JOURNAL OF CATALYSIS **62**, 374–378 (1980)

Incorrect Quantitative Analysis of Cracking Catalysts through Use of Copper Radiation

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Received August 3, 1979

An error can occur in the measurement of synthetic faujasite content of a catalyst by comparing a synthetic faujasite's diffracted intensity to that of a reference standard. The error is due to the failure of all diffracted X rays to emerge from the catalyst particle prior to passage to the powdered sample's surface. The error is not avoided by use of an internal standard. Absorption calculations estimate the synthetic faujasite content of 44 μm-size catalyst particles will be low by 17% if $\text{Cu}K\alpha$ is used. Use of more penetrating $\text{Mo}K\alpha$ indicates the $\text{Cu}K\alpha$ analysis is actually low by 26%.

INTRODUCTION

Processing of natural gas and crude oil requires the use of zeolitic sorbents and zeolitic-cracking catalysts. Measurement of their crystalline zeolite content by X-ray diffraction is perfomed by the oil industry to check purchased materials and to gauge the condition of used zeolites. The object of this paper is to show that inaccurate, low-zeolite-content measurements can be obtained using the copper radiation most commonly available in laboratories. Proper choice of X rays and sample particle size is required to avoid this analysis error.

EXPERIMENTAL

X-ray procedures. Diffraction work was done using a molybdenum tube operated at 50 kV and 32 mA and a copper tube operated at 35 kV and 20 mA. Samples were mounted on a Norelco goniometer. Diffracted intensity was detected with a scintillation counter. Canberra amplifiers and pulse height analyzer were used. Data were obtained using step scan operation controlled by Canberra electronics. Number of counts (40,000–90,000) accumulated in 90 sec was measured every 0.05° (2θ). Scans were made so as to include synthetic faujasite's (533) line and the (111) line of the internal standard elemental silicon.

Samples. Water-washed Davison Chemical Company AGZ-200, Resid 30, Super D Magnum, and Engelhard X1966 cracking catalysts were used as samples. Samples were allowed to air-equilibrate overnight. Samples were generally ground to pass through a 325-mesh screen. The Davison AGZ-200 was examined also after being ground to pass through a 20-μm-screen. In addition, particles of this catalyst that were too large to pass through a 200-mesh screen were examined. The screens are obtainable from Buckbee Mears Company, St. Paul, Minnesota. Elemental silicon having particle sizes less than 10 μm was added in weighed amounts to each weighed portion of sample to serve as an internal standard. The silicon was obtained from A. D. McKay, New York. Samples were not heated because a 17% loss of synthetic faujasite was observed by X-ray diffraction after calcination at 538°C.

Analysis of X-ray data. Synthetic faujasite content, X, was analyzed for by applying the equation given by Klug and Alexander (*1*) to synthetic faujasite's (533) and silicon's (111) diffraction lines:

$$X = k(w/W)(I(z)/I(Si)). \qquad (1)$$

The proportionality constant k was obtained by analyzing mechanical mixtures of pure synthetic faujasite (REY) with kaolin-

0021-9517/80/040374-05$02.00/0

ite of known composition. The synthetic faujasite was that used to make Davison AGZ-200. The constant k determined is appropriate for the other rare-earth catalysts studied. It has been found that the number of rare-earth ions per synthetic faujasite unit cell can vary between 5 and 28 without affecting k. If measurement of content for a catalyst containing NaY or HY were to be made, another standard would be necessary. The value of k depends in part on experimental setup. When Mo$K\alpha$ radiation was used, k was found to be 6.0 ± 0.3; when Cu$K\alpha$ radiation was used, k was found to be 5.1 ± 0.3. These constants are therefore known to within a standard error of ± 0.1 since seven or more measurements of k were made. w is weight of elemental silicon added as an internal standard and W is weight of sample. I(z) is the intensity of synthetic faujasite's (533) diffraction line. I(Si) is the intensity of silicon's (111) diffraction line. Intensity of these lines was measured as a product of peak height and width at half-maximum intensity.

Correction of synthetic faujasite content to dry basis. Synthetic faujasite contents were corrected to dry basis in the following manner. The fractional loss on ignition (LOI) of a catalyst, L, was measured by heating the catalyst to 870°C for 1 hr. The fractional LOI of the matrix material, L_{nz}, was calculated using Eq. (2):

$$L = XL_{\mathrm{z}} + (1 - X)L_{\mathrm{nz}}. \tag{2}$$

X is the measured synthetic faujasite content on a wet basis. L_{z} is the fractional LOI of the synthetic faujasite used to make the catalyst. L_{z} was measured to be 0.242 for the REY used to make Davison AGZ-200. The synthetic faujasite content on a dry basis, Y, was then calculated using Eq. (3):

$$\frac{(1/Y) - 1}{(1/X) - 1} = \frac{1 - L_{\mathrm{nz}}}{1 - L_{\mathrm{z}}}. \tag{3}$$

There is a small error in assuming L_{z} is 0.242 for catalysts other than Davison AGZ-200. Thus, for example, for a catalyst containing a synthetic faujasite with a composition $(\mathrm{RE(OH)})_5\ \mathrm{H}_{45}\mathrm{Na}_5\ \mathrm{AlO}_2)_{60}(\mathrm{SiO}_2)_{132}(\mathrm{H_2O})_{270}$, L_{z} is 0.281. For a composition $(\mathrm{RE(OH)})_{30}(\mathrm{AlO}_2)_{60}(\mathrm{SiO}_2)_{132}(\mathrm{H_2O})_{270}$, L_{z} is 0.231. Using these L_{z}'s for a catalyst containing 15% synthetic faujasite on a wet basis and having an L of 0.200, Y is calculated to be 13.5 and 14.4% respectively. Knowledge of a catalyst's synthetic faujasite composition permits one to eliminate this error entirely.

