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Plenary Lecture II

## Dynamics of Small Molecules in a Nano Space of Layered Silicates and Zeolites

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First, dynamics of guest molecules in kaolinite intercalation compounds with formamide (FA), formamide-N,N-d<sub>2</sub> (FA-d<sub>2</sub>), N-methylformamide (NMF) and N,N -dimethylformamide (DMF) has been investigated through <sup>2</sup>H NMR spectra and <sup>2</sup>H and <sup>13</sup>C spin-lattice relaxations. <sup>2</sup>H NMR spectra of kaolinite/FA-d<sub>2</sub> in the temperature range 200-350K are composed of a narrow central peak, a resolved Pake doublet (RD1) and a distribution of Pake doublets (RDs). Quadrupole coupling constants and asymmetric factors obtained by fitting the spectral patterns indicate that RD1 is ascribed to the host hydroxyl group formed through H-D exchange during the synthesis and RDs to the guest molecules in the interlayer. Temperature dependence of the quadrupole coupling constant reveals that the guest molecules undergo librational motions, and that the librational amplitude increases with temperature. Variable-temperature <sup>13</sup>C spin-lattice relaxation times T<sub>1</sub> of kaolinite intercalates with FA, FA-d<sub>2</sub>, NMF and DMF were recorded at two magnetic fields. T<sub>1</sub> decreases with increasing temperature in all the samples, and increases at the higher magnetic field in the order of FA > FA-d<sub>2</sub> > NMF > DMF, where it is almost independent of the field in kaolinite/DMF. <sup>13</sup>C spins relax through dipole-dipole interactions with <sup>1</sup>H and <sup>14</sup>N by the librational motions of the molecules. The field dependence indicates that the correlation times are of the order of nano seconds, and that they are in the order of FA > FA-d<sub>2</sub> > NMF > DMF. The temperature

dependence of the relaxation time is caused by the amplitude change of the librational motions.  $^2\text{H}$  spins relax mainly through paramagnetic impurities being assisted by spin diffusion at low temperatures, and fluctuation of quadrupole interaction caused by the librational motions contributes to the relaxation at higher temperatures.

Second, molecular motions of benzene-d<sub>6</sub>, cyclohexane-d<sub>12</sub> and n-hexane-d<sub>14</sub> sorbed at loading levels of 1 molecule per channel lobe in KL zeolite have been studied by  $^2\text{H}$  NMR. The spectra were recorded in the temperature range from 124K to 373K, and they were successfully simulated. At low temperatures, benzene molecules rotate fast around the C<sub>6</sub> axis, and cyclohexane molecules rotate fast around the C<sub>3</sub> axis of the chair form, where the directions of the rotation axis are fixed. With increase in temperature, benzene, cyclohexane, and n-hexane molecules start jumping among the six equivalent sites on K<sup>+</sup> ions. Further increase in temperature results in the increase in the fraction of molecules locating at the central space of the micropore which undergo isotropic motions and exchange with the molecules on the K<sup>+</sup> ions. The mean residence time on the K<sup>+</sup> ion is in the following order; benzene-d<sub>6</sub> > cyclohexane-d<sub>12</sub> > n-hexane-d<sub>14</sub>. The apparent activation energies derived from the mean residence times are  $28.0 \pm 1.6$  kJ/mol ( $220\text{K} < T < 373\text{K}$ ) for benzene-d<sub>6</sub>,  $9.6 \pm 1.2$  kJ/mol ( $160\text{K} < T < 260\text{K}$ ) and  $44.3 \pm 3.6$  kJ/mol ( $280\text{K} < T < 373\text{K}$ ) for cyclohexane-d<sub>12</sub>, and about 10 kJ/mol for n-hexane-d<sub>14</sub>. The large activation energy at the high temperatures in cyclohexane-d<sub>12</sub> might be caused by the conformation inversion of the cyclohexane ring. The ratios of the numbers of molecules in the central space to those on the K<sup>+</sup> ions are in the order of benzene-d<sub>6</sub> < cyclohexane-d<sub>12</sub> < n-hexane-d<sub>14</sub>. In conclusion, the interaction between the guest molecules and KL zeolite is in the following decreasing order; benzene-d<sub>6</sub> > cyclohexane-d<sub>12</sub> > n-hexane-d<sub>14</sub>.