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แต่ยังอยู่ในภาวะรอการพิจารณาการลงตีพิมพ์

## Preparation of Ni/SiO<sub>2</sub> Catalysts Using Microemulsion and TEOS Hydrolysis

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### Abstract

Ni/SiO<sub>2</sub> catalysts were prepared by synthesizing Ni-hydrazine complex nanoparticles inside the water pools of water-in-oil microemulsion consisting of water, 1-hexanol, and a non-ionic surfactant Brij-35, and then immobilizing them onto SiO<sub>2</sub> support formed via the hydrolysis of tetraethyl orthosilicate (TEOS). After that, the precipitate was washed, calcined and reduced, and consequently a Ni/SiO<sub>2</sub> catalyst was obtained. The TEM photograph of the catalyst showed small and uniform Ni particles dispersed over small rod-like SiO<sub>2</sub> particles when the molar ratio of water to surfactant (the w/s value) was 6 and the Ni content in the catalyst was around 1 wt%. It was found that when the water amount of the mixture in the stage of microemulsion formation was increased, the morphology of Ni/SiO<sub>2</sub> catalyst changed. The effect of water amount to the morphology of Ni/SiO<sub>2</sub> catalyst is discussed. It was found also that if the Ni amount inside the micelles increased when the w/s was fixed, the probability for the observation of relatively large Ni clusters in the catalyst also increased.

*Keywords:* A. Nanostructures, B. Sol-gel chemistry, C. Electron Microscopy

### 1. Introduction

In recent years, there is drastic increase in attention to the synthesis of nanoparticles in water-in-oil (w/o) microemulsion. The synthesized particles include both metal nanoparticles [1-4] and metal compound nanoparticles [5-7]. This is because nanomaterials are expected to be utilized in various ways [8-9]. From catalysis point of view, many catalysts have been prepared using microemulsion [10-19]. During the synthesis of these catalysts, there were different types of metal (i.e., water-soluble metal complex or insoluble metal compound) which were confined in the water pool of microemulsion, and also there are various ways in immobilizing them onto a support. Therefore there are quite many methods in catalyst preparation using microemulsion. The immobilization processes can be summarized as follows.

The first one is to use the microemulsion, inside which metal ions are confined in the micelles, with a support in impregnation process [10].

The second one is to add a support to the microemulsion having metal ions or metal or metal compound nanoparticles inside the water pools, and let the adsorption of those ions or nanoparticles onto the support occur [11-12].

The third one is to synthesize metal ions or metal compound nanoparticles in the water pools of microemulsion, and then immobilizing them onto a support synthesized in-situ by the hydrolysis of metal alkoxide, the starting material of metal oxide support [13-19].

To avoid confusion, in this paper we will use the terms "ME-impregnation", "ME-adsorption", and "ME-alkoxide" methods, respectively, to describe the above-mentioned three microemulsion-assisting catalyst preparation methods.

The ME-impregnation method has a strong point in that, many parts of metal particles in a prepared catalyst locate outside the pores of the support, which make the catalyst very suitable for a particular reaction such as combustion [10].

The ME-adsorption method is, among the above-mentioned three methods, appeared first in the literatures. Many catalysts have been synthesized using this technique [11-12]. This catalyst preparation method resulted in catalysts having metal nanoparticles with a narrow size distribution [12].

The ME-alkoxide method was developed by Kishida et al. recently [13]. He and his colleagues in Wakabayashi's group used this method to prepare many catalysts and reported that besides the narrow size distribution of metal nanoparticles [14], the catalysts prepared in this way exhibited other characteristic features. They found that their catalysts have very strong interaction between metal particles and support [15]. Besides, the metal particles in the catalysts have high resistance to sintering [16]. Moreover, they found that in many cases the catalysts prepared in this way exhibited higher catalytic activities than conventional impregnation catalysts [13, 16-19].

Due to the interesting characteristic features of the catalysts prepared from the ME-alkoxide method, in this paper we report the investigation of the synthesis of Ni/SiO<sub>2</sub> catalysts by the ME-alkoxide method. The results obtained showed that a Ni/SiO<sub>2</sub> catalyst with small and uniform Ni size could be obtained by this method, and when the water amount in the stage of microemulsion formation increased, the morphology of the Ni/SiO<sub>2</sub> catalyst changed completely.

