JOURNAL OF CATALYSIS 9, 289-294 (1967)

Heating-Oscillating X-Ray Diffractometer Study of Selected Catalysts

JAMES L. McATEE, JR.

From Baylor University, Waco, Texas 76703

Received August 10, 1967; revised October 18, 1967

In many materials used as catalysts, isomorphous substitutions within the lattice, lattice defects, and differences in exchangeable cation composition are significant with regard to the properties of the catalysts. Many of these minor changes in the atomic structure cannot readily be detected by regular X-ray diffraction methods. Heating-oscillating X-ray diffractometry often can give insight into these problems. The heating-oscillating method combines features of differential thermal-analysis with X-ray diffraction wherein a specimen is heated at a controlled rate while oscillating over a diffraction maximum. By this means, the temperature and rate at which structural changes take place can be readily observed. This method has the advantage over conventional X-ray methods in that the changes are observed at the temperature at which they actually take place. That is, the samples are not heated and then cooled to room temperature and the subsequent X-ray diffraction patterns obtained. Often, heating-oscillating is carried out over several of the diffraction maxima, thus resulting in a series of diagrams which when composited represent the diffraction pattern at any temperature within the range studied. Heating-oscillating diffractometer studies have been carried out on a variety of catalysts. It has been found that structural differences can be detected that were not observed from regular X-ray diffraction patterns obtained at room temperature.

In the study of solids, it is often desired to be able to distinguish structural differences that are quite minor in nature. Slight differences within the crystal lattice and lattice defects often lead to considerable differences in the properties of a given material.

Many solids have been studied by X-ray diffraction by heating the samples to various temperatures and cooling them to room temperature before examining them by regular X-ray methods (*1*). Such procedures do not generally give sufficient information regarding the exact temperature at which phase changes take place nor information regarding the rate of the changes. Many others have studied samples at elevated temperatures, obtaining the X-ray diffraction pattern at the temperature to which the sample has been subjected (*2*, *3*, *4*). There are many commercial cameras available for such study and these have been used extensively.

The heating-oscillating X-ray method described herein takes advantage of a continuous X-ray diffraction pattern over selected diffraction maxima, while simultaneously heating the sample at a desired rate. It is thus, a union of differential thermal analysis and high-temperature X-ray diffraction. A further advantage of the method is that the sample can be X-rayed while under various atmospheric conditions such as under N_2 or CO_2 atmosphere or under dry or water-saturated atmospheres. Such X-raying conditions allow the diffraction pattern to be obtained in such a manner that minor differences in the substance can be detected. The chief advantage with the heating-oscillating method lies in the ease by which the X-ray data from various samples can be compared so that differences can be readily seen.

EXPERIMENTAL

The original details of the apparatus as used in this laboratory were adapted from a furnace built by L. S. Birks and H. Friedman at the U. S. Navy Research Laboratory. Many modifications were made by Rowland (*5*) and further modifications made in the author's laboratory. The heating block was purchased from the Robert L. Stone Company, Austin, Texas and was mounted in a platinum holder which in turn was mounted on the camera base as shown in Fig. 1. This sample holder–heating unit was mounted inside an aluminum case fitted with beryllium windows to minimize absorption of the incident and the diffracted radiation. The beryllium windows were 1.3 cm in width and 4.5 cm in length, affording sufficient area to obtain patterns at diffraction angles from 0° 2θ to 90° 2θ. Alignment of the sample holder for para-focusing conditions of X-ray diffraction was accomplished by means of the mounting screws within the aluminum case. It should be emphasized that any commercially available high-temperature assembly can be used in such experiments as described herein and this is only one of many types.

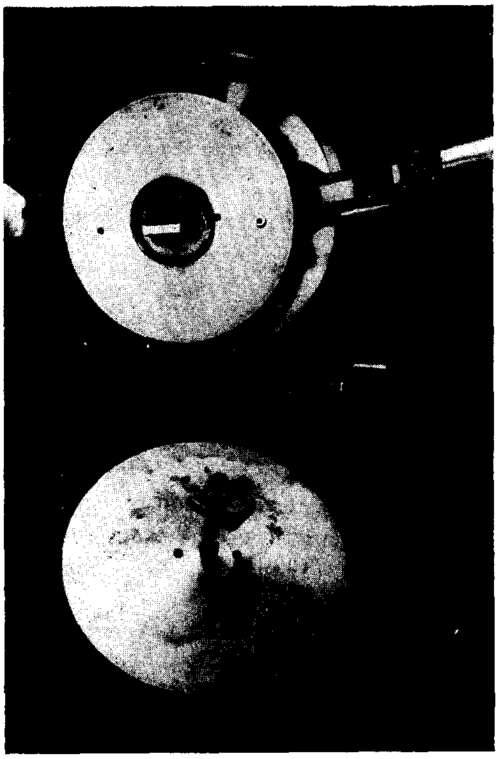

FIG. 1. Heating camera shown with cover removed.

