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The Microwave Direct Heating of Zeolite FAU in an Open System

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Abstract: Zeolite FAU was heated directly by microwave irradiation at 2450 MHz in an open system without special loading materials. It was discovered that zeolite X was heated to 1473 K about 90 seconds at power output of 400 W. HY type zeolite was also heated to 1373 K although it needed relative long time (about 11 minutes). Influences of exchangeable cations and adsorbed substances on zeolite s ability to absorb microwaves were also discussed.

Keywords: Microwave, dielectric heating, zeolite FAU.

Microwaves are electromagnetic waves between infrared rays and radio waves. The frequencies used in microwave dielectric heating are 918 MHz and 2450 MHz. Domestic microwave ovens employ 2450 MHz. The principle of the microwave dielectric heating has been reported by S. A. Galema[1]. Its basic viewpoint is that microwave irradiation induces charged particles to migrate or rotate, which results in polarization of polar particles, and the lag between this polarization and rapid reversals of the microwave field creates friction among molecules to generate heat. Microwave irradiation makes the rate of some organic reactions 1240 times higher than that of classical methods[2].

Zeolite is a family of porous crystalline solid. The anion framework structure is formed by connecting SiO_4 with AlO_4 tetrahedra through oxygen bridge, which give rise to many channels and cavities where exist a certain amount of exchangeable cations to balance the negative electron of AlO_4. Zeolites have a high electric conductivity compared with the normal inorganic crystalline solid[3].

Whittington *et al.*[7] have done some work on the microwave heating zeolites. In their experiments, the zeolite samples (approximately 3.9 g) were heated in a commercial microwave oven (2450 MHz, 700 W) and 300 mL of water was also placed in the oven to avoid damage to the oven. The whole apparatus is an insulated system. During this process, 300 mL of water also absorbs a certain amount of microwave energy, which makes zeolite samples absorb microwave energy incompletely. So the result of the experiment can not reflect the microwave absorption by zeolites themselves. In this point of view, we tried to heat the test zeolite samples directly without loading water.

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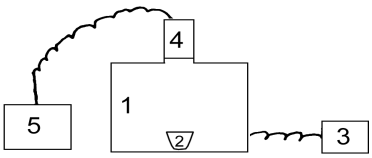
The result is reported in this paper.

Experimental

Zeolite samples used in our experiments were: zeolite X (Nanjing Refinery Catalyst Co., Ltd, Si/Al = 1.18); zeolite Y (Wenzhou Huahua Group Co., Ltd, Si/Al = 2.52); Li-X, K-X, Ca-X, Mg-X, Ba-X, HY and NH_4Y zeolites were obtained by ion exchange. The experimental apparatus was shown in **Figure 1**. All the zeolite samples at temperature higher than 0 K can radiate infrared energy proportional to the temperature of the samples, so the temperature of the samples can be measured by a thermoscope with the temperature range of 273-1473K. The working mechanism of the thermoscope is that lens of it collect the infrared energy on the infrared detector to give a voltage signal which is directly proportional to the temperature of the zeolite surface. The measurement can be done without contact of thermoscope with the sample. What need emphasize is that the sight must be aimed at the center of the surface of zeolite samples. The thermoscope has quick response in 350 mili-seconds, and it does not disturb the field. These are the advantages over the thermocouple.

10 g zeolite sample was placed into a 25 mL open ceramic crucible, then it was set on the microwave cavity and heated. The changes of temperature on the surface of samples were measured continuously by our method, while Whittington *et al.* only got several temperature points at certain intervals[7].

Figure 1 Schematic diagram of experimental apparatus



(1). Altered commercial microwave oven with frequency of 2450 MHz; (2). Crucible (for containing samples); (3) Booster; (4) Thermoscope IRT-1200; (5) Recorder

Results and Discussion

The differences of our results and Whittington s are compared in **Table 1**. It is obvious that our experimental results really reflect the nature of zeolites. The result showed that the zeolite samples with monovalent exchangeable cations are easy to be heated by microwave irradiation. HY type zeolite was also heated to the high temperature after being irradiated for 11.3 minutes. NaY zeolite takes longer time for reaching the highest temperature than NaX zeolite, and the highest temperature of NaY zeolite is not as high as NaX zeolite. The reason is that the content of Si in NaY zeolite is relatively high. The Y type zeolite can also be heated to high temperature in our experiment, whereas under Whittington′s condition can not. It is due to the competition of the microwave absorption between zeolites and water in the experimental system. H_2O has higher dielectric constants 78 (298 K) and can effectively absorb microwave energy as mentioned above.