## 2. Experimental

### 2.1 Catalyst preparation

Water-in-oil microemulsion containing Ni ions in its micelles was prepared by adding 2.556 ml of 0.4 mol/l NiCl<sub>2</sub> aqueous solution into a 47.33 ml solution of 0.5

mol/l of polyoxyethylene dodecyl ether (Brij-35) in 1-hexanol. After that 247.87  $\mu$ l of hydrazine hydrate was added so that Ni-hydrazine complex was synthesized. Then 37.51 ml of tetraethyl orthosilicate (TEOS), the starting material of  $\text{SiO}_2$ , was added to the mixture with 8 ml of water, and then TEOS was hydrolyzed to  $\text{SiO}_2$  for 2 h. The precipitate was washed with 2-propanol three times before dried overnight and then calcined in air flow at 550°C for 1 h before reduced in hydrogen flow at 450°C for 1 h. The resulted catalyst is denoted as Cat. 1. Ni/ $\text{SiO}_2$  catalysts with different Ni loadings from Cat. 1 were prepared either by changing the amount or the concentration of the  $\text{NiCl}_2$  aqueous solution.

## 2.2 TEM observation

TEM photographs of the catalysts were obtained using a JEOL JEM 2010 transmission electron microscope with a LaB6 filament as the source of electrons operated at 200 kV. Samples were mounted on a carbon coated microgrid supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid followed by drying at room temperature.

## 3. Results

Fig.1 shows the TEM photograph of Cat. 1. In this case, the molar ratio between water and Brij-35 (the w/s value) of 6 was employed in the preparation, and the Ni content in the catalyst was around 1 wt%. It can be observed that the catalyst contained small rod-like  $\text{SiO}_2$  particles. For Ni particles, only some of them were seen spreading over the  $\text{SiO}_2$  particles, due to their small size.

