obtain the X-ray pattern from one component in the mixture is developed. The method is applied to the X-ray pattern from the catalyst mixture of 9.5% Co on a ZSM-5 support to obtain the diffraction pattern from metallic cobalt. Analysis of the details of the cobalt pattern shows the cobalt to be hexagonal in structure and dispersed with an average particle size of 220 Å. The shapes of the profiles indicate that the cobalt particles are heavily faulted on the basal plane.

INTRODUCTION

The problem of satisfactorily separating the X-ray diffraction pattern of one component from the diffraction pattern of a mixture, when the pattern of the remaining components is known, is often encountered in diffraction experimentation. The pattern separation problem becomes more complex when the mixture pattern contains a large number of overlapping Bragg peaks. The presentation of a method developed to unfold a complex pattern from a mixture, using Fourier transforms of the patterns, is the main objective of this research. The cobalt pattern obtained from a catalyst containing 9.5% metallic cobalt on ZSM-5 zeolite using the Fourier unfolding technique is presented.

A similar Fourier unfolding technique has been reported for quantitative mineralogical analysis (*1*) and infrared characterization of polymeric materials (*2*). The results obtained in this investigation indicate that this technique is very satisfactory for unfolding an X-ray diffraction pattern from a multiphase material.

THEORY

If an X-ray pattern from a mixture is composed of n components, $f_1(x)$, $f_2(x)$, . . . , $f_n(x)$, having Fourier transforms represented by $f_1(s), f_2(s), \ldots, f_n(s)$, respectively, then the mixture has a Fourier transform equal to $f_1(s) + f_2(s) + \ldots f_n(s)$. This can be expressed (*3*) as

$$\int_{-\infty}^{\infty} \left[\sum_{m=1}^{n} f_m(x) \right] \exp(-2\pi i x s) dx = \sum_{m=1}^{n} \left[\int_{-\infty}^{\infty} f_m(x) \exp(-2\pi i x s) dx \right] = \sum_{m=1}^{n} f_m(s). \quad (1)$$

Therefore if $M(s)$ represents the transform for the mixture of n components, knowing the transforms of $(n - 1)$ component(s), the transform of the remaining component can be found. The subtraction of $(n - 1)$ component(s) can be done individually or collectively by simple subtraction of Fourier coefficients at equal harmonic values.

To prepare the data for unfolding it is necessary to scale each pattern prior to calculating the Fourier transforms. Although the peak intensity of a component is proportional to the concentration of the component in the mixture, the peak-to-background ratio depends upon changes in concentration. For this reason a well-defined diffraction peak from the component to be isolated must be identified in the pat-

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tern from the mixture. This well-defined peak and the identical peak in the component pattern are normalized such that the peak intensity above background is unity. To accomplish this the maximum intensity of the selected peak in each pattern, $f(pk)$; and the background in each pattern, $f(bg)$, are identified, see Figs. 1 and 4. The entire pattern, $f(x)$, is then corrected using

$$f(x)_{\mathrm{corr}} = \frac{f(x) - F(bg)}{f(pk) - f(bg)} + C \qquad (2)$$

where C is a constant intensity added to ensure the background remains above zero.

Finally, due to variations in sample positioning, the peak positions of the individual component and the peak from the component in the mixture may not be at identical 2θ positions. If the positions are different, one of the patterns can be shifted using the Fourier shift theorem (*3*). This theorem states that if $f(x)$ has a Fourier transform $f(s)$, then $f(x - a)$ has the transform $f(s) \exp(-2\pi ias)$.

Thus a given function can be shifted, to increasing values, by an amount "a" simply by multiplying each coefficient by the factor $\exp(-2\pi ias)$. If the shift is known this can be conveniently and economically incorporated in the computations after the transforms have been obtained.

Direct and inverse Fourier transforms were calculated employing the fast Fourier subroutine (*4*). The input X-ray diffraction intensities obtained by step scanning were used directly without any intermediate smoothing.

EXPERIMENTAL TECHNIQUES

X-Ray diffraction patterns were obtained from a catalyst of ZSM-5 zeolite support impregnated with 9.5% cobalt (precipitated from a cobalt nitrate solution). The ZSM-5 is approximately 70% crystalline with an orthorhombic structure, which produces a large number of diffraction peaks in its diffraction pattern. To obtain the diffraction pattern from the cobalt it is necessary to subtract the zeolite diffraction pattern from the pattern of the cobalt–ZSM-5 mixture. The as-received catalysts were calcined in air for 1 hr at 200°C which put cobalt in the form of Co_3O_4. Reduction of the Co_3O_4 was carried out under hydrogen at 350°C in an *in situ* camera on a Picker X-ray diffractometer outfitted with a single bent graphite diffracted beam monochromator. X-Ray diffraction intensity data were obtained using a copper tube operated at 35 kV and 16 mA by step scanning at $(1/30)^\circ$ in 2θ.

