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Small-Angle X-Ray Scattering Study on the Growth of Metal Silicate Polymers in Solution

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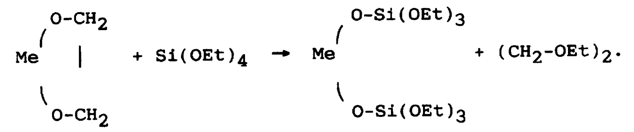
(Received October 8, 1992)

The development of metal silicate polymers in mixed solutions of nickel and iron 1,2-ethanediolates, water, and tetraethoxysilane was studied using a small-angle X-ray scattering (SAXS) method. The effects of the added metals on the growth of the silicate polymers and the correlation between the structure of the gel and metal particle of the catalyst prepared by calcining and reducing the gel are discussed.

It is well-known that the activity and selectivity of a metal-supported catalyst depend on the size of the metal particles;[1)] many attempts have thus been made to develop techniques to control the size of these particles. It was found by Ueno et al.[2)] that catalysts with a homogeneous metal size can be obtained by the hydrolysis of a mixed solution of metal 1,2-ethanediolates and tetraethoxysilane, $\mathrm{Si(OEt)_4}$ (TEOS). This is called the alkoxide method. In this procedure metal is integrated into the silicate network through the formation of metal silicates, eventually transforming to gel:[3)]



$$\mathrm{Me}\begin{matrix}\diagup\ \mathrm{O\text{-}CH_2}\\ |\\ \diagdown\ \mathrm{O\text{-}CH_2}\end{matrix} + \mathrm{Si(OEt)_4} \rightarrow \mathrm{Me}\begin{matrix}\diagup\ \mathrm{O\text{-}Si(OEt)_3}\\ \\ \diagdown\ \mathrm{O\text{-}Si(OEt)_3}\end{matrix} + \mathrm{(CH_2\text{-}OEt)_2}. \qquad (1)$$

Here, Me means metal. The catalysts can be prepared by drying and calcining the gel, followed by reduction.[2—6)]

Although structural changes at several stages of this catalyst preparation procedure have been studied by EXAFS spectroscopy and electron microscopy,[3)] the three-dimensional growth of silicate polymers in a mixed solution cannot be probed by these methods.

Small-angle X-ray scattering (SAXS) measurements comprise one of the most direct ways to study the structure of polymers in solution. In recent studies, the SAXS technique has proven to be useful for determining the fractal structure and size of polymers.[7—10)] In the present work, the growth of polymers in the presence of metal was studied by the SAXS method in relation to the structure of the resultant catalysts.

Experimental

Two kinds of solutions including nickel silicates, called NiA and NiB, were prepared as follows: 2.478 g of $\mathrm{Ni(NO_3)_2{\cdot}6H_2O}$ was dissolved into 20 ml of ethylene glycol at 25°C (p-1); subsequently, 28.7 ml of water was added within 2 min after p-1(p-2). Finally, 16.7 ml of TEOS was added within 2 min after p-2 at 25°C with vigorous stirring (p-3). In the case of NiB, 0.5 ml of $\mathrm{HNO_3}$ was added after p-2. A solution including iron silicates, called FeA, was also prepared in the same manner as that for NiA, except that 3.617 g of $\mathrm{Fe(NO_3)_3{\cdot}9H_2O}$ was dissolved into ethylene glycol. The weight ratio, $\mathrm{Me:SiO_2}$, was 1 : 9 in all samples. The water used for the preparation was deionized and distilled. Ethylene glycol and TEOS of reagent grade with a 99.9% purity were used without any further purification.

The dissolution times of TEOS were as follows: NiA= 16.7±0.1 h, NiB=0.8±0.1 h, and FeA=0.6±0.1 h. Hence, the SAXS of each sample before the time indicated above could not be observed. The pH values of each sample, measured using a glass electrode immediately after the TEOS was dissolved, were as follows: NiA=3.8, NiB=0.9, and FeA=1.0. After dissolution of TEOS, each sample was kept in a cell made of Cu and having about 0.1 mm-thick mica windows. The thickness of the sample was 2.5 mm. The temperature of the sample was kept at 25±0.5°C by a cell holder coupled to a bath circulator.