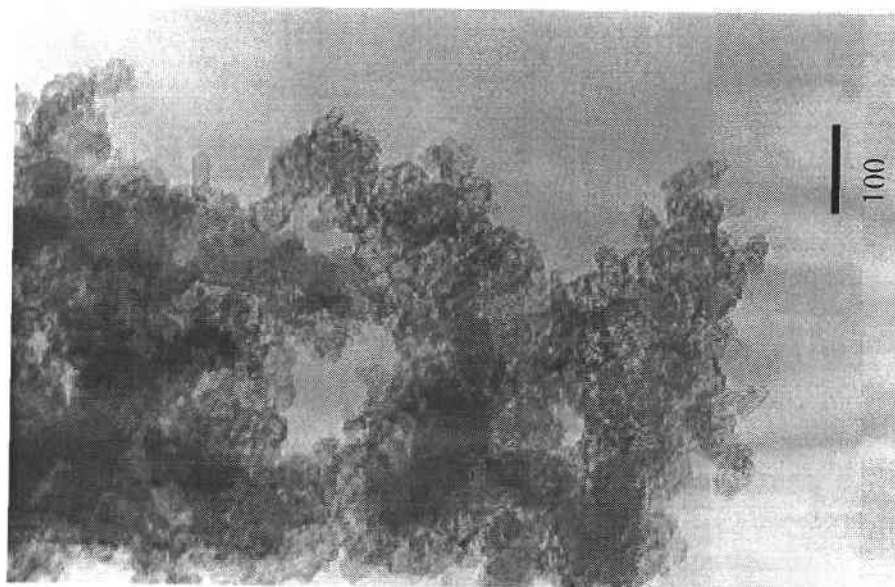
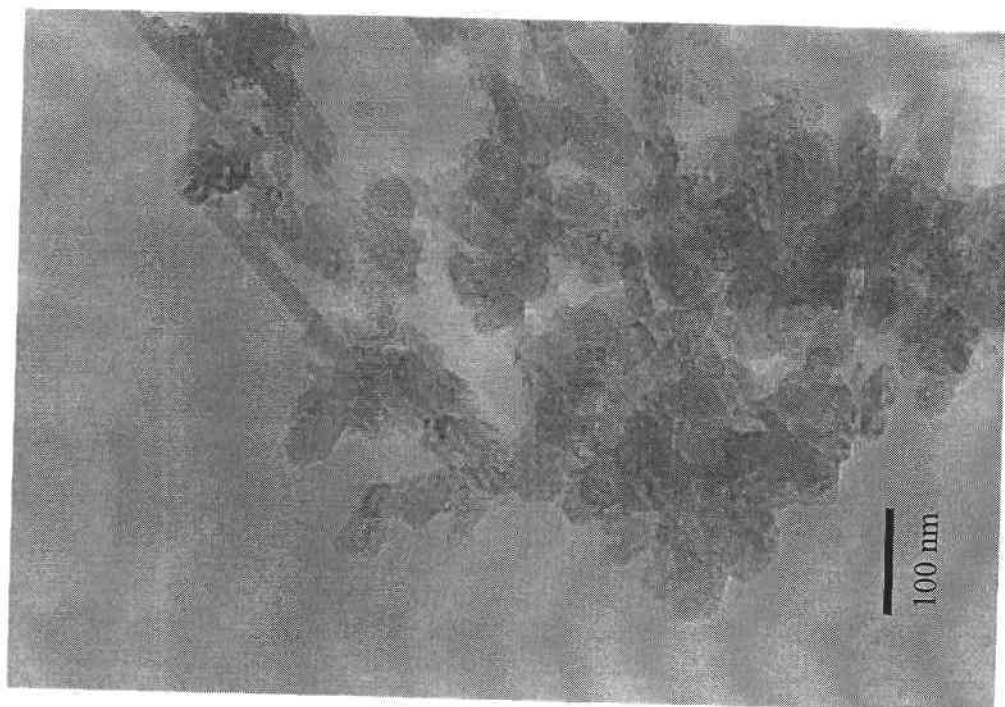
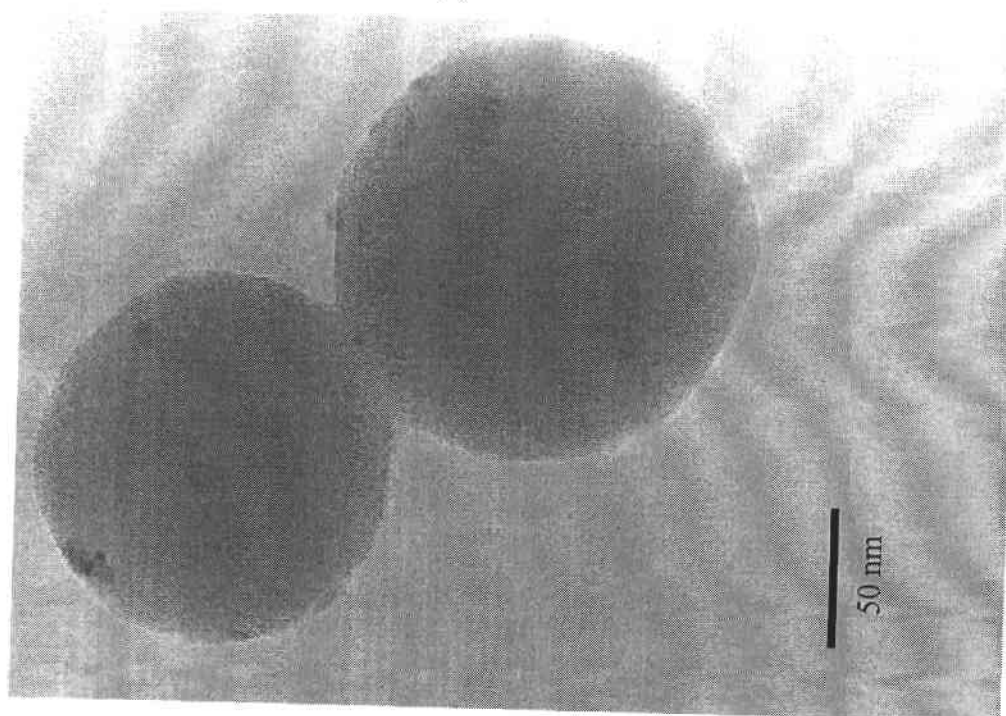


Fig. 1 TEM photograph of the Ni 1 wt% Ni/ $\text{SiO}_2$  catalyst (Cat. 1) prepared by the ME-alkoxide method using w/s value of 6.

In order to increase the Ni content in the catalyst so that the Ni nanoparticles could be seen more clearly, the amount of the  $\text{NiCl}_2$  solution used in the microemulsion was increased to 2 times and 5 times. It was found that the morphology of the obtained  $\text{Ni/SiO}_2$  catalysts changed completely from that shown in Fig. 1. These results are shown in Fig.2 a-c for the catalyst prepared with 2 times Ni solution amount, and in Fig.3 a-c for the catalyst prepared with 5 times Ni solution amount.



