Absorption spectra of selenium clusters and chains incorporated into zeolites

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Abstract. Absorption spectra are reported for Se adsorbed in faujasite (X or Y) as a function of x, where x is the Al-to-(Al + Si) ratio. The amount of adsorbed Se increases with increasing x for small x and is saturated for $x \geq 0.1$. The results are interpreted using the model in which the finite number of Se atoms are physically adsorbed by each permanent dipole which consists of $(AlO_4)^-$ in a zeolite framework and cation. The energy of the lower absorption edge changes with x and the spectral shapes are classified into three types. Spectral differences are also observed for Se incorporated into Linde type A and Linde type L lattices. From a comparison with the spectrum of the isolated Se chain in mordenite, the structures of Se in A and L are expected to be isolated clusters and double parallel chains, respectively.

1. Introduction

Zeolites are crystals having open structures and have the capability of adsorbing various kinds of material (Bogomolov 1978). Mordenite (M), one of these materials, has one-dimensional channels whose diameter is about 0.67 nm. Bogomolov *et al* (1983a) have measured the absorption spectra of isolated Se chains stabilised in the single crystal of natural M and clearly found the blue shift of the absorption edge compared with that of trigonal Se (t-Se). Electron microscopy studies have confirmed that the Se in M exhibits the structure of an isolated chain stabilised in the main channel (Terasaki *et al* 1987, 1988).

Zeolite is constructed by the linking of $(AlO_4)^-$ and SiO_4 tetrahedra with shared oxygen atoms. It contains cations, such as Na^+, for neutrality with $(AlO_4)^-$. The chemical formula is given by $R_{x/m}^{m+}Al_xSi_{1-x}O_2 \cdot nH_2O$, where R is a cation. The Si-to-Al ratio varies according to the method of the synthesis or de-alumination treatment. Various molecules are adsorbed by the permanent dipole formed by the cation and $(AlO_4)^-$. However, whether the amount of Se loaded into zeolite depends on the Si-to-Al ratio or not is as yet unknown, and the correlation between the structure of Se and the Si-to-Al ratio is also not known. Such questions are very important in the discussion of the properties of Se loaded into zeolite.

In section 3 of the present paper, it is shown that the amount of adsorbed Se strongly depends on the Si-to-Al ratio in faujasite (X or Y). The results are interpreted using the

model of physical adsorption of the finite number of Se atoms by the permanent dipole of $(AlO_4)^-$ and the cation, and these Se atoms cover 15 $(AlO_4)^-$ or SiO_4 sites facing the inner surface of the zeolite cages. The absorption spectra change with the Si-to-Al ratio and are interpreted using a tentative model of the structural difference of adsorbed Se chains or clusters. In section 4, the spectral shapes are compared with those of Se incorporated into M, a Linde type A lattice (A) and a Linde type L lattice (L), and we discuss them in terms of the structural difference of Se in each zeolite.

2. Experimental procedures

We used the following powders of synthetic zeolites: HY(7.3–340), NaY(2.8), NaX(1.25), MgX(1.25), NaA(1), MgA(1), KL(3.1) and NaM(10), where the symbol before X, Y, etc, indicates the kind of cation and where the number in parentheses denotes the Si-to-Al ratio. The IUPAC-recommended names of X or Y, A, L and M are FAU, LTA, LTL and MOR, respectively. The size of the powder particles was about 1 μm. MgX(1.25) and MgA(1) were obtained by ion exchange of NaX(1.25) and NaA(1), respectively, using immersion in a $MgCl_2$ aqueous solution.

Zeolites were dehydrated by heating gradually in glass ampoules up to 270 °C on a vacuum line and kept in vacuum for 2 h. The dehydrated zeolite powder and Se (99.999% purity) were sealed in the ampoule without exposing them to air. The ampoule was heated uniformly at 250 °C for 20 h and cooled to room temperature gradually. All the optical measurements were made at room temperature. The samples, however, showed some change in the absorption spectrum in the ultraviolet region with time over the scale of a year. The present measurements were made within several weeks after sample preparation.

Diffuse reflection spectra were measured by using a Nikon G250 monochromator and Si photodiode for the longer-wavelength region, or a Jobin–Yvon U-1000 double monochromator and Hamamatsu Photonics R-106UH photomultiplier for the shorter-wavelength region. The light source for the measurement of the diffuse reflection was a tungsten–halogen incandescent lamp.

