QUARTERLY PROGRESS REPORT (10/1/95-12/31/95)

Contract No. DE-FG22-94PC94215
Project Title: Conversion of Coal Wastes into Waste-Cleaning Materials
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INTRODUCTION

We have been investigating the conversion of fly ash into mesoporous materials in the last several months. Although lamellar phase has been observed, the hexagonal phase has not. According to the literature, only the hexagonal phase survives after calcination. Therefore, our goal is to synthesize hexagonal mesoporous materials with fly ash. It was pointed out by Chen et al.[1] that the Si/Al molar ratio in the precursor solution must be larger than 74 in order for the hexagonal mesoporous phase (MCM-41) to be formed. On the other hand, the Si/Al molar ratio in the fly ash is lower than 74. It is possible that it is due to the low Si/Al molar ratio in the fly ash solutions, the MCM-41 phase was not formed. However, it is not clear why Si/Al molar ratio in the precursor solution has to be larger than certain value for the MCM-41 phase to be formed. In the last three months, we did a systematic study on the effect of Si/Al molar ratio on the formation of MCM41 phase.

In the study, the silicon source is sodium silicate only instead of tetramethylammonium silicate solution and silica as done in Chen et al.[1] The Si/Al molar molar ratio was varied from 148 to 1, the smallest ratio allowed by the Loewenstein rule.[2] It was found that the amount of Al in the precursor solution can be as high as Si/Al=1 without disrupting the formation of aluminosilicate mesoporous materials (MCM-41). As the Si/Al ratio in the precursor solution was varied, the structure and the physical properties of the MCM-41 materials were changed. Lower Si/Al ratios tend to have a smaller shrinkage in the d_{100}-spacing after calcination and have higher X-ray diffraction intensity. Our results indicate that as the Al content increases, the MCM-41 materials tend to have a thicker cell wall.

EXPERIMENTAL SECTION

The experiments began with preparing the surfactant solution first. 10.9 g of surfactant, $C_{16}H_{32}(CH_3)_3NBr$, were mixed with 32.7 g distilled water at room temperature. The 25 wt% aqueous surfactant solution was heated to 38°C and stirred for 5 minutes. After the surfactant were fully dissolved, 7.25 ml of 4.96 N NH_4OH solution was added to the surfactant solution and then diluted by adding 200 ml of distilled water. The pH value of the solutions was typically at 11. After the surfactant solution was made, 41.8 g of sodium silicate (PQ Co., 28.7 wt% SiO_2, 8.9 wt% Na_2O, 62.4 wt% H_2O) was added to the surfactant solution prepared earlier. At the same time, different amount of aluminum hydroxide (Aldrich) were added so that the Si/Al molar ratios are 148, 74, 37, 18.5, and 1 respectively. The mixture solutions were stirred for 30 minutes at room temperature. The mixture solution with different Si/Al molar ratios were then hydrothermally cured at 10 psi (corresponding to 115°C). Samples were taken at various curing times and were washed with distilled water two times and then centrifuged to collect the powders. The centrifuged sediment was dried in the range of 60-80°C for 12 hours. After grinding, the solid powders were studied with X-ray diffractometer. The powders were calcined at 540°C for 7 hours at 1 °C/min. The calcined powders were studied with X-ray diffraction and BET.

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RESULTS and DISCUSSION

The X-ray diffraction patterns of aluminosilicate mesoporous materials cured at 115°C for 4 hours for Si/Al ratios ranging from 148 to 1 are shown in Fig.1. It is shown that as the Si/Al molar ratio decreases, the (110) and (200) peak intensity reduces although the (100) peaks remain strong. The d_{100}-spacing changes with the Si/Al molar ratio and the samples with smaller ratios have a larger d_{100}-spacing. It is seen that the higher Si/Al ratio tends to give clearer hexagonal structure pattern before calcination. However, the X-ray diffraction patterns of calcined samples show the opposite trend. Fig.2 shows the X-ray diffraction patterns of samples in Fig.1 that were calcined at 540°C for 7 hours in air. It is seen that calcined samples of smaller Si/Al ratios have clearer X-ray diffraction patterns. In fact, the calcined Si/Al=148 sample shows only one broad (100) peak whereas the calcined Si/Al=1 sample shows the strongest (100) peak. The d_{100}-spacing of the mesoporous materials after calcination showed similar trend as that before the calcination and the samples with smaller Si/Al ratios have a larger d_{100}-spacing. The X-ray diffraction results for samples cured for 9 hours, 22 hours, 49 hours, and 60 hours show similar trend as the results of curing for 4 hours. Namely, the samples with higher Si/Al molar ratios have a stronger (100) peak intensity before calcination but a weaker (100) peak intensity after calcination than that with lower Si/Al ratios. However, the behavior of d_{100}-spacing before and after calcination varies with the curing time and no systematic trend can be deduced as in the case of 4-hour curing.

