Study on the Surface Free Energy of Ground CaO by IGC *

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Abstract:　CaO formed by decomposing $CaCO_3$ at 1450℃ was ground in a vibrational mill, then the long-time ground sample was reheated at different temperatures. Inverse Gas Chromatography (IGC) was used to measure the variation of the sample's surface free energy under grinding and reheating. It is concluded that the total surface free energy and the London dispersive component of the surface free energy increases with grinding, while the polar component first increases with grinding, and then decreases, and finally disappears. When the long-time ground sample was reheated, its total surface free energy decreases, among which the London component decreases, but the polar component appears again.

Key words:　surface free energy; ground CaO; IGC

1　Introduction

Many methods were proposed for the analysis of powder's surface properties. In Papiere's experiment[1], powders were compressed into discs, and then classical liquid contact angle technique was used to measure the powder's surface energy. Schultz suggested that, for solids with high surface energies, it is preferable to use the two liquids technique[2]. Morever, surface energy values were evaluated by the measurement of immersion heat and adsorption isotherm[3]. Inverse Gas Chromatography (IGC) as an effective gas - solid chromatographic technique to analyze the properties of the stationary phase was first used by Gray for the characterization of the surface properties of powders[4]. Papier[5] successfully used IGC technique to analyze cellulose fibers.

CaO is an important component for silicate materials. In this work, fine crystal structure CaO which simulates free-CaO in cement was made by decomposing $CaCO_3$ at 1450℃ for 2 hours. Then the samples were ground in a vibrational mill. Long-time ground samples were reheated at different temperatures. IGC was used to analyze the surface properties of CaO samples under grinding and reheating.

2　Principle of the Method

The surface free energy of powders can be separated into two parts: London dispersive component and Nondispersive component. The latter includes the contributions arising from polar force, dipole-induced force, electrostatic force, π—bonds and hydrogen bonds, etc. While considering about the interaction between the powder and another phase, the free energy of interaction between them is – W_A, where W_A is the work of adhesion, then[6]:

$$W_A = W_A^d + W_A^h + W_A^p + W_A^i + W_A^\pi \qquad (1)$$

where the superscripts refer to London dispersion forces, hydrogen bonds, dipole-dipole interactions, dipole-induced dipole interactions and π—bonds. If the other phase has its internal interaction limited to London dispersive force (as in saturated hydrocarbons), the interaction between the two phases is chiefly London dispersive force (for the other forces are usually negligibly small), so W_A is essentially egual to W_A^d[7]. For such systems the saturated hydrocarbon can be used as a probe to measure the dispersive force field of powders[8]. This is the basis to use n-alkanes as probes to measure the London dispersive component of the surface free energy of the stationary phase in IGC experiment.

In general, the surface free energy of CaO is mainly made up of two parts: London dispersive part and polar part, all the other terms can be neglected[2]. In this work polar probes were also used to analyse the polar action of the stationary phase. The difference between the IGC and the ordinary GC is that the former take the stationary

phase as its studying object and the known pure volatile probe together with carrier gas as mobile phase. To the probe under the same driving force, if the stationary phases are different, the retention actions will be different. Thus, the surface properties of different stationary phases which control the retention action can be analyzed.

The specific retention volume $\overset{r}{V}_g$ (the net retention volume for unit weight of stationary phase) is an important factor in IGC analysis. Since the concentration of probe in the gas phase is very small, if the n-alkanes are retained solely by surface adsorption on the adsorbent, the adsorption is in Henry's Law region. For the adsorption process form an ideal gas phase to an ideal adsorbed phase, if the increment per CH_2 in the molar free energy of adsorption is $\Delta G_A^{(CH_2)}$, Gray[4] demonstrated a linear relationship between $\ln V_g$ and the number of carbons of n-alkanes injected in the GC, the slope of the straight line is

$$-\frac{\Delta G_A^{(CH_2)}}{RT}.$$

According to Fowkes[5], the work of adhesion W_A between a saturated hydrocarbon and a second phase is given by the geometric means of the London components of the surface free energies of cohesion ($W_C = 2\gamma$) of the two pure phases, such that:

$$W_A = (W_{C,1} \cdot W_{C,2})^{1/2} = 2(\gamma_1 \cdot \gamma_2)^{1/2} \qquad (2)$$

Since phase 1 is a saturated hydrocarbon, γ_1 is equal to surface tension, while γ_2 represent the London dispersive part of the surface free energy of phase 2 (stationary phase).