The pure zeolite had no absorption within the present energy region of the observation. The absorption spectra of Se-loaded zeolite powder were obtained from the following analysis of the diffuse reflection spectra.

We assume that the zeolite powder is filled for the layered region $-l < z < 0$, and the light goes into the powder in the $-z$ direction. The light energy flows toward the $-z$ and z directions are indicated by $A(z)$ and $B(z)$, respectively. The differential equations are given by

$$- dA(z)/dz = - (K + S)A(z) + SB(z) \tag{1}$$

$$dB(z)/dz = - (K + S)B(z) + SA(z) \tag{2}$$

where K is the absorption coefficient of the powder and S is the scattering rate for light. The value of S is inversely proportional to the powder size. The above equations hold under the following two conditions. The powder size is larger than the wavelength, and the scattered light rays from powder particles do not interfere with each other. The other condition is the weak absorption limit where the ordinary reflection of each powder particle is smaller than that of the scattered or the transmitted light. The present experiments were made under these conditions.
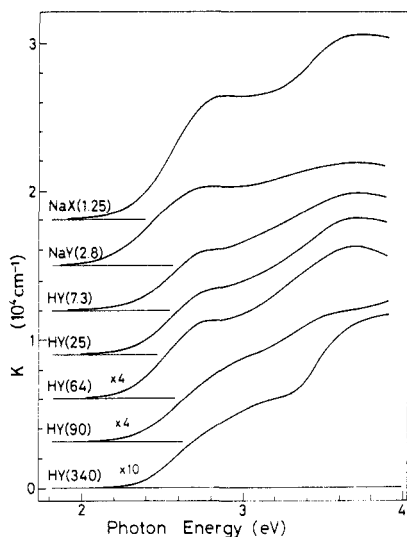
Figure 1. Absorption spectra of Se incorporated into faujasite (X or Y) and the dependence on the Si-to-Al ratio.

The boundary condition in equations (1) and (2) is given by

$$B(-l) = 0. \tag{3}$$

The diffuse reflection $r(\omega)$ is defined by

$$r(\omega) = B(0)/A(0). \tag{4}$$

In the case when $l = -\infty$, we get the relation

$$K = SF(\omega) \tag{5}$$

where $F(\omega)$ is the so-called Kubelka–Munk function (Kortüm 1969):

$$F(\omega) = [1 - r(\omega)]^2/2r(\omega). \tag{6}$$

Therefore the absorption coefficient K is proportional to $F(\omega)$. In the case of no absorption where $K = 0$, $r(\omega)$ becomes unity.

The absolute value of K, however, depends on S. If we need the absolute value of K, we evaluate the value of S as follows. The transmission rate T is given by $A(-l)/A(0)$ and calculated from equations (1)–(3) for a white powder ($K = 0$) as

$$T = 1/(Sl + 1). \tag{7}$$

Thus, S is determined from T for each zeolite powder before the adsorption of Se. Finally, the absolute value of K is given by equation (5).

3. Absorption spectra of Se adsorbed in zeolites with various Si-to-Al ratios

The absorption spectra of Se in X or Y are shown in figure 1. The pore structure of X or Y is constructed by the nearly spherical cages which are connected in the diamond structure with each other through the windows of each cage. The inner diameters of the cage and the window are 1.35 nm and 0.7 nm, respectively, where the size of cations is
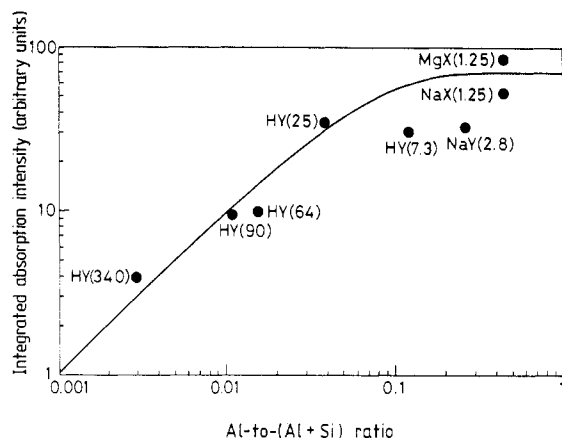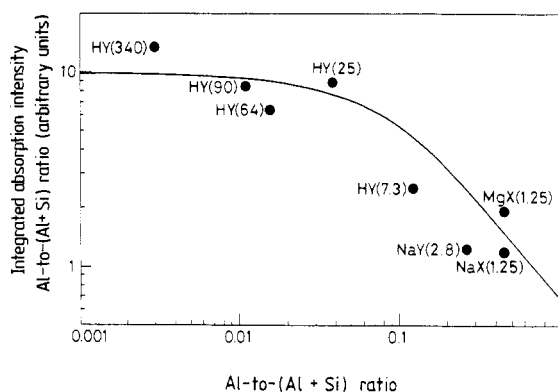
Figure 2. Integrated absorption intensity as a function of Al-to-(Si + Al) ratio (●): ———, results based on the model calculation.