For this work, a chromel-alumel thermocouple was inserted from the rear of the camera shield into the sample compartment and the thermocouple bead was placed in intimate contact on the sample plate.

The output signal of the thermocouple was fed to a West Model JSBGB-1 temperature controller which was used to control the heating rate of the sample. The program cams used for these studies provided a heating rate of approximately 2.5° or 5° per minute over the entire range of the experiment.

The samples to be X-rayed were first dispersed in water using a Spex mill and sufficient material was then placed on 1 × 1-inch stainless or platinum slides to completely cover the metal surface. These slides were 0.66 mm thick and were of a height so that when they were placed in the sample holder of the diffractometer it was in optimum X-ray alignment. The sample, after drying at room temperature, was placed in the diffractometer holder and the thermocouple positioned so that it was in contact with the upper surface of the metal plate.

In order to calibrate the actual temperature of the assembly, the following procedure was used: A small portion of a pure compound was spread in a thin layer on one of the platinum slides and the X-ray goniometer set at one of the strongest diffraction lines for the compound under study. The slide was then heated at a rate of approximately 2.5° per minute and the chosen *d* spacing was followed by manual operation of the goniometer. The melting point of the material was taken as the temperature at which there was a loss of the intensity of the diffraction peak. The materials used for this calibration were sulfur, m.p. 112.8°C; potassium bisulfate, m.p. 210°C; succinic acid, m.p. 185°C; sodium nitrate, m.p. 308°C; potassium iodate, m.p. 560°C; and sodium bromide, m.p. 755°C. In all cases the temperature indicated on the West controller was within ±5°C of the literature value of the melting point of the compound being X-rayed.

During a heating oscillating run, the verification of the diffractometer alignment is made by checking the position and intensity of one of the diffraction peaks of the platinum or stainless steel plates. It has been found on such checking that the para-focusing alignment remains constant through the temperature range used in these experiments.

The heating-oscillating device was mounted in a Philips high-angle Spectrogoniometer. The X-radiation used in these experiments was Ni-filtered, Cu, $K\alpha$ radiation with the unit operated at 35 kV and 18 ma. The oscillating device on the Philips unit was altered by replacing the screws on the oscillating pressure plate with screws of 4-52 threads so that the trip position could be controlled more accurately.

After preparing the dried sample on the slide, the slide was placed on the heating device and the cover placed in position. If an atmosphere other than air was desired, the desired gas was flowed into the sample chamber. Generally, the flow was continued for about 10 min before the actual diffraction run was started. After equilibrating the sample with the desired atmosphere, the sample was run over a sufficient range of the diffractometer to obtain the overall diffraction pattern of the sample under investigation. By so doing, the position and intensities of the diffraction maxima that were to be studied by the heating-oscillating technique could be determined. Generally, the height of the diffraction maxima to be further studied was then adjusted by utilizing the controls of the Philips diffractometer amplifier system so that it was approximately 90% of full scale on the Brown strip-chart recorder.

The oscillating control of the spectrogoniometer was then positioned so that the goniometer would oscillate automatically over the desired range while the sample was being heated at the desired rate. Usually the range oscillated was approximately 1° either side of the particular diffraction maximum to be studied. However, in many samples where it was known that the diffraction peak would shift in its position during the course of the heating, the oscillating range was increased so that the peak could be observed throughout the changes in peak position which would take place.

With the oscillation of the diffractometer set, the actual heating-oscillating run was then completed automatically. Occasionally the temperature of the furnace as read from the controller was noted on the strip chart along with the 2θ position of the maximum.

RESULTS AND DISCUSSION

Some typical heating-oscillating results for various montmorillonites are shown in the first several figures. Figure 2 shows the heating-oscillating trace for a calcium montmorillonite, while Fig. 3 gives the graphical presentation of the changes in the *d* spacing with temperature for this sample.