(a)



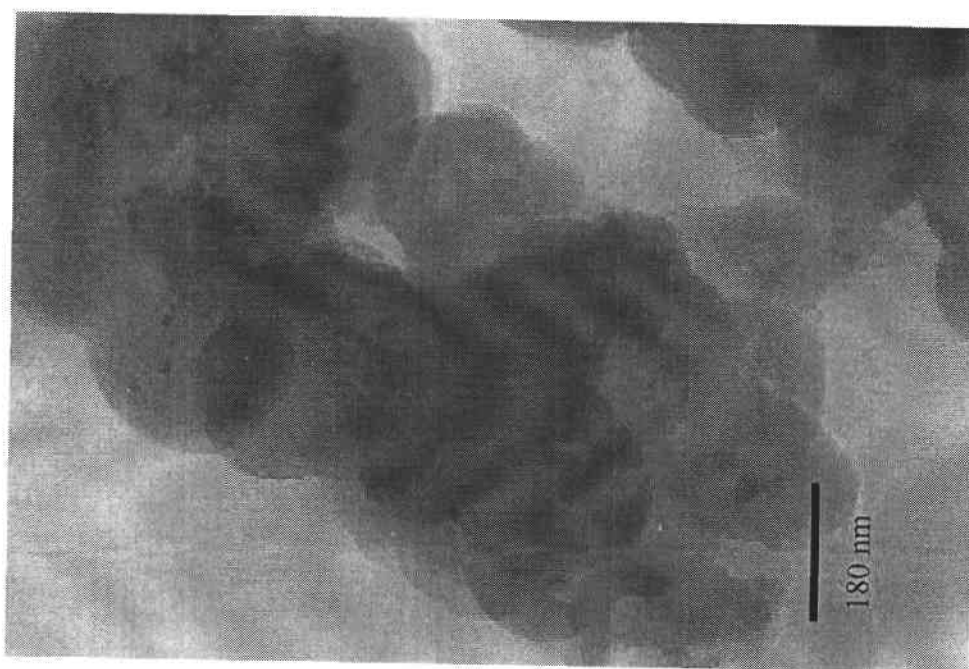
(b)



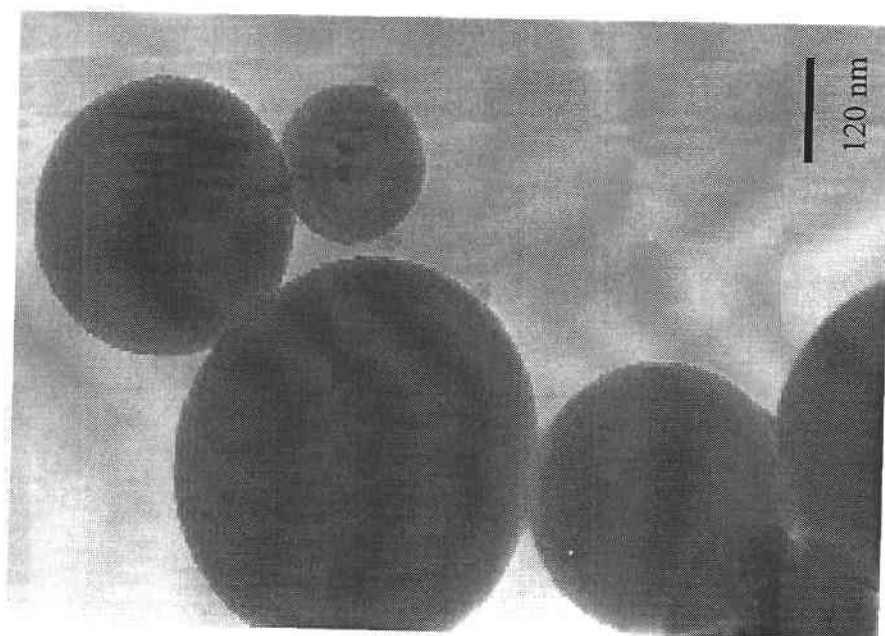
(c)

Fig. 2 TEM photographs of the Ni/SiO<sub>2</sub> catalyst prepared by using the amount of NiCl<sub>2</sub> solution two times as compared to that of Cat.1 shown in Fig. 1. (a)-(c) indicate different parts of the catalyst.