Pure cobalt can exist in both hcp (a_0 = 2.507 Å , C_0 = 4.069 Å) or fcc (a_0 = 3.552 Å) forms or as a mixture of both at room temperature (*5*). ZSM-5 crystallizes in the idealized orthorhombic system with space group *Pnma* and lattice constants $a = 20.1$ Å, $b = 19.9$ Å, and $c = 13.4$ Å. The unit cell contents of the Na form are $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O)$ where $n < 27$ and typically about 3 (*6*). The structure of ZSM-5 produces numerous peaks spread over the entire diffraction range which makes it difficult to observe the diffraction pattern from the low concentration of cobalt in the form of a fine-particle dispersion.

RESULTS AND DISCUSSION

The as-received material showed only ZSM-5 peaks which indicates the cobalt nitrate to be either noncrystalline or of very fine particle size (<20 Å). After calcination well-formed (220), (311), (511), and (440) peaks were observed from the cubic Co_3O_4. From the analysis of these peaks the particle size of the Co_3O_4 was determined to be about 300 Å. No diffraction peaks from metallic cobalt or any other cobalt oxide form were observed at this stage.

Following the reduction under hydrogen at 350°C for 16 hr metallic cobalt diffraction lines were observed; the details of these will be discussed below. Diffraction lines from the (111), (200), and (220) planes of cubic CoO were the only other lines observed after reduction.

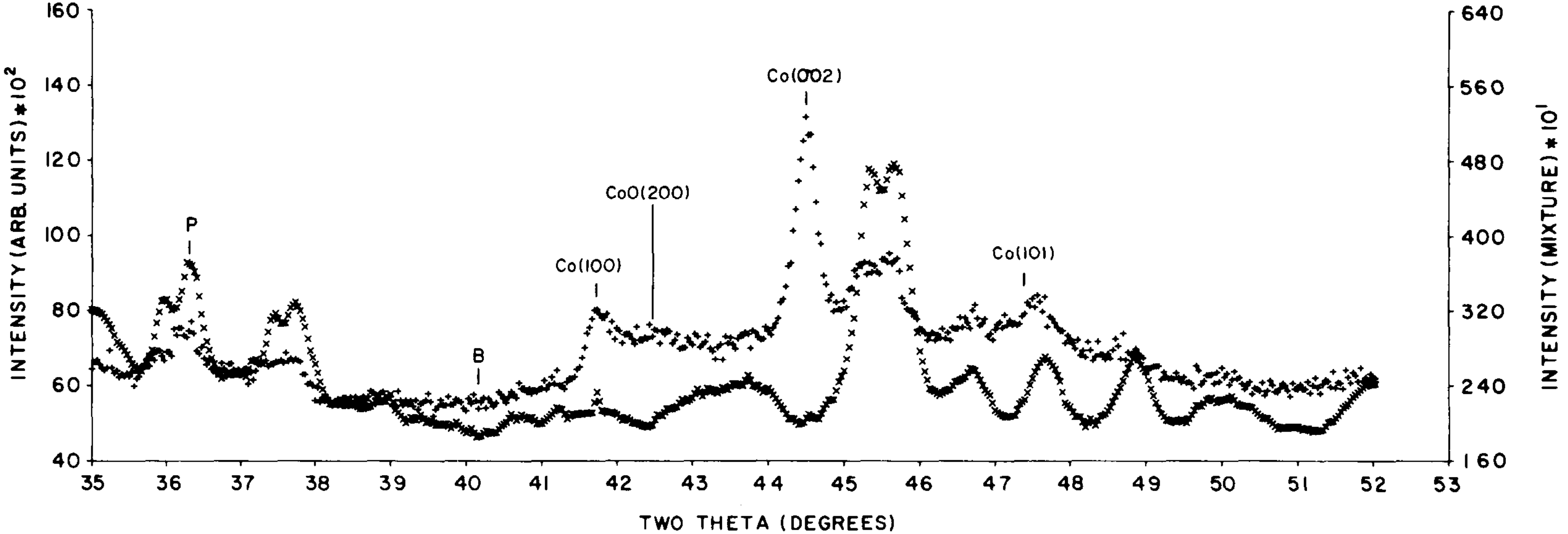

FIG. 1. Diffraction patterns from 9.5% CO + ZSM-5 mixture (+) and ZSM-5 (x) before unfolding. Note that P and B are peak and background positions, respectively, used for scaling the ZSM-5 pattern. Reduction was carried out under H_2 at 350°C for 16 hr.