neglected. There appears to be a remarkable change in the absorption intensity and a slight difference in the spectral shape on changing the Si-to-Al ratio (see figure 1). The spectral difference is discussed in the next section. In the present section, we remark on the absorption intensity. When the shape of the absorption spectrum has no change, the absorption intensity is known to be proportional to the total amount of material contained in the matrix, because of the sum rule in the optical transition. In the present case, the spectral difference is so small in the present spectral region that the integrated absorption intensity is expected to be proportional to the amount of Se loaded into the zeolite matrix.

The integrated absorption intensity is shown in the logarithmic scale by full circles in figure 2 as a function of Al-to-(Al + Si) ratio. Hereafter, we define x as the Al-to-(Al + Si) ratio. In the figure, the result for MgX(1.25) is also shown. It is seen that the integrated absorption intensity is proportional to x at small x and saturates at large x.

The full curve indicates the calculated results based on the following simplified model. The permanent dipole consisting of $(AlO_4)^-$ and a cation adsorbs a finite number N of Se atoms, and these N Se atoms cover the n sites of $(AlO_4)^-$ or SiO_4 which face the inner surface of the zeolite cage. The coverage rate is given by the probability that one $(AlO_4)^-$ or more are found in n sites. It is given by $1 - (1 - x)^n$, where $(1 - x)^n$ is the probability that all sites are SiO_4. If we assume that the Se atoms do not cover the surface doubly for any value of x, the amount of Se is proportional to $1 - (1 - x)^n$, because the lattice constant of zeolite scarcely depends on x. However, $(AlO_4)^-$ and SiO_4 in zeolites are connected with each other under the Loewenstein rule that the nearest neighbour of $(AlO_4)^-$ is always SiO_4, i.e. bonding such as Al–O–Al does not occur and the maximum value of x is 0.5. This rule is important only in the case of large x and is ignored for simplicity here. The full curve in figure 2 shows $1 - (1 - x)^n$ as a function of x, where n is assumed to be 15. The ordinate is changed to fit the experimental results. The experimental results are roughly reproduced by this model. By comparison between the sizes of Se atom and the zeolite lattice, N is estimated to be about 10–20 from the value of n. It is expected that Se is an isolated cluster consisting of about 10–20 atoms for sufficiently small x where the distance between $(AlO_4)^-$ is much larger than the size of

Figure 3. Integrated absorption intensity normalised by the Al-to-(Si + Al) ratio as a function of the Al-to-(Si + Al) ratio ($\bullet$): ——, results based on the model calculation.

the Se cluster. The spectral difference is discussed later in terms of the relation with the structure of Se.

The full circles in figure 3 show the integrated absorption intensity normalised by the amount of Al, and the full curve represents $[1 - (1 - x)^n]/x$ where $n = 15$. In this, the experimental results show that the number of Se atoms per Al is constant for small x and decreases for large x. The number of Se atoms per cage is known to be about 21 in NaX (Bogomolov *et al* 1985). This value means that the number of Se atoms per Al is 2 by assuming that the Si-to-Al ratio is 1.25. We normalise the ordinate to be about 2 for NaX(1.25) in figure 3. Then, we can estimate the number of Se atoms per Al to be about 20 for small x. This value is roughly equivalent to the value of N, which is 10–20.

