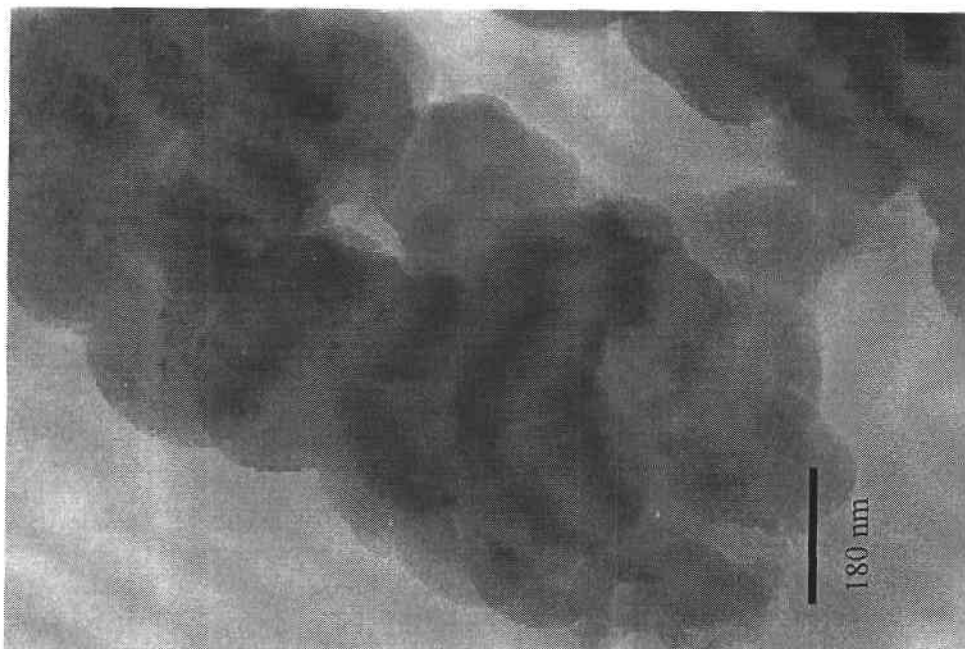
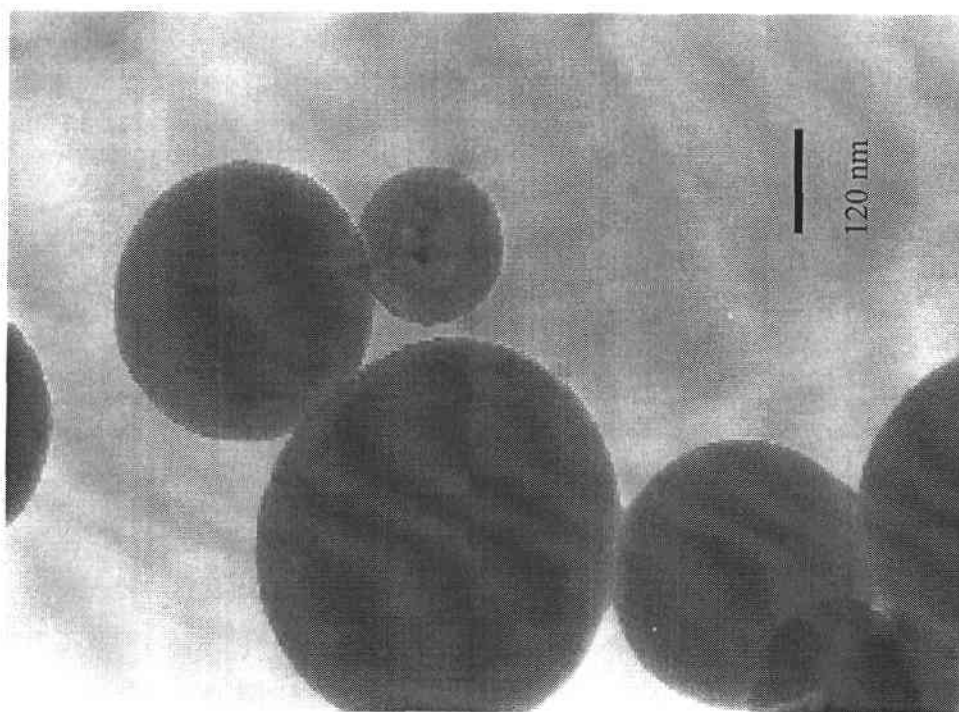