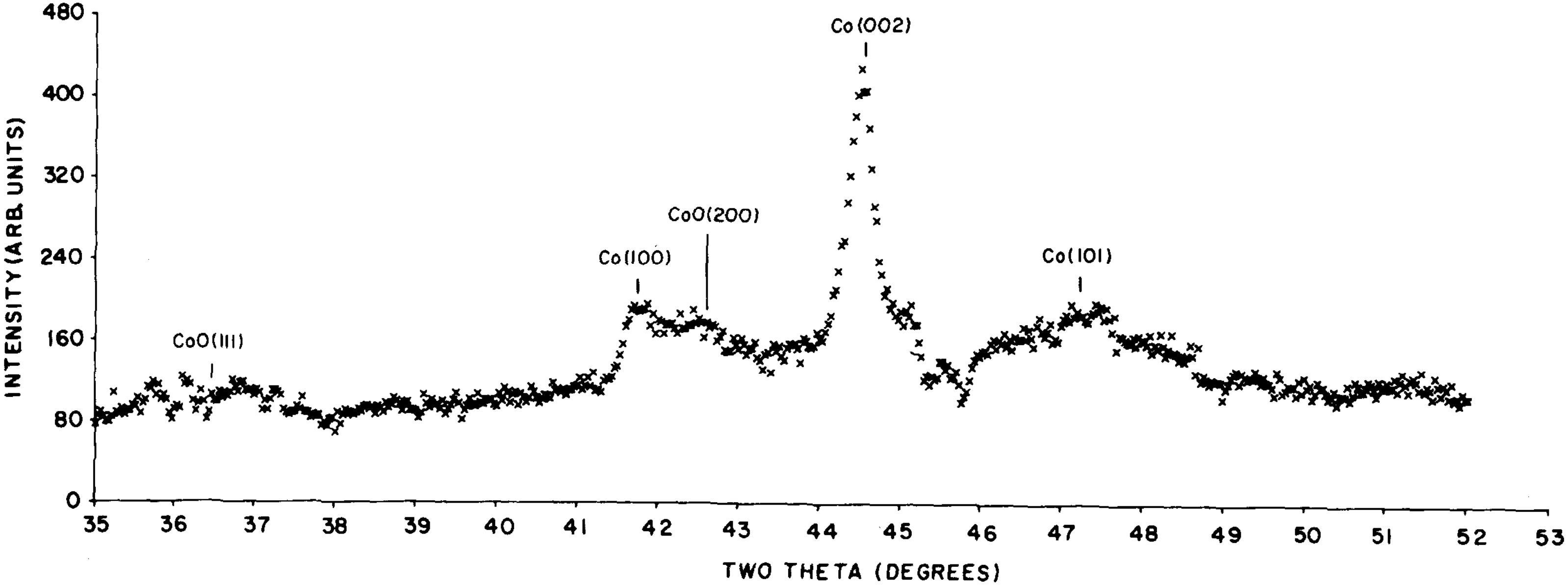

FIG. 2. Hexagonal cobalt lines and two CoO lines after subtraction of the unshifted ZSM-5 pattern from mixture pattern shown in Fig. 1 employing a shift of 0°.