To ordinary interface, the molar area of CH_2 group can be used as an adjusting parameter, the work of adhesion in Fowke's formula can be substituted by the free energy of desorption (equals to the adsorption free energy) per unit area of methylene.

$$\frac{-\Delta G_A^{(CH_2)}}{N \cdot a_{CH_2}} = 2(\gamma_{CH_2} \cdot \gamma_S^D)^{1/2} \qquad (3)$$

Where N is Avogadro number, a_{CH_2} is the area of adsorbed CH_2 group ($0.06 \times 10^{-18} m^2$) and γ_S^D is the London dispersive component of the surface free energy of the stationary phase.

From the temperature dependence of the surface tension of a linear polyethylence, the surface tension of a CH_2 surface, γ_{CH_2} at low temperature may be obtained by extrapolation[7]. Gaines got the value $\gamma_{CH_2} = 35.6 mNm^{-1}$ at 20°C. Now, from Eq. (3), the London dispersive component of the surface free energy of the stationary phase (γ_S^D) can be calculated.
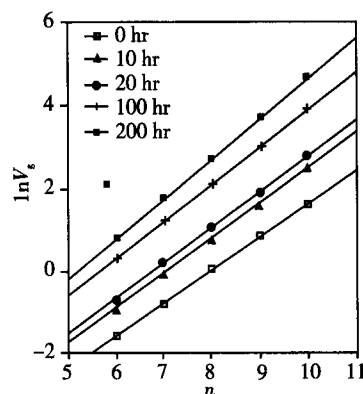

Fig.1   Retention volume vs number of C atoms of n-alkanes for the ground CaO

3   Experimental Procedures

CaO produced by heating $CaCO_3$ at 1450°C for 2 hours was ground in a vibrational mill (up to 200 hours), the samples were taken at regular intervals and stored in glass bottles which were sealed by wax. To perform an IGC experiment, the stationary phase must have a certain grain size. In his experiment with $CaCO_3$, Papiere[5] used hydrothermal treatment and aggregation from a methanol. Neither of them are suitable to CaO powders which are easy to hydrate. In this experiment, CaO powders were compressed (under a pressure 1 MPa) into small discs. The discs were then ground and sieved to particles in the size range 0.20 - 0.40mm. The grains formed in this method have uniform size distribution, high strength and the process has little effect on the sample's surface properties.

Shimadzu GC-9A Gas Chromatograph and Shimadzu C-R2AX Chromatograph Recorder were used. The column is made of glass, 3.2mm in diameter and 1600 mm in length. Hydrogen was carrier gas. The optimum working conditions were flow rate of the carrier gas was 30mL/min, column temperature was 100°C, detector temperature was 180°C, and vaporization chamber temperature was 180°C. Before the injection of the probes, the column was treated at a temperature of 150°C, with dry hydrogen running through it for 15min, to remove the water which might be adsorbed by the sample. The amount of probe injected into the IGC was $2\mu L$.

4   Results and Discussion

Fig.1 relates the specific retention volume (V_g) to the number of carbons of n-alkanes (n). From the slope of the straight line, the increment of the molar free energy of adsorption per CH_2 is known. According to Eq. (3), the London dispersive component of the surface free energy of

the ground CaO can be calculated. For the conversion between column temperature and room-temperature, the relation $d_\gamma/d_T = -0.056 \text{mJm}^{-2}\text{K}^{-1}$ was used[8]. The results are collected in Table 1. As grinding continues, the London dispersive component of the surface free energy of ground CaO increases.

Table 1   Variation of γ_S^D of Ground CaO with Grinding Time

Grinding time /hr	0	10	20	100	200
γ_S^D at 100℃ /(ergs/cm$_1^2$)	37.9	44.1	45.0	50.0	56.3
γ_S^D at 20℃ /(ergs/cm^2)	42.4	48.6	49.5	54.5	60.8

Three polar molecules (Benzene, Toluene and Xylene) were also used to analyse the variation of the polar component of ground CaO. From the values of the retention time, it is found that the retention time increases with grinding, which means that the adorability of the ground sample to the probes or the total surface free energy increases. The contribution includes London dispersive part and polar part.