The typical results of the microwave heating various ion-exchanged zeolite X and SiO_2 at the output power of 400 W are shown in **Table 2**. All the samples calcined and dehydrated at 773 K for 5 hours, then they were placed in a desiccator for later using. From **Table 2**, it is found that the temperatures of zeolite samples are much higher than that of the inorganic material — SiO_2. It indicated that there exist rotation or migration of ions or bounds inside zeolites. This induced the zeolites to absorb the microwave energy more strongly. From the microscopic point of view, the exchangeable cations or unbalanced charges distributed in the zeolites caused the zeolites' microwave absorption.

Table 1 The differences of our results and Whittington′s

Zeolite samples (dry)	Temperature (K)*	time (min)*	Temperature (K) after heating 6 min$^{\Delta}$
NaX	1473	1.50	>1473
NaY	1428	6.00	353
KY	1473	3.73	313
HY	1373	11.3	313
NH_4Y	1273	2.50	–

* Our results (400 W) expect HY being heated at 600 W . $^{\Delta}$ Whittington s results (700 W).

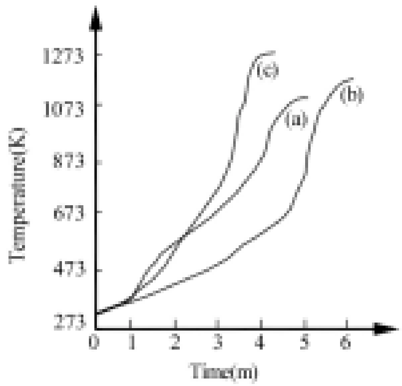
From **Table 2**, we can see that dehydrated zeolite LiX, NaX and KX absorb microwave energy much more effectively than dehydrated zeolite CaX, MgX and BaX. The order of calefactive rate of these zeoltes is LiX > NaX > KX > MgX > CaX > BaX, the order of the highest temperature of these zeolites is KX > NaX > LiX > CaX > MgX > BaX. One may estimate the property of exchanged cations according to the microwave absorption ability of zeolites. Infrared spectram of these zeolite samples show that the feature of hydroxyl groups are similar, but the ability of microwave energy absorption is different, it may be inferred that surface hydroxyl groups in zeolites are not responsible for the heating. The absorption ability of microwave energy of the same kind of zeolite depends on the exchanged cations, in other words, the ability of microwave energy absorption of zeolites with the same crystalline structure is directly related to the unbalanced sites caused by AlO_4^- .

Table 2 The effect of exchangeable cations

Zeolites	NaX	LiX	KX	CaX	MgX	BaX	SiO_2
Temperature (K)	1473	1273	>1473 (molten)	1073	948	418	403
Time (s)	90	70	130	300	153	310	240

For proving whether the water in zeolites is the reason of strong microwave absorption, we carried out following experiment. The zeolite samples calcined and dehydrated at 773 K for 5 hours, then was divided into three portions: one portion was kept in a desiccator, another was placed in a humidistat for 24 hours, the third portion adsorbed *iso*-octane. The experiment was operated at low power output of 200 W to avoid occurrence of the spurting. From **Figure 2**, it is found that temperature-time curves are nonlinear. One can predict that the desorption of water takes off heat energy more rapidly than the heat diffuse of zeolite X, the temperature of wet sample should rises slower than that of dry sample. When the temperature is over 623 K water combined with the framework of zeolites can be removed, so the dehydrated zeolite X should be heated faster. Our experimental results agreed with this prediction well. The temperature of zeolite X absorbing non-polar molecular *iso*-octane is the highest than other two portions of samples. It could be considered that the polar molecular H_2O in zeolite is not responsible for the strong microwave absorption of zeolite.

Figure 2 Curves of the microwave heating of zeolite X
(a). dry sample (b). wet sample (c). sample adsorbed *iso*-octane



Conclusion

Strong microwave absorption is the nature of zeolite which may be used as a measurement to characterize zeolites. Exchangeable cations exert heavy influences on zeolite absorbing microwave energy. Zeolites accomplish rapid absorption in a microwave oven and it is forecasted that zeolites can be used as catalysts for rapid chemical reaction.

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