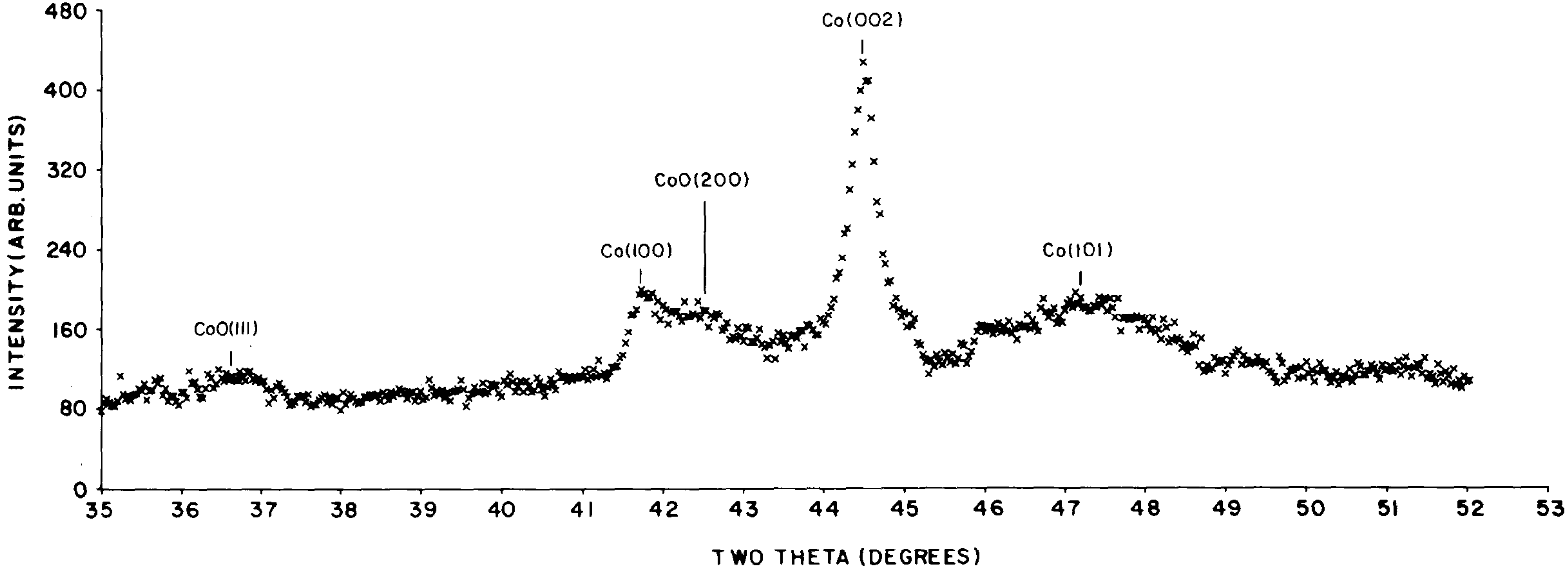

FIG. 3. Hexagonal cobalt lines and two CoO lines obtained by subtraction of the ZSM-5 pattern from the mixture pattern employing a shift in the ZSM-5 of 1/15°.

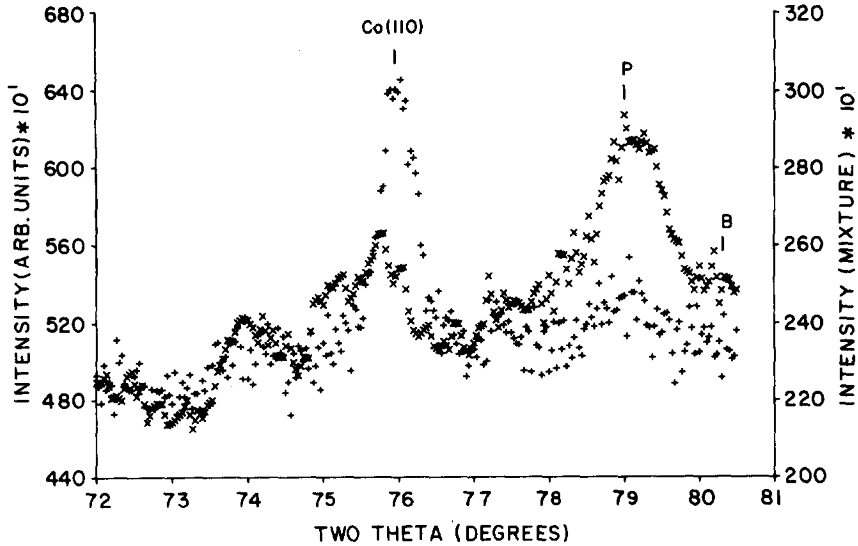

FIG. 4. Diffraction patterns from 9.5% CO + ZSM-5 mixture (+) and ZSM-5 (x) before unfolding in the range 72 to 81°; the position of the Co(110) is 76°. Note that P and B are peak and background positions, respectively, used for scaling the ZSM-5 pattern. Reduction was carried out under H_2 at 350°C for 16 hr (x) and 24 hr (+).