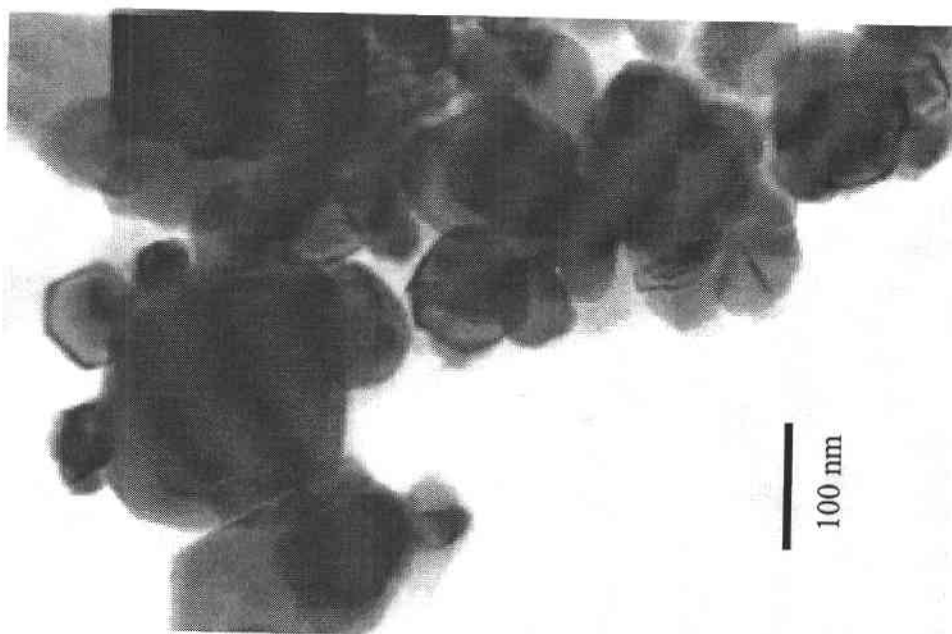
When the amount of NiCl<sub>2</sub> solution was increased to two times, most part of the obtained catalyst had a morphology as shown in Fig. 2a or Fig. 2b. That is, there were parts in the catalyst that the SiO<sub>2</sub> had a rod shape, and parts where SiO<sub>2</sub> were spherical particles. Ni nanoparticles spread in these SiO<sub>2</sub> particles. However, as indicated in Fig. 2c, there were few parts in the catalyst that Ni clusters (as large as 50 nm) were observed also.



(a)



(b)



(c)

Fig. 3 TEM photographs of the Ni/SiO<sub>2</sub> catalyst prepared by using the amount of NiCl<sub>2</sub> solution five times as compared to that of Cat.1 shown in Fig. 1. (a)-(c) indicate different parts of the catalyst.

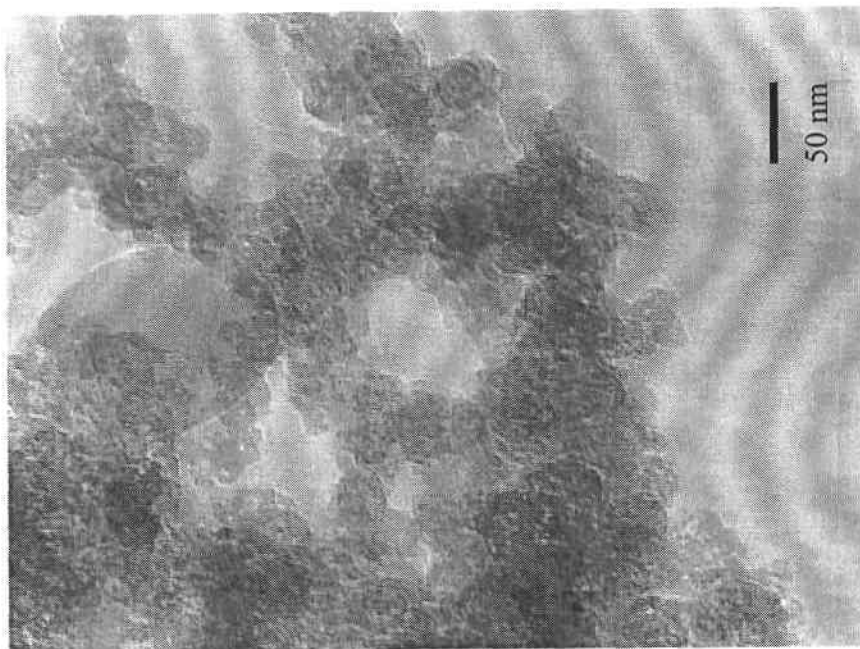
When the amount of NiCl<sub>2</sub> solution was increased to five times, the rod-shape SiO<sub>2</sub> disappeared. That is, some SiO<sub>2</sub> particles were bulk SiO<sub>2</sub> or agglomerated SiO<sub>2</sub>, like that seen in Fig. 3a, while other SiO<sub>2</sub> particles were spherical ones inside which there were some Ni nanoparticles observed, like that seen in Fig. 3b. Moreover, as shown in Fig. 3c, the size of Ni clusters observed in the catalyst became larger (some were larger than 100 nm).

