CHEMISTRY LETTERS, pp. 1339 - 1342, 1984.

EFFECT OF PREPARATION VARIABLES ON MORPHOLOGICAL AND CATALYTIC PROPERTIES OF PRECIPITATED NICKEL-SILICA CATALYSTS

Yuriko NITTA, Teruo UTSUMI, Toshinobu IMANAKA, and Shiichiro TERANISHI*
Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

Composition of the precursors and its effect on the crystallinity of Ni-SiO_2 catalysts were studied using thermal gravimetry and X-ray diffraction measurement. The severer preparation conditions led to the lower proportion of $NiCO_3$ in the precursor. The mean crystallite size of Ni in H_2-reduced catalysts, and hence the activity and enantioselecivity of modified catalysts, were found to depend on the proportion of $NiCO_3$.

Precipitation of metal salts with sodium carbonate is one of the typical methods for the preparation of supported metal catalysts. Activity and selectivity of these precipitated catalysts are known to vary considerably by changes in preparation conditions, probably because of the change in composition of the precipitate(i.e., basic metal carbonate). In the preparation of Ni-SiO_2 catalyst for enantioselective hydrogenation of methyl acetoacetate(MAA), we have shown that almost all preparation variables affect the selectivity of the modified catalyst, and suggested a change in crystallite size distribution(CSD) of Ni in the catalyst with a change in preparation conditions.1) However, dependence of the CSD on the composition of the catalyst precursors and also dependence of the composition on preparation conditions still remain ambiguous. In the present study, we examined the chemical composition of various precursors of the Ni-SiO_2(1:1) catalysts by means of the differential thermal gravimetry(DTG). The X-ray diffraction(XRD) patterns of hydrogen-reduced catalysts were also measured in order to reveal the influence of preparation variables on the CSD of Ni in the catalysts.

The Ni-SiO_2(1:1) catalyst precursors were prepared by a precipitation method with Na_2CO_3 from aqueous $Ni(NO_3)_2$ solution suspended by silica gel. In preparing a standard sample precipitation was carried out at 75 °C by use of equimolar alkali with nickel salt, followed by aging for 15 min and washing three times with warm distilled water. Other details for the preparation of precursors were described elsewhere.1) The precipitate was dried at 50-120 °C for 20-45 h and reduced in a hydrogen stream of 8 l/h at 400 °C for 3 h. The reduced sample was modified with aqueous tartaric acid solution according to the method described by Izumi et al.2) and used for the hydrogenation of MAA.1) The optical yield(OY) of methyl 3-hydroxybutyrate(MHB) determined from the optical rotation of distilled product was employed as a measure of the selectivity of the catalyst. The XRD patterns of the catalysts were obtained with a Shimadzu VD-1 diffractometer after separation from the reaction mixture. The mean crystallie size ($\bar{D}_c$) of Ni was calculated from the half-width of the peak on (111) plane of Ni. The XRD patterns were also measured for the precursors calcined under N_2 at 400 °C for 2 h. The DTG measurements of catalyst precursors were carried out with a Shimadzu DT-30 thermal analyzer under N_2 flow in the range of ambient temperature to 600 °C at a heating rate of 5 K/min.

The DTG profiles of the standard precursors dried at various temperatures are shown in Fig. 1 together with the profiles of commercial nickel hydroxide, basic nickel carbonate, and silica gel. The peak around 70 °C corresponds to the weight loss based on the desorption of water adsorbed mainly on silica gel. The small peak around 150 °C is attributable to the water of crystallization. The dehydration of $Ni(OH)_2$ and the decarboxylation of $NiCO_3$ to nickel oxide are indicated by the peaks around 270 and 320 °C,