The diffraction patterns in the range of 35 to 52° 2θ from both the catalyst mixture of ZSM-5 with 9.5% cobalt and the pure ZSM-5 after exposure to the reduction treatment are shown in Fig. 1. The pattern obtained after unfolding the ZSM-5 spectrum from the pattern of the mixture is shown in Figs. 2 and 3. The pattern in Fig. 3 was obtained by shifting the ZSM-5 spectrum (1/15)°. No shift was employed in obtaining the pattern shown in Fig. 2. Both of the patterns shown in Figs. 2 and 3 contain Bragg diffraction peaks from the (100), (002), and (101) planes of hcp cobalt at 2θ positions of 41.7,

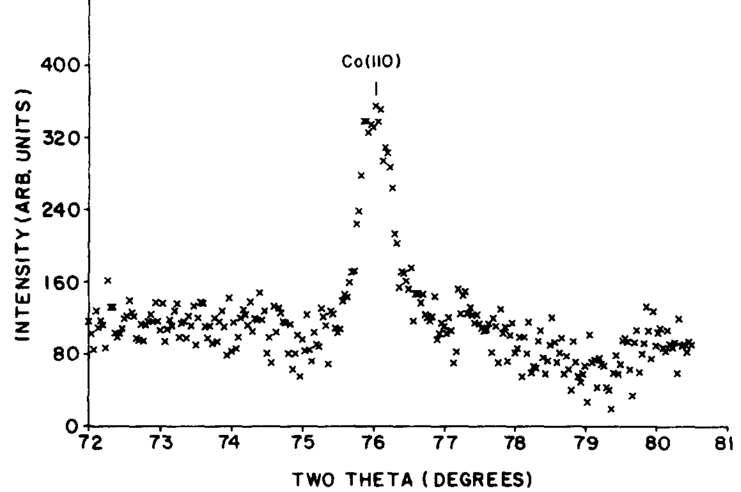

FIG. 5. The hexagonal cobalt(110) peak after unfolding the pattern shown in Fig. 4 and employing a 1/15° shift of the ZSM-5 to lower angle.

44.8, and 47.6°, respectively. There also is a weak peak from cobalt oxide (CoO) which is cubic ($a_0 = 4.26$ Å) at 2θ of 42.5°. No fcc cobalt reflections were observed. The effect of the shift of the ZSM-5 pattern can readily be seen by comparing Figs. 2 and 3. The pattern in Fig. 3 is generally smoother and the high-angle side of the (002) cobalt is of a better form.

The cobalt pattern contains a broad (101) profile and a sharp (002) peak. The exact shape of the (100) is not possible to determine because of the overlap with the CoO(200) peak. This broadening behavior of the profiles from cobalt is consistent with the presence of faults on the (002) planes of cobalt (*7, 8*).

A similar unfolding technique was applied to obtain the (110) peak of cobalt. The results are shown in Figs. 4 and 5. In this case the ZSM-5 pattern was scaled using a peak near 2θ of 80.5° and the pattern was shifted to a lower angle by 1/15°. As expected, this peak is sharp because its broadening is not affected by the existence of faults on the basal plane.

The particle sizes calculated (*9*) from the peaks affected and unaffected by faulting were 30 and 220 Å. This indicated the faulting particle size to be about 35 Å which corresponds to a fault probability of 0.08 (*7*).

Comparisons of the Fourier unfolding technique with direct subtraction of the data sets were made. When the patterns were unfolded by direct subtraction (no shift) of the ZSM-5 pattern from the Co–ZSM-5 pattern the resulting Co–CoO pattern did not give definition to the weak CoO(111) peak. The direct subtraction method does not have the capability of employing arbitrary shifts of a data set as the Fourier technique does. In the direct subtraction method shifts are limited to integer values of the data spacing interval. This serious limitation of the direct subtraction method is eliminated by employing the Fourier method of unfolding.

If there are n ($n > 200$) equally spaced data points in the spectra and an equal number of harmonics are used in developing the Fourier series to fit the data sets, the fit produces an exact reproduction of the data set including the high-frequency noise. If $n/4$ harmonics are employed the high-frequency noise is smoothed out. However, if $n/8$ harmonics are employed, a smooth fit to the data set is obtained which contains unacceptable large-amplitude low-frequency oscillations.

The results obtained from the Fourier unfolding technique presented provide a method, which is superior to direct pattern subtraction, of revealing the X-ray diffraction pattern of a small amount of metal dispersed on a support. In addition the details of the pattern are retained. The shapes of the selected profiles from the cobalt particles indicate that the particles contain faults on the basal plane.

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