#### 4. Discussion

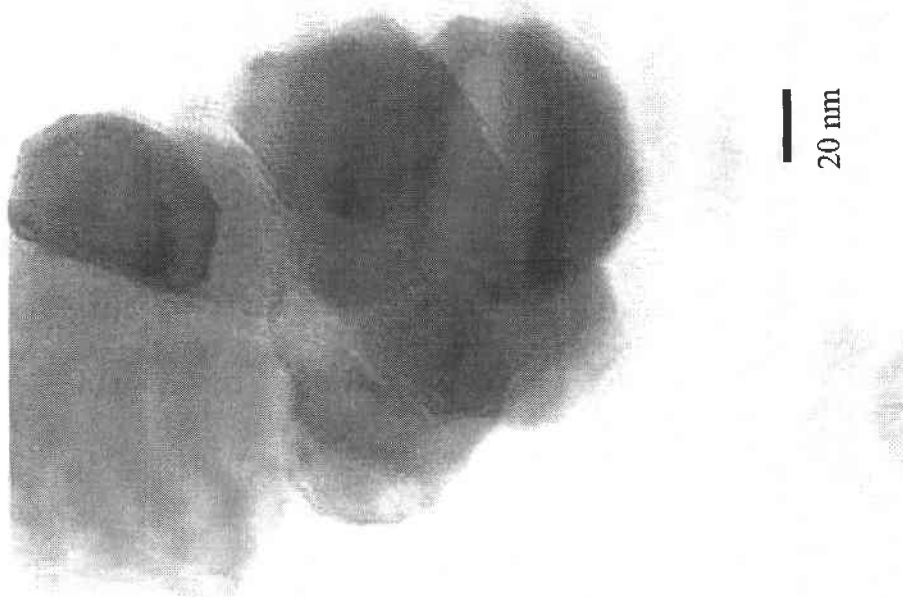
##### 4.1 Confirmation for the cause in the change in catalyst morphology



The difference in catalyst morphology among Figs. 1-3 occurred when the amount of  $\text{NiCl}_2$  solution was varied. When the amount of Ni solution was changed, both Ni amount and water amount in the stage of microemulsion formation were also altered. To investigate each effect, firstly we prepared a catalyst having a Ni content 2.5 times of that of Cat. 1. This was done by performing a preparation procedure like that of Cat. 1 except that 1.0 M  $\text{NiCl}_2$  solution was employed instead of 0.4 M  $\text{NiCl}_2$  solution. The TEM photographs of this catalyst are shown in Fig. 4 a-b.



(a)



(b)

Fig. 4 TEM photographs of the Ni/SiO<sub>2</sub> catalyst prepared by using the concentration of NiCl<sub>2</sub> solution 2.5 times as compared to that of Cat.1 shown in Fig. 1. (a) and (b) indicate different parts of the catalyst.

It can be seen clearly from Fig. 4a that the catalyst prepared in this way had the same morphology as that of the one shown in Fig. 1. There were also, as shown in Fig. 4b, few Ni clusters like those observed in the samples shown in Figs 2c and 3c. The sizes of these Ni clusters were as large as 60 nm. Therefore, it can be said that the Ni amount is not a factor to the change in the morphology of Ni/SiO<sub>2</sub> catalyst prepared by the ME-alkoxide method. Nevertheless, when the amount of Ni ions inside the water pools of the microemulsion increased, the probability of finding large and more Ni clusters also increased. This explanation can also explain the Ni clusters shown in Figs. 2c and 3c. These Ni clusters are considered to be formed through the sintering of small Ni particles in the stages of calcination and reduction in the catalyst preparation.

On the other hand, as the amount of the solution changed, the molar ratio of water to Brij-35 (the w/s value) also changed. When the amount of NiCl<sub>2</sub> solution was changed to 2 times and 5 times of that of Cat.1, the w/s of the mixture before TEOS was added were 12 and 30, respectively.

#### 4.2 Investigation for the microemulsion region

As there was some possibility that when too much w/s values were employed, the mixtures were no longer microemulsion, we then investigated the extent of the microemulsion region by adding different amount of 0.4 M Ni solution into fixed amount of the mixture between Brij-35 and 1-hexanol. The result is shown in Fig.5.