The d_{100}-spacings of samples with various Si/Al molar ratios before and after calcination were compared and the amount of shrinkage can be calculated. The amount of shrinkage of d_{100}-spacing during the calcination is shown in Fig.3. Overall, smaller Si/Al molar ratios give larger d_{100}-spacing and the shrinkage during calcination is smaller, although there existed a few exceptions. Apparently, the Si/Al molar ratio has an effect on the shrinkage of the mesoporous phase during calcination.

The fact that samples with lower Si/Al ratios have a smaller d_{100}-spacing shrinkage indicates that they are more stable. A possible reason for the stable mesoporous materials of lower Si/Al molar ratios is that the hydrolysis and condensation rate of Al is much faster that of Si species.[3] Faster reaction rates produce a stable material at short time. Therefore, the shrinkage of the d_{100}-spacing of lower Si/Al molar ratios is smaller than that of higher Si/Al ratios. However, at longer time, the effects of faster reaction rate of Al will not be as conspicuous as at shorter times. Therefore, the trend observed at 4 hours is not clear at longer times, such as 49 hours and 60 hours.

The surface area of the calcined samples is affected by the Si/Al ratio as well. The surface area measured by a BET meter (Micromeritics, Flowsorb II) is summarized in Table I. The surface area increases with the addition of Al initially but decreases again for higher amount of Al added. The maximum surface area of 1030 m^2/g was obtained for Si/Al=74. The reason for the increase in the surface area as Si/Al ratio is decreased from 148 to 74 is not clear at the moment. However, the surface area decreases with when Si/Al ratio decreases from 74 to 1. The decrease in surface area indicates that the wall of the hexagonal cells of lower Si/Al ratios may be thicker since thicker walls would require more material and as a result have less number of cells per gram of material. A thicker cell wall is also consistent with the results that the materials of lower Si/Al ratios are more stable.

Another evidence of a more stable MCM-41 material with higher Al content can be seen in the acid test of the materials. The MCM-41 materials were subjected to a solution of phosphoric acid (Aldrich, 85 wt%) for several hours and the acid treated samples were taken out for X-ray diffraction study. It was found that the sample with Si/Al=1 still maintained a strong X-ray diffraction pattern after the acid test whereas the sample with Si/Al=74 did not show visible diffraction pattern. This result indicates that the MCM-41 material with Si/Al=1 is more stable or has a thicker cell wall which can sustain the attack of strong acid while that of Si/Al=74 can not.

CONCLUSIONS

In conclusion, it was found that the Si/Al molar ratio in the initial solution can be smaller than previously stated in the formation of aluminosilicate mesoporous molecular sieves. The Si/Al molar ratio can be as small as 1 for the formation of aluminosilicate MCM-41 phase. The addition of Al enhances the X-ray intensity, increases the d_{100}-spacing, reduces the shrinkage of d_{100}-spacing after calcination. Our results are consistent with the picture that increasing the Al content increases the cell wall thickness of the mesoporous materials. Therefore, increasing the Al amount can stabilize and strengthen the mesoporous phase.

PLAN FOR NEXT QUARTER

Since the MCM-41 phase can be formed even for Si/Al molar ratio of 1, it is clear that fly ash can be converted to mesoporous materials. In the next three months, we will focus our attention to the surfactant/Si ratio which is another dominant factor in the formation of MCM-41 phase. It is expected that as the surfactant/Si ratio decreases, the hexagonal phase would be favored. A systematic study on the surfactant/Si ratio will be conducted.