Absorption correction factors. Synthetic faujasite contents were corrected for absorption by multiplying them by absorption correction factors, A^*, listed in a standard table (*2*). The A^* depends on diffraction angle, θ, and the product of mass absorption coefficient, μ/ρ, density, ρ, and particle radius, R.

The diffraction angles, θ, were calculated using the d-spacing of the faujasite (533) line, 3.767 Å, Mo$K\alpha$ wavelength, 0.7107 Å, Cu$K\alpha$ wavelength, 1.5418 Å, and Bragg's equation.

The mass absorption coefficient is calculated using Eq. (4):

$$\mu/\rho = \sum_i (\mu/\rho)_i x_i. \tag{4}$$

Elemental mass absorption coefficients, $(\mu/\rho)_i$, for the ith constituent of the particle were taken from a standard table (*3*). The composition of AGZ-200, x_i, was set at: 0.10% CaO, 0.024% MgO, 2.89% $(\mathrm{NH_4})_2\mathrm{O}$, 2.40% (Ce, La, Nd, Pr, Sm)$_2$O$_3$, 0.28% $\mathrm{Na_2O}$, 22.6% $\mathrm{Al_2O_3}$, 52.7% $\mathrm{SiO_2}$, and balance (approx 19.0%) $\mathrm{H_2O}$. The calculated catalyst mass absorption coefficient for Mo$K\alpha$ is 3.91 cm^2/g; for Cu$K\alpha$, 34.7 cm^2/g.

The density of an air-equilibrated catalyst particle obtained by water displacement, ρ_0, was estimated to be 2.3 g/cm^3, using chemical composition and density of constituents. The measured density was found to be 2.1 g/cm^3. The density the X rays see, ρ, is lower than this because each particle contains an extensive pore system. This density was calculated to be 1.5 g/cm^3 using

$$(1/\rho) = (1/\rho_0) + V(1 - (L_c/100)) - (L_c/100), \quad (5)$$

where V is pore volume in cubic centimeters per gram of dehydrated catalyst, 0.53, and L_c is catalyst LOI, 22.8%.

Breck and Flanigen (*4*) give the crystal size of pure synthetic faujasite as 2–3 μm. The AGZ–200 particles that did not pass through a 200-mesh screen were observed through a light microscope to have a Martin's diameter of 160 ± 40 μm. However, an average size of 108 μm was calculated using sieve analysis data that show that the overall average catalyst particle size is 77 μm, with 2% of the catalyst having a 0–20 μm size, 10% having a 20–40 μm size, 44% having a 40–80 μm size, and 44% having a size in excess of 80 μm. Particles that were passed through a 325-mesh screen were assigned a size of 44 μm even though light-microscope examination indicated a Martin's diameter of 52 ± 15 μm. Particles that were passed through a 20 μm-screen were assigned a size of 20 μm even though light-microscope examination indicated a Martin's diameter of 22 ± 6 μm.

A^* was calculated assuming silicon crystals were located in the center of catalyst void spaces. Actually, they are located on the peripheries of the catalyst voids. Calculation of A^* using the latter location lowers the A^* values. The decrease is negligible when void diameter is small and radiation is Mo$K\alpha$. For a 108 μm-diameter void, the decrease in A^* is 3% when Cu$K\alpha$ is used.

RESULTS

Observed synthetic faujasite content measurements are listed in Table 1 for AGZ–200 having different particle sizes. One should note the decrease in uncorrected synthetic faujasite content with increasing particle size and with use of the softer copper radiation. Correction for absorption alleviates differences between analyses made with Mo$K\alpha$ and Cu$K\alpha$. Uncorrected synthetic faujasite content determined for a sample containing 44 μm particles using Mo$K\alpha$ is some 6 content percentage units higher than that determined using Cu$K\alpha$. The statistical validity of the difference was checked with Student's *t* test. The Mo$K\alpha$-determined content is an average of five runs. The Cu$K\alpha$-determined content is an average of six runs. The pooled mean estimate of standard error, S_p, was in this case ±1.6%. The calculated Student *t*, 6.2, exceeds that required to be 99.5% confident of a difference, 3.7. Table 2 lists data for three other catalysts. The Student *t*'s indicate differences between determinations of synthetic faujasite content that are significant at the 99.5% confidence level. The last entry in Table 2 shows that there is no difference between synthetic faujasite contents measured for a mechanical mix of