A plot of the *d* spacing versus temperature for the same montmorillonite converted to the sodium form is shown in Fig. 4. The differences in the curves of Figs. 3 and 4 are due to the differences in the manner in which water is lost from the clay. For calcium clay, water is both adsorbed on the clay surfaces and coordinated with the calcium ion, thus the change in *d* spacing of the (001) line has two sharp breaks. On the other hand, the sodium clay only has water adsorbed on the basal surfaces, thus only one break in the *d*-spacing curve.

This same montmorillonite was converted to a chromium montmorillonite and the heating-oscillating curve obtained. The *d* spacings and relative intensities from the X-ray tracing are plotted versus temperature and given in Fig. 5. If one compares the data shown in Fig. 5 with those given in Figs. 3 and 4, it will be recognized that the three types of montmorillonite are easily distinguished. It should be emphasized that in all cases the only change in these samples was the type of exchangeable cation associated with the montmorillonite clay.

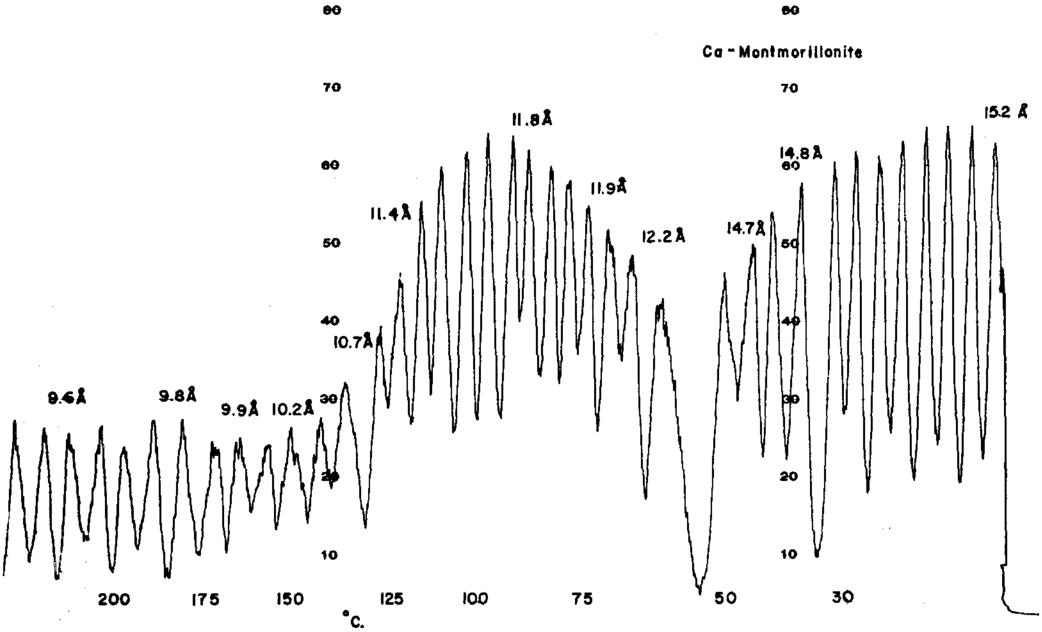

FIG. 2. Heating-oscillating X-ray diagram of (001) spacing for Ca-montmorillonite.