The gelation time (t_g) was determined from the time when the solution was solidified after TEOS was added into the solution: NiA=29 h, NiB=185 h, and FeA=37 h. As long as the same cell was used, the error in t_g was within 3%, but t_g depended on the volume of the cell and showed large values for a sample in a large vessel. Hence, the present t_g values are not absolute, but relative.

For the SAXS measurements, a point-focusing diffractometer with a double-bent LiF monochromator was used. Scattered X-rays were detected by a position-sensitive proportional counter (PSPC). Details have been described elsewhere.[11)] The s-region ($s=4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of X-rays), ranging from 0.038 to 0.40 Å^{-1}, was covered by this diffractometer. The maximum length scale of the present SAXS measurement ($d_{\max}$) was roughly estimated as being $d_{\max}=\lambda/(2\sin\theta_{\min})=2\pi/s_{\min}\approx165$ Å ($s_{\min}$ is the minimum s value, 0.038 Å^{-1}). The accumulation time in a measurement was 1.5—3 h. The data were corrected for background scattering and absorption.

The gels formed in NiA and NiB were dried at 110°C for 24 h, calcined at 450°C for 4 h, and reduced at 450°C for 4 h in a hydrogen stream. The thus-prepared catalysts were photographed with a magnification of 2×10^5 by using a transmission electron microscope (Hitachi, H-800). The average sizes of metal particles within the catalysts were estimated by a hydrogen adsorption study combined with magnetization measurements.[4)]

Results

The SAXS method was used to determine the size of the polymers from the Guinier radius,[12)] and to obtain information about their structure from the Porod slope.[13)] These parameters, originally employed for dilute systems, have recently been widely applied to dense systems, like the present ones.[7—10)]

In the region $sR_G \approx 1$, the SAXS intensity curve ($I(s)$) follows the well-known Guinier law:[12)]

$$I(s) \propto \exp\left[(-1/3)R_G^2 s^2\right], \qquad (2)$$

where R_G is the electronic radius of gyration of the scatterer (Guinier radius). R_G can be calculated from the slope of $\ln I(s)$ vs. s^2 plot (Guinier plot). Figure 1 shows typical examples of Guinier plots for NiB. The R_G values, thus obtained, in each sample are plotted against the normalized time (t/t_g) in Fig. 2. The R_G values in the final stage are listed in Table 1. The s ranges used to determine the final R_G values of NiA, NiB, and FeA were 0.038—0.045, 0.038—0.048, and 0.038—0.048 Å^{-1}, respectively.

In the region $sR_G \gg 1$, $I(s)$ depends on the geometric structure of the scatterer and follows the Porod law as follows:[7—10)]

$$I(s) \propto s^{-\mu}, \qquad (3)$$

where μ is called the Porod slope.[13)] When μ is less than or equal to 3, μ can be related to the mass fractal dimension of the scatter (D): $\mu = D$.[7—10)]

μ can be obtained from the slope of double logarithmic plot of $I(s)$ vs. s (Porod plot). Figure 3 shows typical examples of Porod plots for NiB; the μ values obtained for each sample are plotted against t/t_g in Fig. 4. The μ values in the final stage are included in Table 1. The s ranges used to determine the final μ values of NiA, NiB, and FeA were 0.051—0.400, 0.062—0.400, and 0.125—0.400 Å^{-1}, respectively.