REFERENCES

1. C.-Y. Chen, H.-X. Li, and M. E. Davis, *Microporous Materials* **2**, 17 (1993).
2. W. Loewenstein, *Am. Mineral.* **39**, 92 (1954).
3. D. C. Bradley, R. C. Mehrotra, and G. P. Ganur, **Metal Alkoxide**, Academic Press, New York, 1978).

TABLE I Surface Area of Mesoporous Materials with Different Si/Al Ratios

Si/Al ratio	pure	148	74	37	18.5	1
Surface area (m^2/g)	694.8	905.6	1030.4		715.7	323.9

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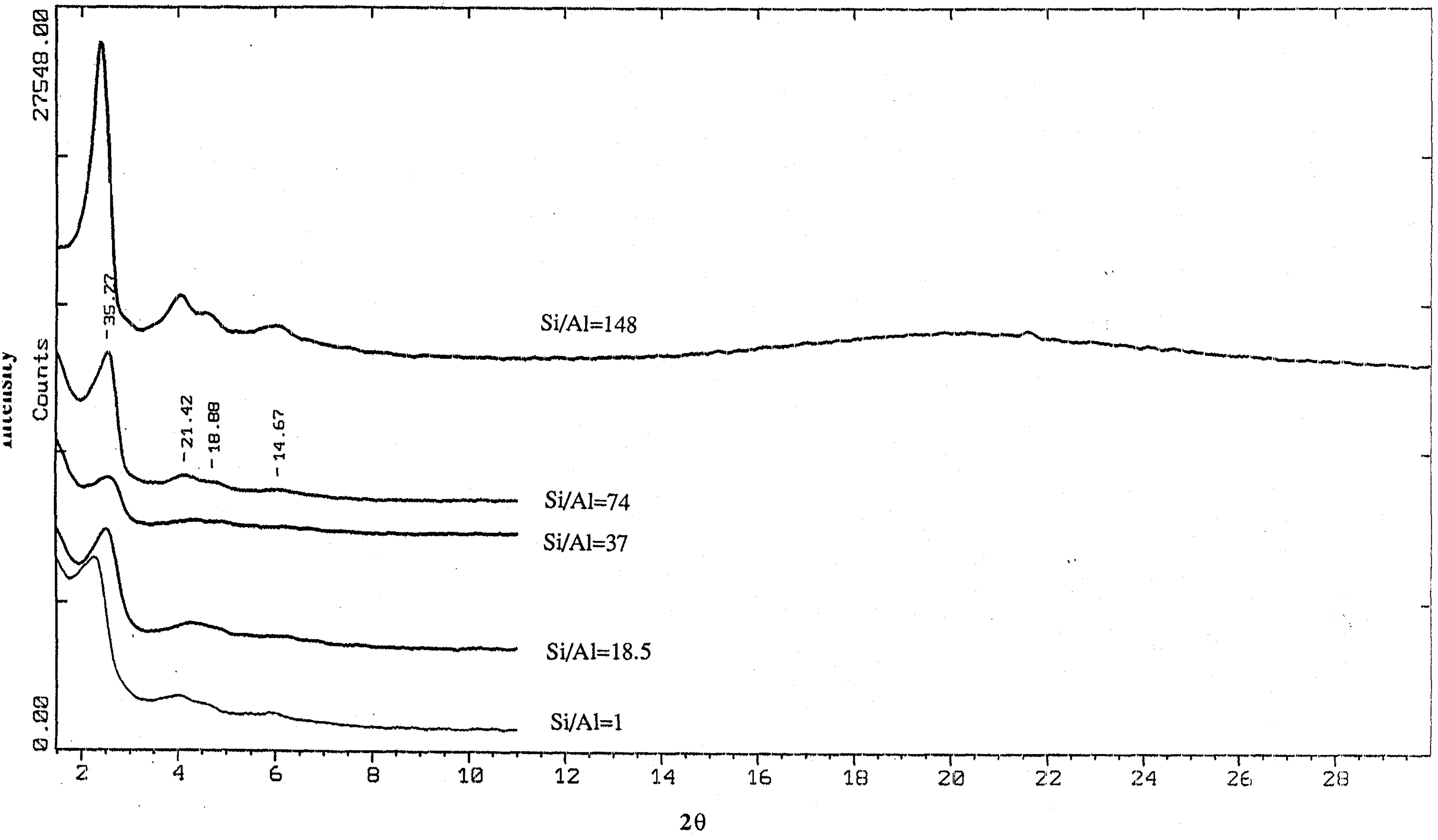

Fig.1. X-ray diffraction patterns of synthesized mesoporous phases with various Si/Al molar ratios after 4 hours of curing at 115°C.