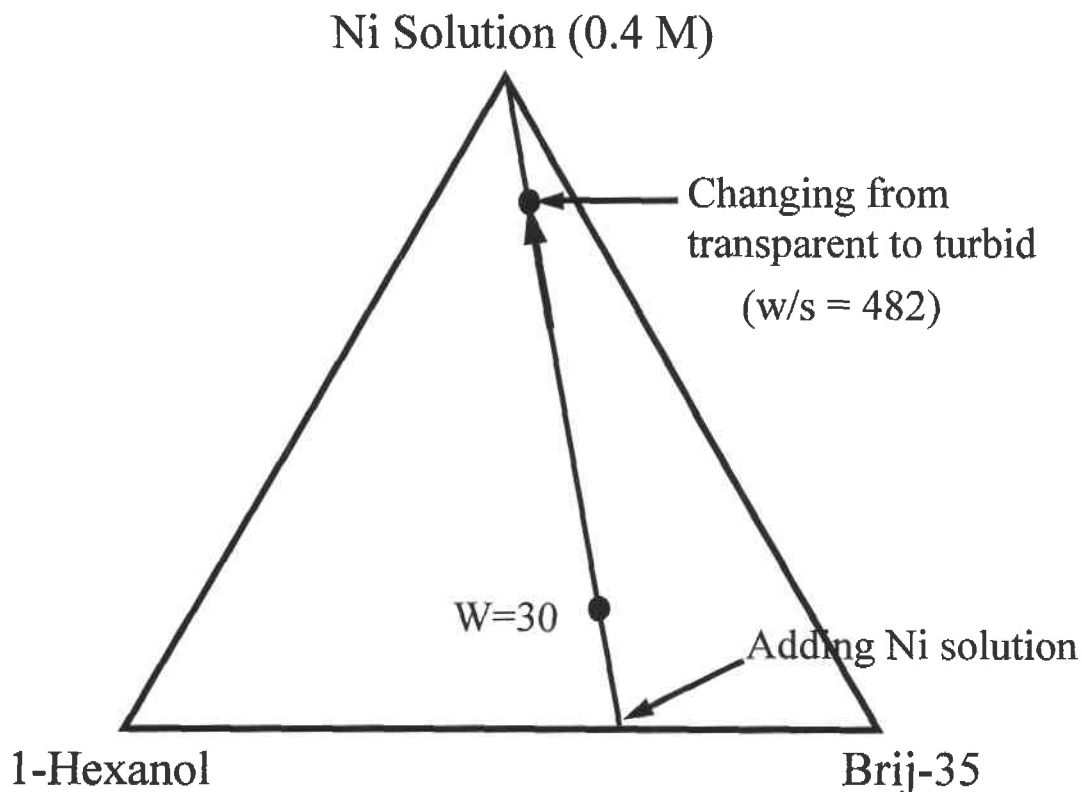


Fig. 5 Transparent and turbid zones when the amount of the mixture between Brij-35 and 1-hexanol was fixed and the amount of 0.4 M Ni solution was varied.



It is clear from Fig. 5 that even the amounts of the Ni solution was changed in the experiment, in all cases the mixtures were microemulsion. Moreover, even water added later (along with TEOS) was calculated in the system, the mixtures were still microemulsion.

### 4.3 Mechanism for the formation of catalysts with different morphology

When the w/s was changed, the concentration of surfactant molecules per a water pool decreased. Therefore, the capacity of the micelles in stabilizing the particles inside the water pools also decreased. This should have resulted in two ways. On one way, the particles still could stay inside the micelles. In this case, they would contact or agglomerate with other particles in other micelles more easily. On the other way, the particles inside the micelles could not stay in the micelles any longer, and thus went out of the micelles. We believe that these would result in different morphology of the catalysts, as illustrated in Fig. 6, and as can be explained in the next paragraphs.

That is, when the w/s was low (6), the SiO<sub>2</sub> particles formed from TEOS hydrolysis grew bigger by using the Ni-hydrazine complex nanoparticles inside micelles as the seeds for their growth. Since the size of each SiO<sub>2</sub> particle was limited by the size of the water pool confining it, each SiO<sub>2</sub> particle was small and had its shape similar to the micelles. Therefore, small rod-like SiO<sub>2</sub> particles were obtained, as can be seen in Figs. 1 and 4.

When a much higher w/s value (30) was employed, on one hand if Ni-hydrazine complex nanoparticles still could stay inside the micelles, the SiO<sub>2</sub> particles containing Ni-hydrazine complex nanoparticles inside micelles would contact with other SiO<sub>2</sub> particles in other micelles more easily. Therefore, a catalyst having agglomerated-SiO<sub>2</sub> morphology would be obtained, as can be seen in Fig. 3a.