Next, we speculate about the structure of Se in X or Y. As mentioned briefly above, the structure of Se is expected to be an isolated cluster for sufficiently small x. The bonding between Se atoms is of the covalent type, and the dangling bond is unstable. It is well known that the structures of Se crystals in the trigonal and monoclinic forms are spiral chains and Se_8 rings, respectively. If the dangling bond does not occur, the possible structure of the Se cluster in zeolite is a ring or a long chain which is pinned to the zeolite framework at the permanent dipole of zeolite. In the present case, the amount of Se is saturated for each zeolite, and the dangling bond scarcely occurs, because the attractive potential at the dangling bond is usually stronger than that at the permanent dipole, and Se atoms will be connected successively at the dangling bond until the Se chain becomes a ring or a sufficiently long chain. In figure 4, the expected structures of Se in X and Y are shown schematically. The possible structure of Se is a ring for sufficiently small x, as shown in figure 4(a). For an intermediate value of x where the Se rings overlap with each other, as shown in figure 4(b), the structure of Se gradually changes to an isolated chain with some deformation. This is because t-Se is most stable in all allotropes, and the chain is considered to be most stable in zeolite, if the structure is geometrically possible. With increasing x, these chains will become neighbours to each other, as shown by figure 4(c). These expectations are confirmed from the analysis of the spectral shapes in section 4.

4. Absorption spectra and the structure of Se in zeolites

The outermost electronic configuration of the Se atom is $4s^2 4p^4$. Two 4s electrons are in a deep state compared with 4p states and localised inside the 4p electrons. Two 4p
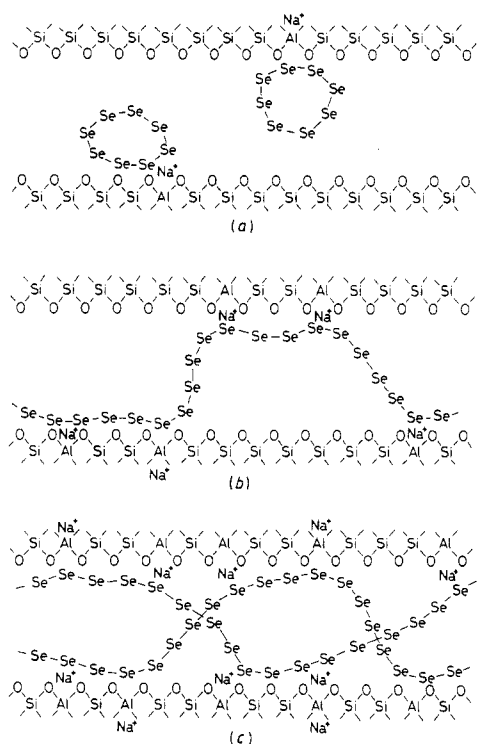
Figure 4. Schematic representation of the expected structures of Se in a zeolite pore for (a) the high-silica case when the Al-to-(Si + Al) ratio is much less than unity, (b) the middle-silica case and (c) the low-silica case when the Al-to-(Si + Al) ratio is about 0.5.

electrons contribute to the covalent bond between Se atoms, which is called the σ-bond. The last two 4p electrons are in the lone-pair state and scarcely contribute to the bond between Se atoms; they form the uppermost valence band. The bonding structure of Se is characterised by the bond length, the bond angle and the dihedral angle. As freedom is permitted in the sign of the dihedral angle, Se atoms form a spiral chain and a ring for same and alternate signs, respectively, of the dihedral angle. Above the Fermi energy, there exists the σ^*-bond state which is the anti-bonding state of the σ-bond. In t-Se, the absorption bands appear at 2 eV and 3.5 eV (Tutihasi and Chen 1967), and they are assigned to the transitions from the lone-pair state to the σ^*-bond state and from the σ-bond state to the σ^*-bond state, respectively (Lingelbach *et al* 1972, Joannopoulos *et al* 1975). Therefore the spectral shape of the lowest absorption band will change in dependence on the lone-pair band and/or the σ^*-bond band. The absorption edge of monoclinic Se (m-Se) is known to be higher than that of t-Se. The origin of the blue shift of the absorption edge is the decrease in the intermolecular interaction, because the intermolecular distance in m-Se is larger than the interchain distance in t-Se and the energy width of the lone-pair band is expected to decrease in m-Se (Bayliss and Liang 1982).

The isolated Se chain in M is reported to show a blue shift of the absorption edge compared with that in t-Se (Bogomolov *et al* 1983a). This result is interpreted as due to the absence of intermolecular interaction, as in m-Se.