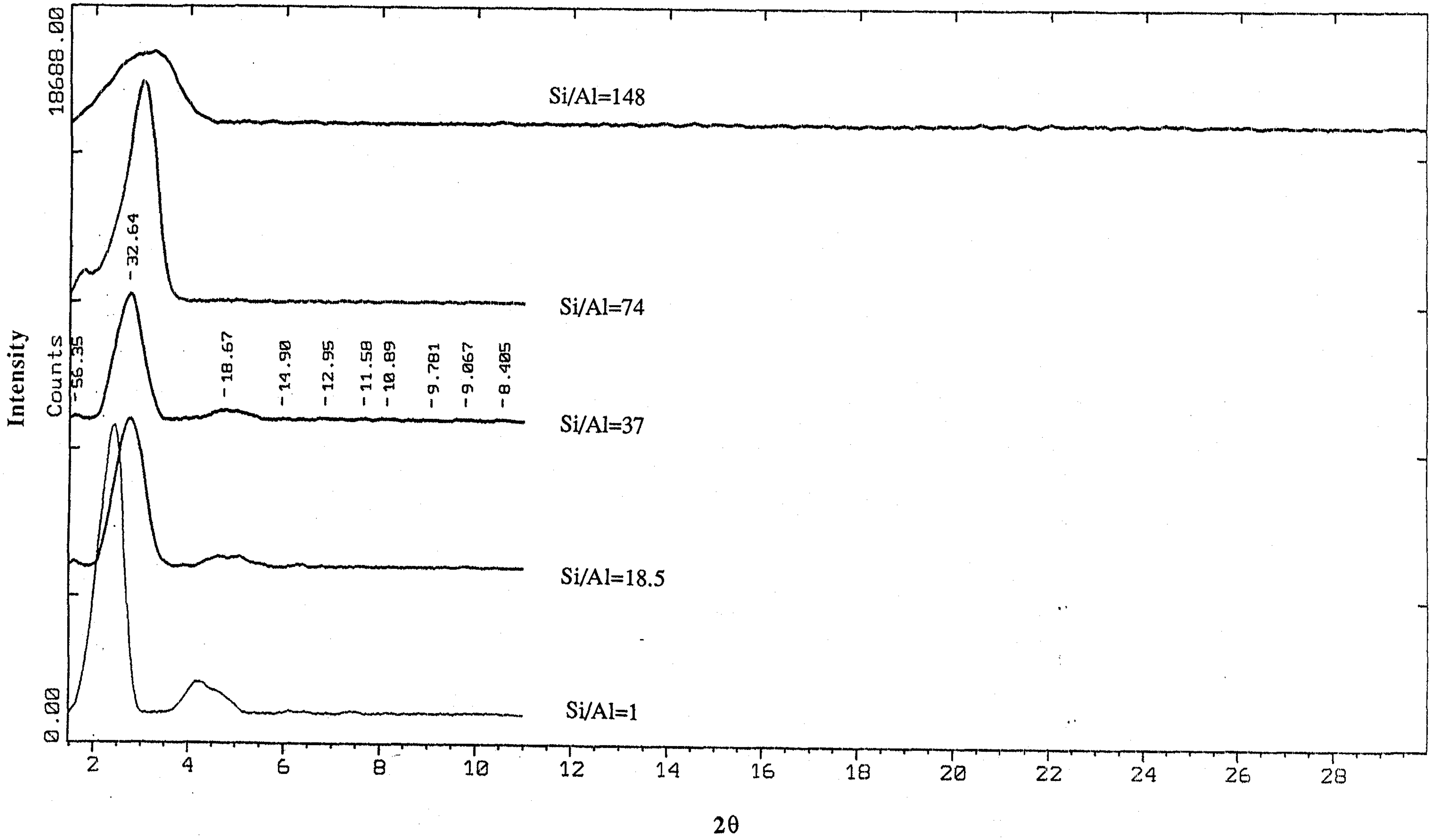

Fig.2. X-ray diffraction patterns of mesoporous phases with various Si/Al molar ratios after 4 hours of curing at 115°C and calcined at 540°C for 7 hours.