TABLE 1

Synthetic Faujasite Contents

Radiation	Catalyst particle size (μm)	Synthetic faujasite content (%)		Correction factor	
		Uncorrected	Corrected	A^*	Based on Mo$K\alpha$ analysis
Mo$K\alpha$	20	23	23	1.01	1.0
	44	23	23	1.02	1.0
	108	19	20	1.05	1.2
Cu$K\alpha$	20	19	21	1.08	1.2
	44	17	20	1.18	1.4
	108	16	24	1.50	1.4
Average			22 ± 2		

TABLE 2

Synthetic Faujasite Contents of Other Catalysts

Catalyst	Synthetic faujasite content (%)		$S_p((1/N_1) + (1/N_2))^{1/2}$	t	
	Mo*K*α	Cu*K*α		Obs	Required for 99.5% confidence
Davison Resid 30	36.2 ± 1.0(3)[a]	30.8 ± 0.9(3)[b]	0.81	6.7	5.6
Davison Super D Magnum	20.4 ± 0.3(3)	18.2 ± 0.4(3)	0.30	7.5	5.6
Engelhard X1966	17.9 ± 0.7(3)	15.2 ± 0.6(4)	0.53	5.1	4.8
Mechanical mix of 23% faujasite and matrix material	22 ± 1 (6)	22 ± 1 (4)	—	—	—

[a] Bracketed numbers indicate number of observations, N_1.

[b] Bracketed numbers indicate number of observations, N_2.

synthetic faujasite and matrix material using the two radiations.

DISCUSSION

The effect of particle size on X-ray fluorescence measurements has been noted by Wagman *et al.* (*5*). The effect of particle size on quantitative X-ray diffraction analysis is not generally appreciated. However, the effect of particle size on quartz-diffracted Cu*K*α X-ray intensity can be seen in Klug and Alexander's data (*6*).

It is well recognized that in the passage of X rays in and out of a powdered sample some X-ray intensity is lost due to absorption. This loss varies from sample to sample. An internal standard such as silicon is added to each sample in an attempt to compensate for this loss. If the synthetic faujasite-diffracted X rays experience the same absorption as the silicon-diffracted X rays, then the ratio of the intensities should be independent of sample absorption and exactly proportional to synthetic faujasite content. Thus, if one measures this ratio for a catalyst having a 20% synthetic faujasite content, an equal ratio should be obtainable by preparing a mechanical mix of 20% synthetic faujasite and matrix material. This will be so if the w and W of Eq. (1) are the same for both samples.

The object of this paper is to show that unless precautions are taken, this equality will not be realized. This can be understood by examining Fig. 1. This shows schematically paths followed by X rays in and out of a powdered catalyst during diffraction by synthetic faujasite and silicon. Total path lengths are the same. The distances l mark identical passages of X rays through catalyst material. The diffraction paths differ in that synthetic faujasite diffraction occurs in a solid sphere of radius R that attenuates the diffracted X-ray beam, whereas the silicon diffraction occurs in a catalyst void that does not attenuate the X-ray beam. In contrast, for a mechanical mix, environments of synthetic faujasite and silicon are identical. It is the inability to compensate for loss of diffracted intensity within a catalyst particle that leads to the inequality of I_z/I_{Si} ratios.

One can avoid sample absorption problems by:

(1) Reducing catalyst particle size to the point that calculation shows each particle transmits all X-ray intensity.

(2) Using X rays with sufficient penetrating power so that all are transmitted by each sample particle.

(3) Compacting the sample to remove void spaces.

(4) Matching reference's particle size to that of sample.

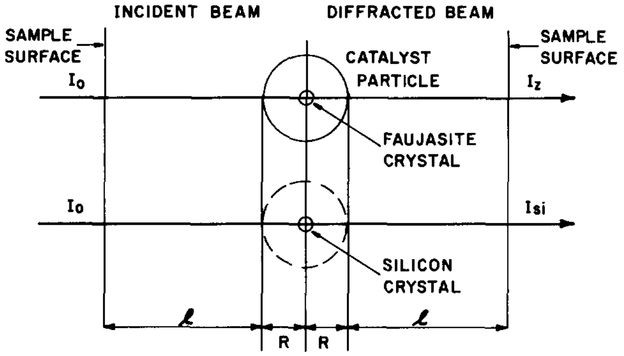

FIG. 1. Paths followed by X rays in and out of a powdered catalyst during diffraction by synthetic faujasite and silicon.

(5) Correcting content measurements for inadequate X-ray penetration.

Of these, (4) is impractical. To correct content measurements for inadequate X-ray penetration, (5), requires good knowledge of sample particle size, density, and composition.

While the effect of radiation wavelength and sample particle size on content measurement has been demonstrated for a special case, a cracking catalyst, the effect on content measurement will occur whenever X-ray penetration of a sample particle is different from the penetration of a reference material particle. This will occur whenever the particle sizes are very different, and both sample particle density and sample mass absorption coefficient are high.

ACKNOWLEDGMENT

The writer wishes to thank members of Texaco's Port Arthur Research Laboratory Catalysis Section for their helpful criticism of this work.

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