From the comparison with the assignment of the absorption spectrum in t-Se, the absorption bands located at from 2.5 to 3 eV and at 3.5 eV in figure 1 are assigned to the
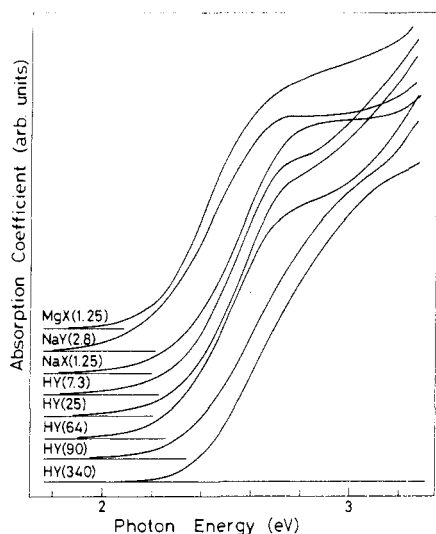
Figure 5. Detailed absorption spectra of Se incorporated into faujasite (X or Y) shown in figure 1. The ordinate scale of each curve is changed for comparison.
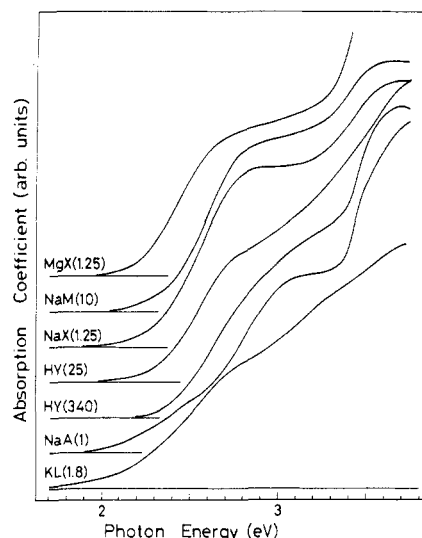
Figure 6. Absorption spectra of Se incorporated into various zeolites: faujasite (X or Y), mordenite (M), A and L.

transitions from the lone-pair state to the σ^*-bond state and from the σ-bond state to the σ^*-bond state, respectively.

Figure 5 shows the magnified part of figure 1. The ordinate of each curve is changed for comparison. It is seen that energies of the absorption edge are classified into three groups; the lowest two, the middle four and the highest two curves. From the expectation in section 3, these lowest, middle and highest groups are tentatively ascribed to the isolated cluster, to the isolated chain and to chains with adjacent chains, respectively.

Figure 6 shows the absorption spectra of Se adsorbed in various zeolites. Here, we try to interpret the spectral difference from the point of view of the Se structure in each zeolite. The spectrum of Se in NaX(1.25) quite resembles that of Se in NaM(10) but is different from that of Se in MgX(1.25). The only possible structure of Se in M is the isolated chain. Therefore the structure of Se in NaX(1.25) is expected to be the isolated chain irrespective of the difference in the framework. The real structure of Se in NaX(1.25) may have some alternation of the sign of the dihedral angle, and the chain will bend, because the framework of X has no straight channel as in M. The middle four spectra in figure 5 including NaX(1.25) resemble each other. Therefore the most plausible structure for Se in NaX(1.25), HY(7.3), HY(25) and HY(64) is the isolated chain also from the spectral point of view.

The absorption edges of Se in MgX(1.25) and NaY(2.8) are shifted to the lower-energy side compared with those in NaX(1.25) and NaM(10). This fact suggests that an interchain interaction occurs.