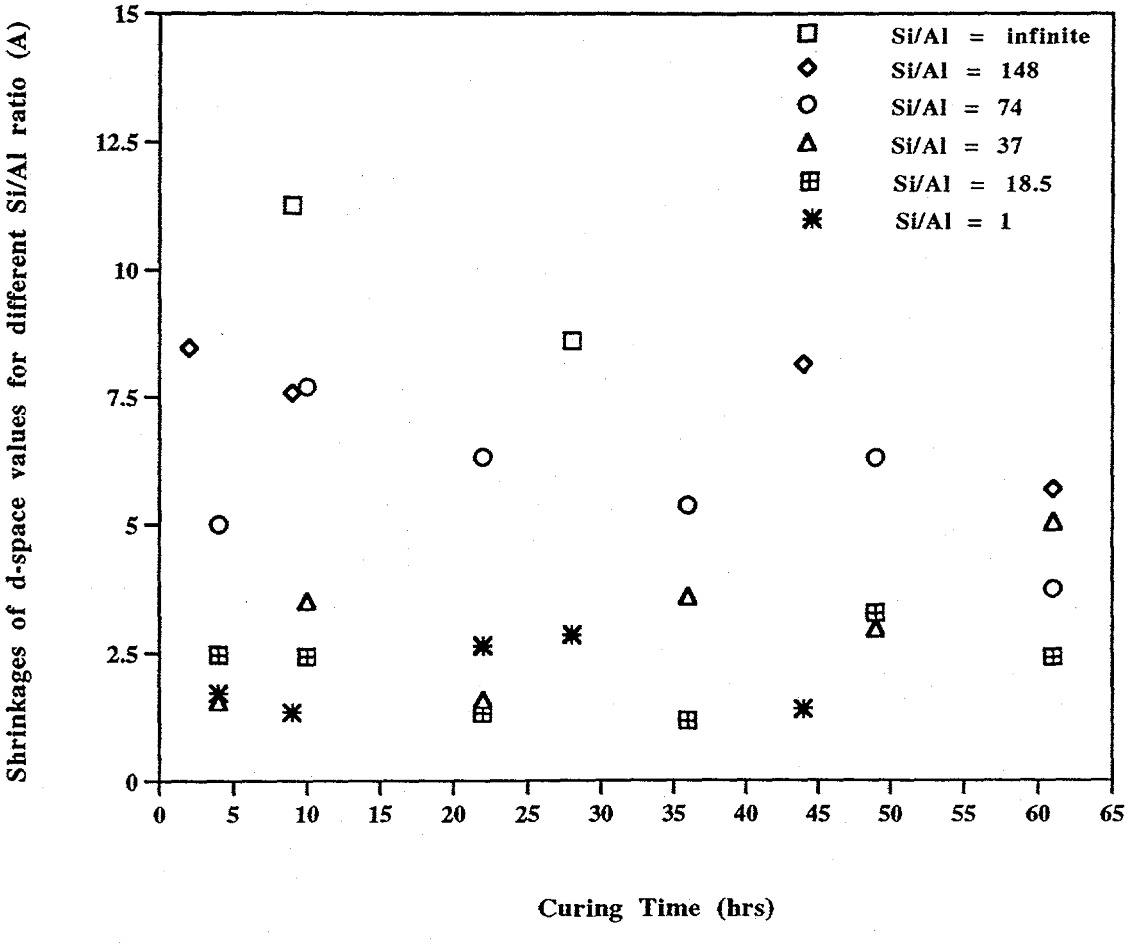

Fig.3. The shrinkage of d_{100}-spacing of mesoporous phases due to calcination as a function of curing time.