On the other hand, if Ni-hydrazine complex nanoparticles could not stay inside micelles any longer, as the growth of SiO<sub>2</sub> particles used Ni-hydrazine nanoparticles as their seeds, SiO<sub>2</sub> particles then grew bigger outside the micelles. Since in the system, there should be many long micelles swinging around, SiO<sub>2</sub> particles would grow bigger in all directions while the agglomeration among them should be limited to some extent. Therefore, spherical SiO<sub>2</sub> particles having some Ni nanoparticles inside were obtained, as can be seen in Figs. 2b and 3b.

We note here that at an intermediate w/s value (12), the morphology with rod-like SiO<sub>2</sub> particles and the morphology with spherical SiO<sub>2</sub> particles were both observed (Figs. 2a and 2b). The SiO<sub>2</sub> rods became longer than the ones seen in Figs. 1 or 4 because the microemulsion having much water was employed in the preparation.

## 5. Conclusion

When the w/s of 6 was employed, the preparation of Ni/SiO<sub>2</sub> by the ME-alkoxide method resulted in a catalyst having small and quite uniform Ni nanoparticles dispersed on small rod-shape SiO<sub>2</sub> particles. However, when the w/s was increased, the capacity of the micelles in stabilizing the materials inside decreased. Therefore, catalysts with different morphologies were obtained. Moreover, when the Ni content of the catalyst was increased, the probability in finding Ni clusters in the catalysts also increased.

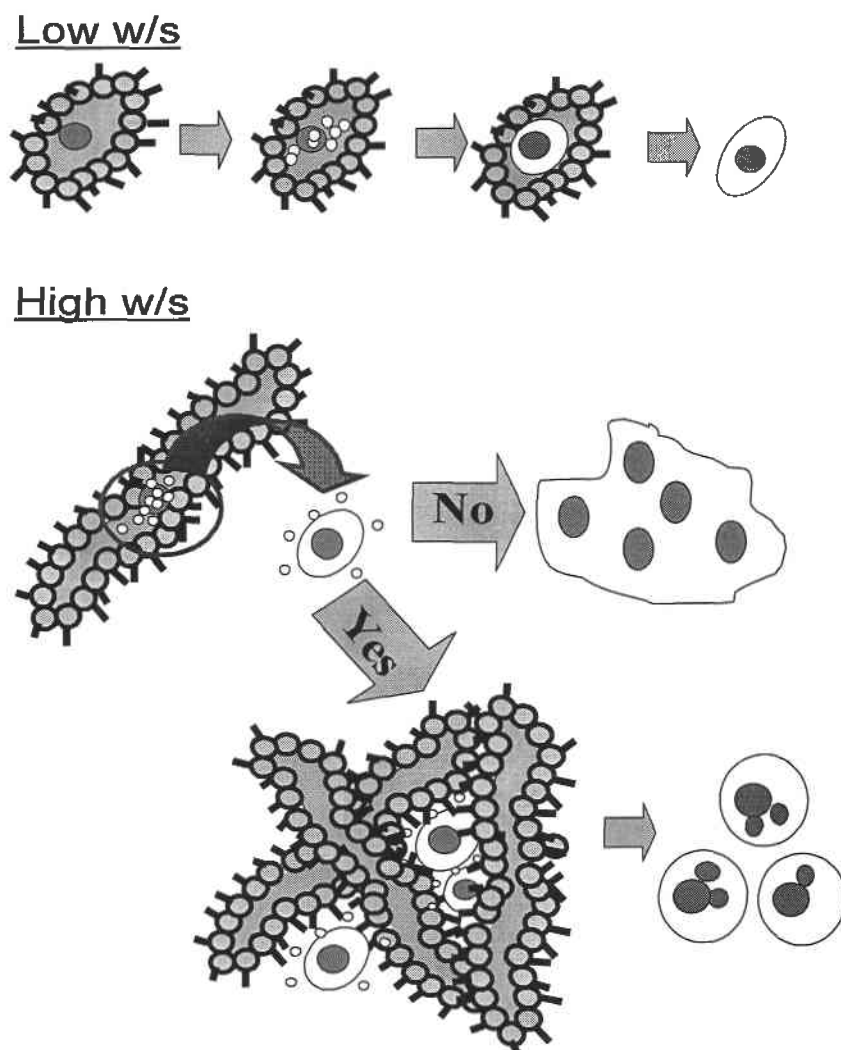


Fig. 6 The proposed mechanisms for the formation of  $\text{SiO}_2$  when different w/s values were employed in the preparation.

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