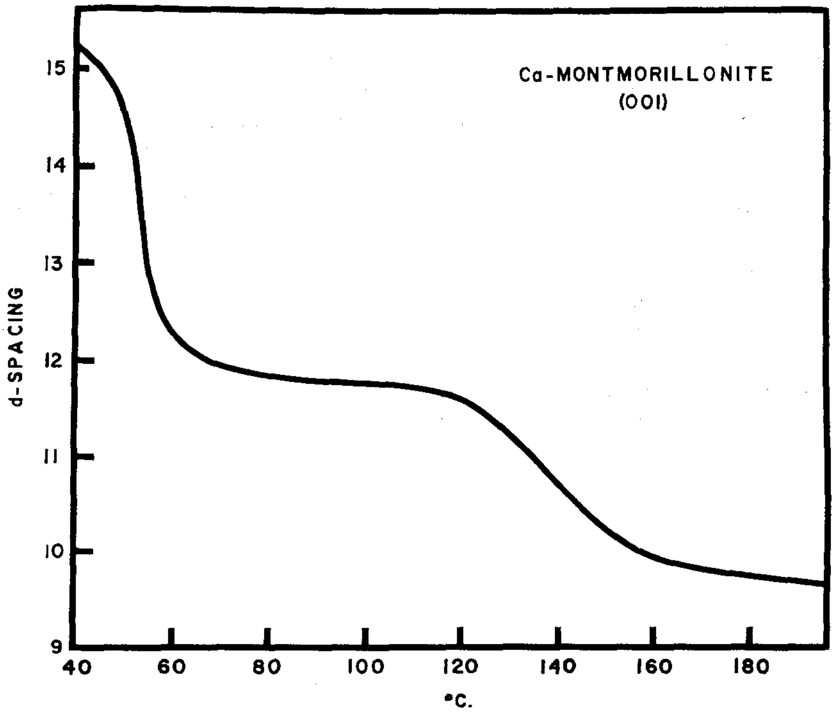

FIG. 3. Change in *d* spacing with increasing temperature of (001) spacing for Ca montmorillonite.

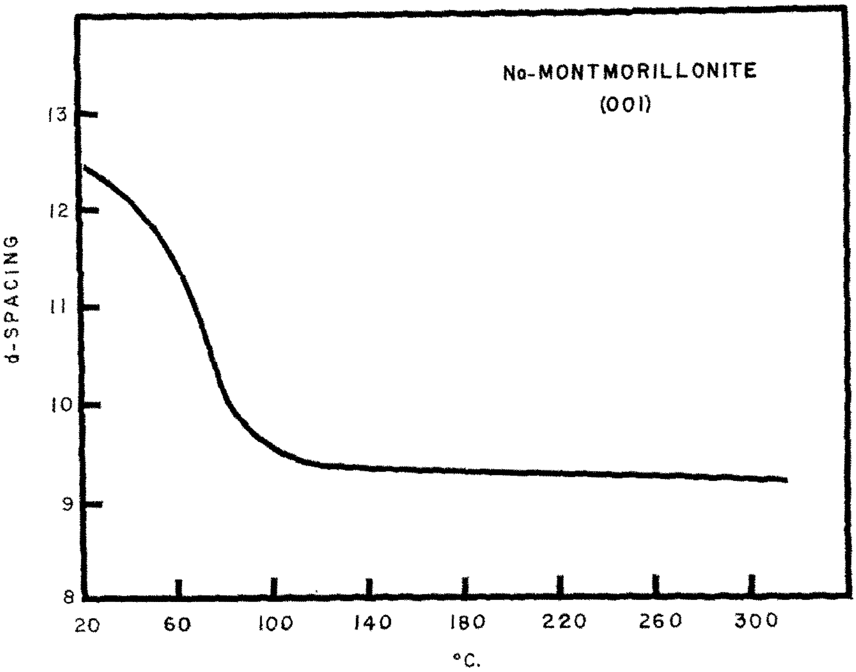

FIG. 4. Change in *d* spacing with increasing temperature of (001) spacing for Na montmorillonite.

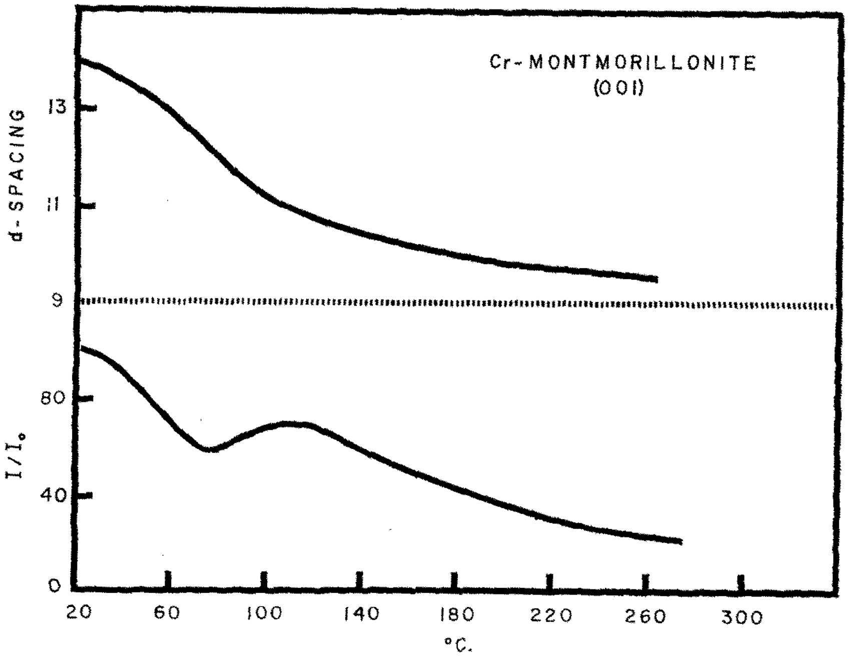

FIG. 5. Change in *d* spacing and relative intensity of (001) spacing for Cr montmorillonite.