in the system there were many long micelles swinging, which acted as barriers for the agglomeration of  $\text{SiO}_2$  particles, each  $\text{SiO}_2$  particle therefore became bigger with relatively little agglomeration. Consequently, a catalyst with morphology like that in Fig. 4b was obtained.



(a)



(b)

Fig. 4 TEM photographs of the  $\text{Ni/SiO}_2$  catalyst prepared using Brij-35 as a surfactant and hydrazine as a complex-forming reagent when the w/s value of 30 was employed and only water was used in TEOS hydrolysis. (a) and (b) indicate different parts of the catalyst.

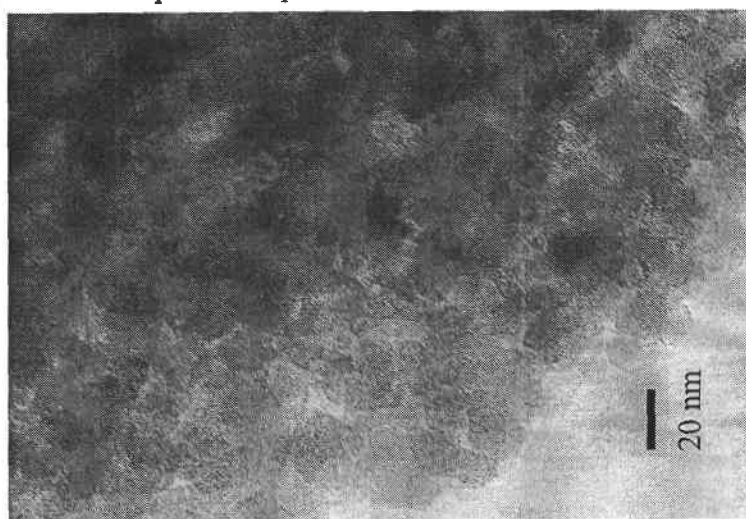
When comparing Fig. 3 with Fig. 1, it is observed that when some  $\text{NH}_3$  was also used to promote the TEOS hydrolysis, the morphology of the resulted catalyst changed from the one having rod-like  $\text{SiO}_2$  particles to the one with agglomerated- $\text{SiO}_2$  particles, like that when the w/s value was raised higher as mentioned above. Therefore, the key factor for the change in catalyst morphology in this case should be the change in the stabilization power of micelles in the microemulsion also. It is considered that the larger size of  $\text{NH}_4^+$  from  $\text{NH}_4\text{OH}$  solution than  $\text{H}^+$  of water, was the reason for the decrease in the stabilization power of the micelles because this would result in the larger size of water pools in the microemulsion while the amount of surfactant molecules remained the same.