These results are expected from the difference in the window size of the framework. The cations in zeolite, such as Na^+ and Mg^{2+}, have no chemical reaction with Se, because no absorption band of such compounds appears, but geometrically affect the structure of Se. It is well known that the effective window sizes of CsA, KA, NaA and CaA are 0.2 nm, 0.3 nm, 0.4 nm and 0.43 nm, respectively. The radii of Na^+ and Mg^{2+} are
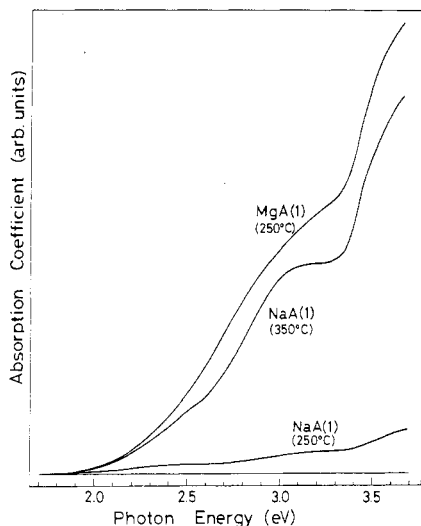
Figure 7. Absorption spectra of Se incorporated into zeolite NaA(1) and MgA(1), and the dependence on the loading temperature of Se.

0.097 nm and 0.065 nm, respectively. The size of Mg^{2+} is much smaller than that of Na^+, and the number of Na^+ ions is twice that of Mg^{2+} ions for the equivalent Si-to-Al ratio. Therefore the effective sizes of the cage and window in NaX(1.25) are expected to be smaller than those of MgX(1.25) and NaY(2.8). Two Se chains probably cannot pass through the window in NaX(1.25), and the probability of neighbour chains is small. On the other hand, the window sizes of MgX(1.25) and NaY(2.8) may be large enough for two chains to pass through, and the probability of neighbouring chains may increase.

In zeolite A, the nearly spherical cages with a diameter of 1.15 nm are connected in simple cubic form through the window having a diameter of 0.42 nm. As shown in figure 7, NaA(1) loaded with Se at 250 °C shows weak colouration compared with that at 350 °C, while MgA(1) loaded with Se at 250 °C shows strong colouration. In this figure, the absorption intensities can be compared with each other because the original powder is equivalent. The smallest molecular structure of Se is Se_2 in a vapour phase. The present results indicate that any Se molecules scarcely pass through the window in NaA(1) at 250 °C, while Se molecules can do so in NaA(1) at 350 °C or in MgA(1) at 250 °C. It is anticipated that molecules which are slightly larger than that of window size can pass through the window at high temperatures, since the zeolite framework vibrates violently, and the vibration increases the chance that Se molecules pass through the window. The effective window size of MgA(1) is considered to be larger than that of NaA(1), and Se molecules can pass through the window of MgA(1). The above results lead to the expectation that any Se atom in NaA(1) is not located inside the window, and the possible structure of Se is only an isolated cluster located inside the cage. The structure of S loaded into NaA is reported to be double parallel S_8 rings which are separated from each other in the cage (Seff 1972). In the case of Se, the double parallel Se_8 rings can be expected by analogy with S, but intermolecular interaction between two rings may occur because the Se atom is larger than the S atom. The absorption spectrum of NaA(1) resembles that of HY(340) except for the lower-energy absorption around 2.4 eV in figure 6. The lower-energy absorption may be caused by partial intermolecular interaction. Therefore the most plausible structure of Se in NaA is double parallel Se_8 rings which are partly in contact with each other. From the weight change of Se-loaded

NaA, the number of Se atoms is estimated to be about 18 per cage (Bogomolov *et al* 1983b). This value is nearly the same as the present value of 16.

The absorption spectrum of Se in KL(1.8) is quite different from others in figure 6. The pore structure of L is constructed by spheroidal cages which are connected in one dimension, and the window size is 0.75 nm. The possible structure of Se is one dimensional, but there is the possibility of double parallel chains because of the large window size. The absorption spectrum shows the structure at about 2.7 eV as observed in NaM(10), while the strong absorption tail appears to be continued in the infrared region. This lower tail is stronger than that in MgX(1.25). This fact suggests that the structure of Se in KL(1.8) is double parallel chains.

5. Summary

The amount of Se incorporated into X or Y strongly depends on the Si-to-Al ratio and is interpreted using the model in which the permanent dipole consisting of $(AlO_4)^-$ and a cation adsorbs the finite number of Se atoms, about 10–20. The spectral change of Se in X or Y is interpreted under the assumption that the structures of Se are isolated clusters, isolated chains and chains with neighbouring chains for high-, middle- and low-silica zeolites, respectively. The most plausible structures of Se in A and L are double parallel Se_8 molecules and double parallel chains, respectively. The molecular sieve effect on Se molecules is observed in NaA at a loading temperature of 250 °C.

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