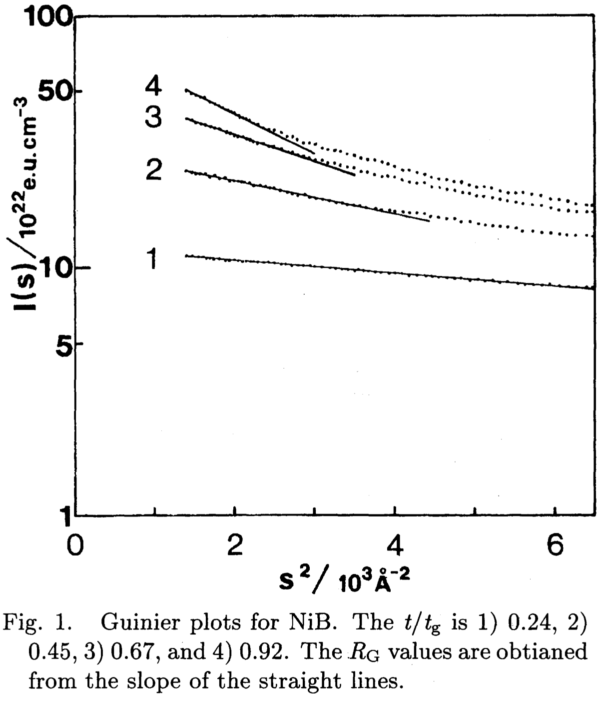


Fig. 1. Guinier plots for NiB. The t/t_g is 1) 0.24, 2) 0.45, 3) 0.67, and 4) 0.92. The R_G values are obtianed from the slope of the straight lines.

Discussion

The purpose of the present study was twofold; to determine the effects of added metals on the growth of silicate polymers, and to correlate the structure of the formed gel with the metal size and metal size distribution of the resultant catalyst.

Several SAXS studies have been reported concerning the growth of TEOS and TMOS (tetramethoxysilane) polymers under various pH and concentration ranges.[8—10)] All of the studies agree in that R_G increases with time, reaching a constant value at the later stage of gelation. R_G values of 20—200 Å have been reported, depending upon the conditions employed.[8,9)] μ is always close to 2 over a wide pH range ($0.65 < \mathrm{pH} < 8.2$),

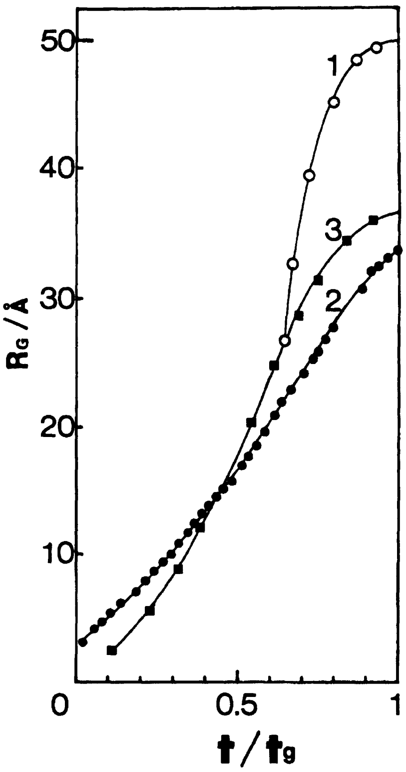


Fig. 2. R_G values plotted against t/t_g: 1) NiA, 2) NiB, and 3) FeA.

Table 1. SAXS Parameters of Metal Silicate Polymers in the Final Stage

Sample	Guinier radius R_G/Å	Porod slope μ
NiA	50.1	1.61
NiB	33.6	1.50
FeA	36.2	1.27

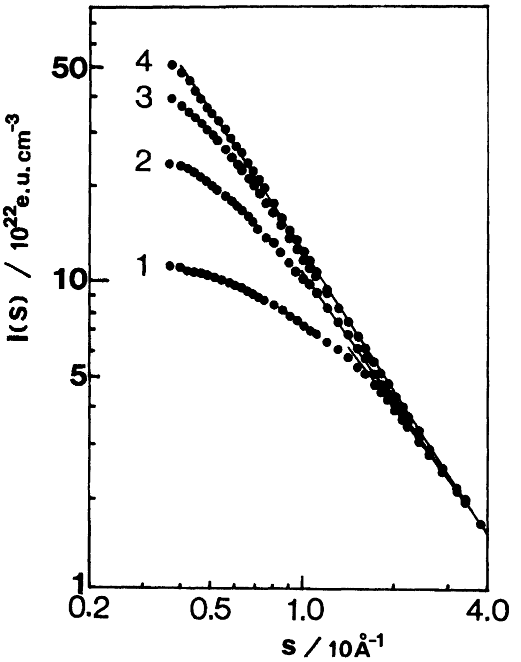


Fig. 3. Porod plots for several data of NiB. The t/t_g is 1) 0.24, 2) 0.45, 3) 0.67, and 4) 0.92. The μ values are obtained from the slope of the straight lines.