#### 4.2 Concerning the EDA-Ni/SiO<sub>2</sub> and DCPD-Ni/SiO<sub>2</sub> catalysts

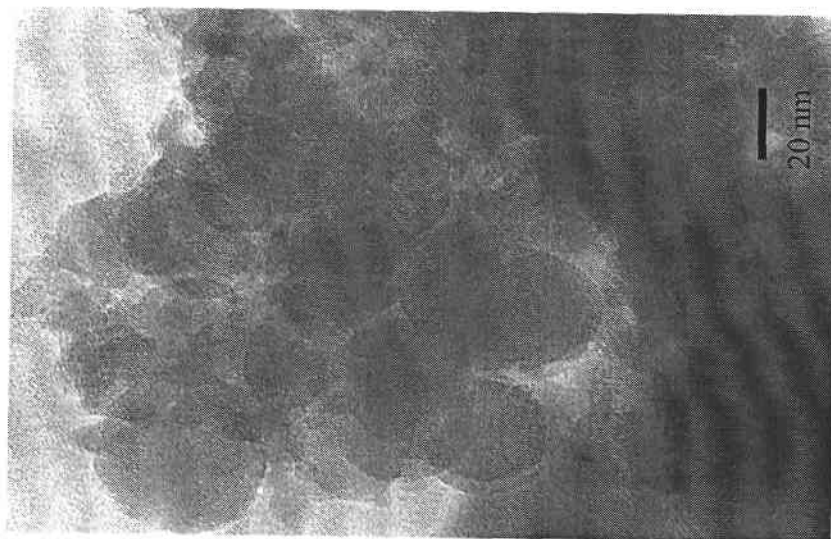
From Figs. 2 and 4b, it can be seen that both EDA-Ni/SiO<sub>2</sub> catalyst and DCPD-Ni/SiO<sub>2</sub> catalyst had their morphology similar to the one with spherical SiO<sub>2</sub> particles observed in some parts of the catalyst prepared using a high w/s value in the stage of microemulsion formation. Therefore, according to the discussion explained in Section 4.1, it seems reasonable to think that some Ni-ethylenediamine or Ni-dicyclopentadiene complex nanoparticles went out of the micelles and acted as the seeds for the SiO<sub>2</sub> growth as in the case of the catalyst shown in Fig. 4b. This is considered to be because they were too large or too heavy to stay inside the micelles.

Nevertheless, there may be some possibility that the Ni-ethylenediamine or Ni-dicyclopentadiene complex nanoparticles had nothing to do with the formation of spherical SiO<sub>2</sub> particles, i.e., spherical SiO<sub>2</sub> particles might have formed inside micelles having their shapes altered from rod-like to spherical ones due to the presence of ethylenediamine or dicyclopentadiene. We then prepared two catalysts by exactly the same preparation methods of EDA-Ni/SiO<sub>2</sub> and DCPD-Ni/SiO<sub>2</sub> catalysts except that in these cases water was used instead of 0.4 M NiCl<sub>2</sub> solution. Therefore, there was no Ni in these catalysts, which are denoted as EDA-SiO<sub>2</sub> and DCPD-SiO<sub>2</sub> catalysts respectively.

Fig. 5 shows the TEM photographs of the EDA-SiO<sub>2</sub> and DCPD-SiO<sub>2</sub> catalysts. These pictures revealed that these catalysts had the agglomerated-SiO<sub>2</sub> morphology. Therefore it can be concluded that the spherical-SiO<sub>2</sub> morphology for the EDA-SiO<sub>2</sub> and DCPD-SiO<sub>2</sub> catalysts stemmed from the formation of Ni-ethylenediamine and the Ni-dicyclopentadiene complex nanoparticles as described earlier.



(a)



(b)

Fig. 5 TEM photographs of (a) EDA-SiO<sub>2</sub> catalyst and (b) DCPD-SiO<sub>2</sub> catalyst.

#### 4.3 *The important role of hydrazine*

Fig.6 shows the TEM photograph of No-Reagents-Ni/SiO<sub>2</sub> catalyst, which is the catalyst prepared by exactly the same way as the catalysts shown in Figs. 1 and 2 except that in this case no complex-forming reagents was added in the preparation.