Papiere[5] related the $\ln V_g$ to the logarithm of the vapour pressure (P_0) of the probe to compare the London dispersive and polar interactions between the probes and the stationary phase, for in an IGC experiment the volatility of the probe is very impotent. Fig. 2 shows the variations of $\ln V_g$ with $\lg P_0$ for ground samples. For the untreated CaO, all alkanes fall on a line, the polar molecules are above the line which means the polar molecules are retained more strongly than hypothetical alkanes having the same vapour pressure. Because CaO is a polar component, there is polar interaction between the surface of CaO and the polar probe molecules as well as London dispersive interaction. As grinding continues, the points of polar molecules become farther and farther above the n-alkane line, which means the polar action of the stationary phase to the probe molecules is increasing. Surely in this period, the total surface free energy is increasing. After 20 hour grinding, the points of polar moleculars become closer and closer to the n-alkane line, which means that there is only London dispersive interaction between CaO and the probe molecules (polar or not), almost no polar interaction.
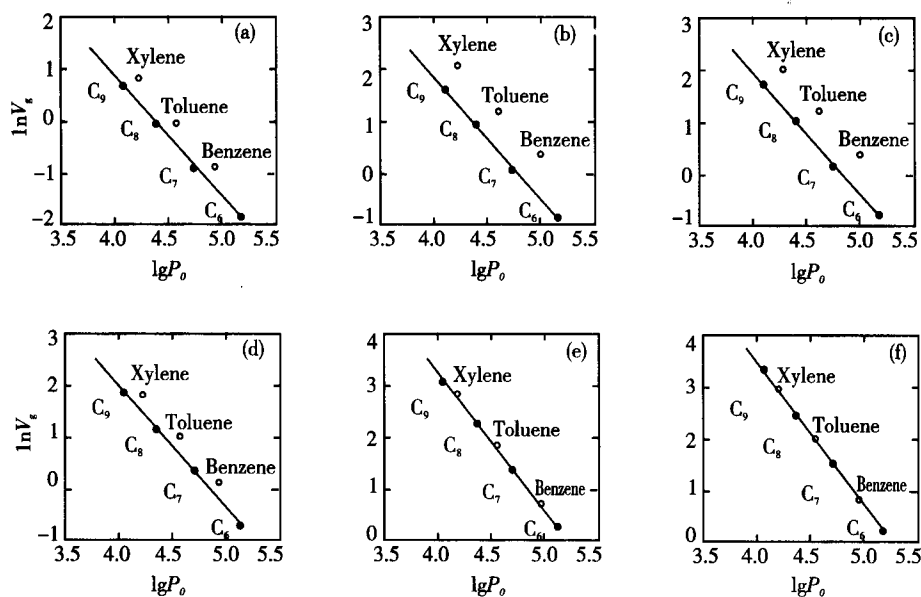

Fig.2   Specific retention volume $V_g(\text{cm}^3/\text{g})$ of ground CaO vs vapour pressure $P_0(\text{Pa})$ of the probes with grinding time: (a)0 hr, (b)5 hr; (c)10 hr; (d)20 hr; (e)100 hr; (f)200hr

CaO samples ground for 200 hours were reheated at different temperatures, then analyzed by IGC. Fig.3 shows the variations of the retention volumes with the number of carbon atoms of the n-alkanes. By the same method mentioned before, the London dispersive component of the surface free energy of the heated CaO can be calculated. From the values in Table 2, it is known that, as the heating temperature rises, the London dispersive component decreases.

Fig.4 shown the relation between $\ln V_g$ and $\lg_{10} P_0$.

Table 2   Variation of γ_S^D of Reheated CaO with Reheating Temperature

Reheating temp. /℃	400	600	800	1000
γ_S^D at 100℃ /(ergs/cm^2)	45.3	40.3	35.5	33.3
γ_S^D at 20℃ /(ergs/cm^2)	49.8	44.5	40.0	37.8

When the heating temperature is above 600℃, the points

of polar molecules begin to leave away from the n-alkane line. The higher the heating temperatures, the farther the points are away from the n-alkane line. The reason is the increase of the polar component of the surface free energy with heating.
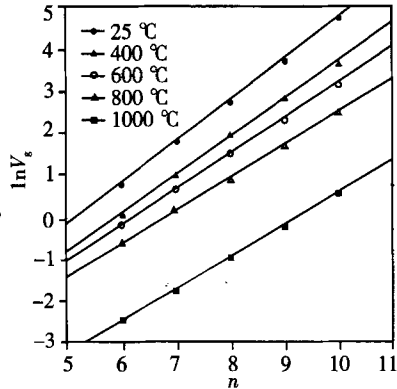