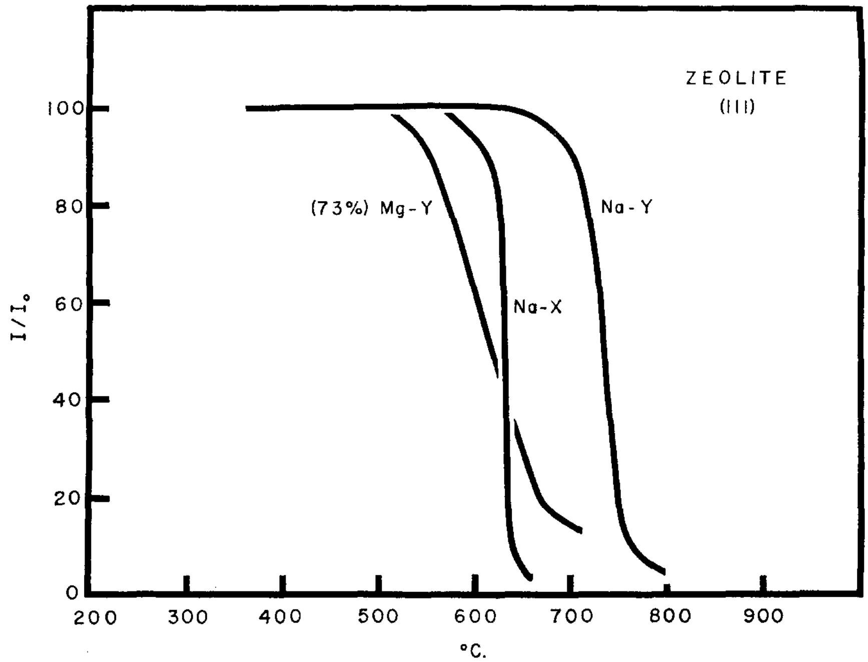

FIG. 6. Change in relative intensities of the (111) spacing for Na X, Na Y, and Mg Y zeolite.

The curves shown in Fig. 6 present another example of the use of the heating-oscillating X-ray diffraction method as applied to catalysts. The curves shown in Fig. 6 are for the (111) zeolite diffraction maximum. It can be seen that there is a pronounced difference between the sodium Y zeolite and the sodium X zeolite. The third curve shown on this graph represents the type of curve that is obtained when 73% of the sodium ion of the sodium Y zeolite was replaced with magnesium ion. These curves show that the heating-oscillating method can be used to differentiate not only between the X and Y types of zeolite but it can also be used to differentiate between the type of exchangeable cation present on the zeolite.

The heating-oscillating method combines salient features of high-temperature X-ray diffraction with differential thermal analysis techniques. The procedure is particularly useful in being able to compare two or more samples that differ only slightly in composition or structure that would usually not be apparent from DTA or X-ray diffraction patterns alone.

ACKNOWLEDGMENT

The heating-oscillating experiments with the montmorillonites were conducted under a Robert A. Welch Grant, for which appreciation is expressed.

REFERENCES

1. KLUG, H. P., AND ALEXANDER, L. E., "X-Ray Diffraction Procedures," p. 226. Wiley, New York, 1954.
2. GOLDSCHMIDT, H. T., "Bibliography on High Temperature X-Ray Diffraction Techniques." Intern. Union of Crystallographic Apparatus, 1964.
3. RASHKIN, J. A., AND PIERRON, E. D., *J. Catalysis* 6, 332 (1966).
4. RASHKIN, J. A., PIERRON, E. D., AND PARKER, D. L., *J. Phys. Chem.* 71, 1265 (1967).
5. ROWLAND, R. J., AND WEISS, E. J., *Am. Mineralogist* 41, 117-127 (1956).