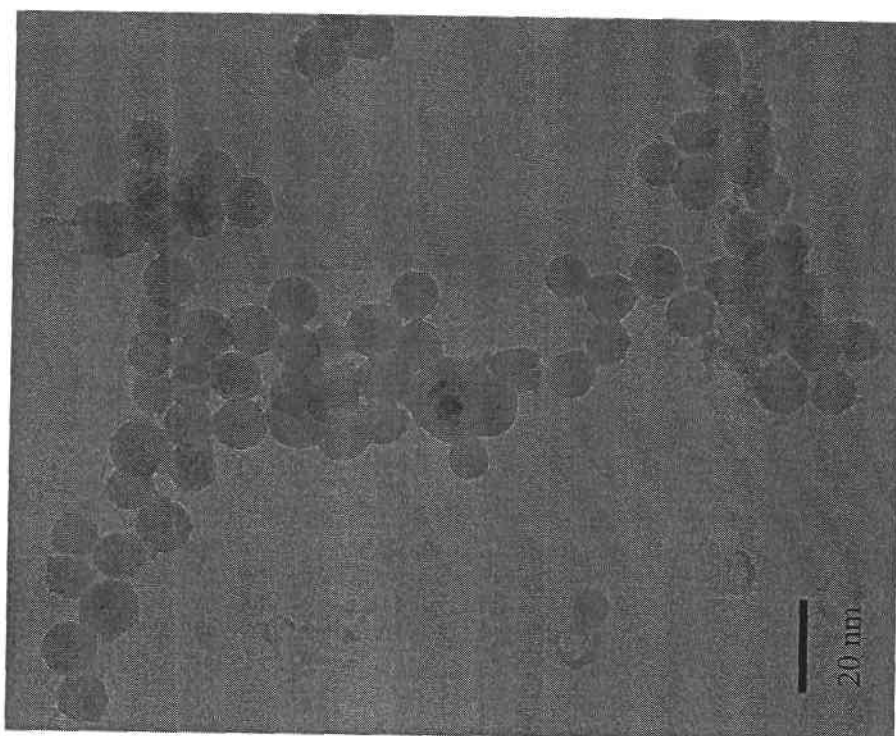


Fig. 6 TEM photograph of No-Reagents-Ni/SiO<sub>2</sub> catalyst.

Even though no reagents was used in the preparation and thus there could not be any Ni-complex nanoparticles formed inside micelles of microemulsion, a catalyst with spherical-SiO<sub>2</sub> morphology was obtained like in the cases when large complex-forming reagents were employed as shown in Fig. 2. It is considered that for the No-Reagents-Ni/SiO<sub>2</sub> catalyst, because Ni ions did not form complex with any reagents and thus stayed freely inside the micelles of microemulsion, they therefore could react easily with OH<sup>-</sup> induced by NH<sub>3</sub>. Consequently Ni(OH)<sub>2</sub> clusters were formed, which then went out of the micelles and later became nuclei for the formation of spherical SiO<sub>2</sub> particles.

When hydrazine was used as a complex-forming reagent, a catalyst with rod-shape SiO<sub>2</sub> morphology was obtained, i.e., there was no Ni complexes or compounds that went out of the micelles. It therefore can be concluded that hydrazine played a very important role in confining all Ni ions to stay inside the micelles through the formation of Ni-hydrazine complex nanoparticles.

## 5. Conclusion

Hydrazine played an important role as a complex-forming reagent in the preparation of Ni/SiO<sub>2</sub> catalyst by the ME-alkoxide method. When hydrazine was employed in the preparation, a catalyst with agglomerated SiO<sub>2</sub> was obtained. However, either when the complex-forming reagent was changed to ethylenediamine or dicyclopentadiene, or when no complex-forming reagents were employed at all, the morphology of the Ni/SiO<sub>2</sub> catalysts completely changed. This is considered to be because hydrazine could confine Ni ions to stay inside the micelles through the formation of Ni-hydrazine complex nanoparticles. When no reagents or larger reagents were employed, Ni(OH)<sub>2</sub> or Ni-reagent complex nanoparticles that were formed then went out of the micelles, resulting in catalysts with spherical SiO<sub>2</sub> particles.

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