Fig. 3   Retention volume vs number of C atoms of the n-alkanes for the reheated CaO

The surface free energy of CaO depends on the molecular arrangement on the crystal surface. The ionic polarization and rearrangement for stabilization on the new surface formed with grinding lead to stronger polar action. As grinding continues, the number of dipoles formed on the crystal surface increases, which results in the increase

of the degree of polarization and also polar action. The observation mentioned above is just like this, from 0 hours to 15 hours, the polar action of the ground CaO of the probe molecules increases with grinding. After a certain time, the surface crystal structure of CaO is seriously destroyed, amorphous phase formed. The ions on the surface take random motion that the polar force disappears, only London dispersive force exists. The observation shows that, after 20 hour grinding, the polar force of ground CaO to the probes begins to decrease. When the grinding time is more than 100 hours, the stationary phase only has London dispersive force to the polar probes as it is to the n-alkanes.

One fact is that the London dispersive interaction between CaO and the probes is always increasing. That is because the London dispersive force depends on the propagation of the electromagnetic field and the vibrational electric field[9]. The amorphous phase formed on the sample's surface may change the dielectric constant which results in the increase of London dispersive force.

After CaO sample (ground for 200 hours) is reheated, the amorphous phase recrystallizes and the dipoles on the sample's surface appear again, the polar part of the surface free energy reappears.
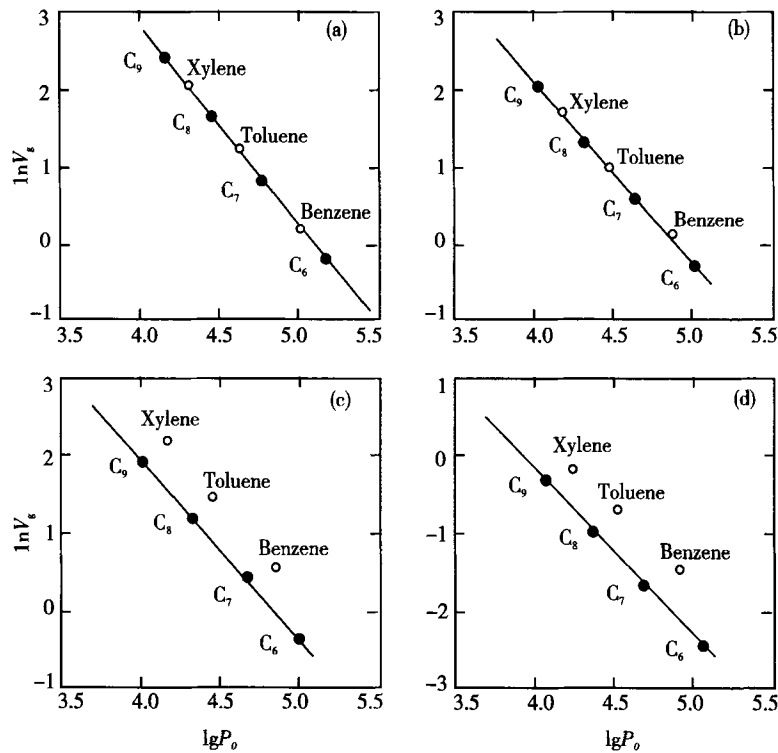

Fig. 4   Specific retention volume $V_g(cm^3/g)$ of reheated CaO vs vapour pressure $P_0(Pa)$ of the probes under different heating temperatures: (a)400℃ (b)600℃ (c)800℃ (d)1000℃

5   Conclusions

With grinding, the London dispersive component of the surface free energy of ground CaO is increasing. The polar component of the surface free energy increases with grinding in the first 15 hours, then decreases with continuous grinding because of the formation of amorphous phase on the surface of the sample. After 100 hours grinding, the surface free energy only has London dispersive component. The total surface free energy is always increasing with grinding.

After the sample (ground for 200 hours) is reheated, with the rising of the heating temperature, the London dispersive component of the surface free energy decreases, while the polar component reappears with the recrystallization of the amorphous phase on the sample's surface.

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