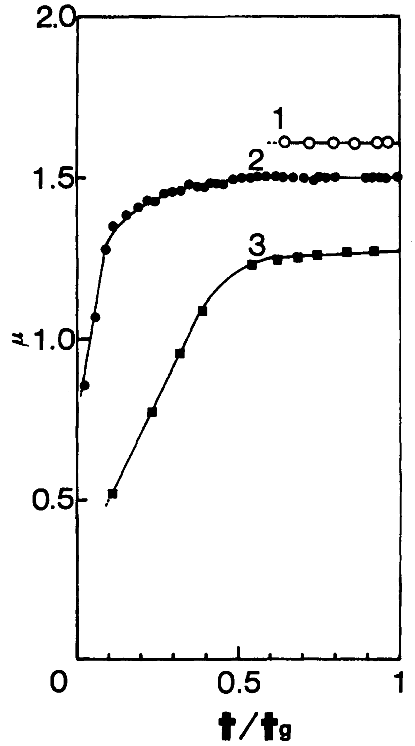


Fig. 4. μ values plotted against t/t_g: 1) NiA, 2) NiB, and 3) FeA.

and shows no marked change during growth.[8—10] From this value the lattice animal model or the randomly branched analog of self-avoiding linear chains model has been proposed for the resultant polymers.[9]

In this study the R_G shown in Fig. 2 increases with time, as is expected. The R_G values at the final stage of gelation largely depend not only on the pH employed, but also on the metal species added. The R_G values of NiA, NiB, and FeA are about 50, 34, and 36 Å, respectively. This indicates that the gels comprise clusters of several decades Å. μ also increases with time during the early stage of gelation, reaching a constant value while R_G is still increasing; in the later stage the growth of the polymers proceeds without any fractal geometry changes. The major difference between the polymers grown with/without metal lies in the final value of μ. Since μ corresponds to the fractal geometry and is considerably smaller than 2 for every sample studied here (Table 1), polymers grown with metal have a tendency to be close to a linear chain, or less well-branched. Thus, the growth of polymers occurs primarily at the tips of the clusters. This may be because the inclusion of metal atoms (expressed in Eq. 1) truncates the growth of the tetrahedral network of SiO_2.

Catalysts with small metal particles with a uniform size distribution can be prepared by the alkoxide method; a homogeneous dispersion of metal atoms in the precursor gel is assumed to be the reason for this.[2—6] Because R_G and μ of NiA are larger than those of NiB, clusters in the gel of NiA are larger and more highly branched. It is natural to expect that large/small metal particles are formed in catalysts prepared by calcining and reducing the gel containing large/small clusters. Electron microscope pictures of the catalysts prepared from NiA and NiB showed that although metal particles are fairly homogeneous, they are too small for a precise evaluation of the sizes and size distributions. Accordingly, hydrogen adsorption combined with a magnetization measurement was carried out in order to determine the average size of the metal particles. It was found that, assuming a cubic shape, the average size in side is larger for a catalyst prepared from NiA (80 Å) than that for one prepared from NiB(40 Å), as is expected. However, the metal particle size distribution of a catalyst prepared from FeA is much broader and the average size much larger,[5] even though the R_G value of FeA is almost the same as that of NiB.

Conclusion

The geometric structure of the silicate polymers is significantly influenced by the presence of metal 1,2-ethanediolates. The resultant gels have smaller μ values, indicating that the polymers are less well-branched than those grown without metal. Apparently, catalysts with smaller metal particles can be prepared from gels with a smaller R_G value.

We thank Dr. T. Mizushima at Toyohashi University of Technology for his advice in preparation of samples, electron microscope photography, and the hydrogen adsorption measurements.

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