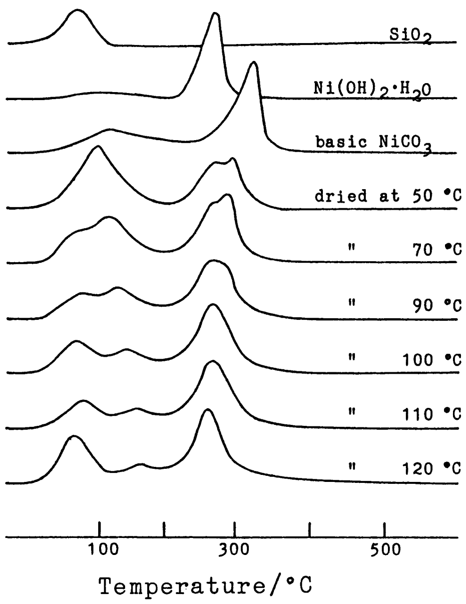

Fig. 1. DTG profiles of the Ni-SiO_2(1:1) catalyst precursors.

Table 1. Effect of preparation conditions on the composition of catalyst precursors

Run No.	Preparation conditions					$NiCO_3$ content^b) in precursor
	Ppt. temp	$\left[\frac{Ni}{Alkali}\right]^{a)}$	Aging time	Drying temp	Drying time	
	°C		min	°C	h	%
1	75	1.0	15	70	20	49
2	75	1.0	15	90	20	45
3	75	1.0	15	100	20	41
4	75	1.0	15	110	20	37
5	75	1.0	15	120	20	34
6	0	1.0	15	110	24	38
7	85	1.0	15	110	24	27
8	75	1.2	15	110	24	41
9	75	0.8	15	110	24	32
10	75	1.0	0	110	24	37
11	75	1.0	60	110	24	30
12c)	0	1.2	0	50	20	61
13d)	85	0.8	30	110	45	18

a) Molar ratio of nickel nitrate to sodium carbonate. b) Molar percentage of $NiCO_3$ in $aNi(OH)_2 \cdot bNiCO_3$. c) Precursor (A). d) Precursor (B).

respectively. The location of the peaks and the extent of weight loss corresponding to the peak around 300 °C showed that the proportion of $NiCO_3$ in the precursors decreases with increase in drying temperature. This is probably because the following reaction is accelerated by a rise in temperature.

$$a\mathrm{Ni(OH)_2 \cdot bNiCO_3 \cdot aq} + 2x\mathrm{H_2O} \longrightarrow (a+x)\mathrm{Ni(OH)_2 \cdot (b-x)NiCO_3 \cdot aq} + x\mathrm{H_2CO_3}$$

Here, the molar percentage of $NiCO_3$ in the basic nickel carbonate was quantitatively estimated from the weight loss in the range of 200 to 500 °C which corresponds to the reactions:[3] $NiCO_3 \rightarrow NiO_{1.2}$ and $Ni(OH)_2 \rightarrow NiO_{1.2}$. Similarly, increases in the amount of added alkali, precipitation temperature, and aging time were found to decrease the proportion of $NiCO_3$ as listed in Table 1: the severer preparation conditions resulted in the lower proportion of $NiCO_3$ in the precursor. This tendency is in harmony with that reported by Mallya and Murthy[4] for unsupported basic nickel carbonates.

Now the selection of preparation conditions made it possible to prepare precursors with desired percentage of $NiCO_3$. Two kinds of precursors, i.e., (A) $NiCO_3$ rich and (B) $Ni(OH)_2$ rich precursors, were prepared to examine the influence of the composition of precursors on the crystallinity of the calcined and/or hydrogen-reduced catalysts. As shown in Fig. 2a, the catalyst obtained from precursor (A) has large $\bar{D}_c$(16 nm) of Ni, whereas the catalyst obtained from precursor(B) has only low crystallinity($\bar{D}_c \leq 4$ nm). Figure 2b shows that the calcined precursors also have much different crystallinity from each other: precursor(A) produced nickel oxide with relatively large $\bar{D}_c$(6 nm) and precursor(B) led to almost amorphous nickel oxide. Moreover, subsequent reduction of these calcined precursors resulted in $Ni-SiO_2$ catalysts having quite similar XRD patterns to that shown in Fig. 2a. Therefore, the difference in $\bar{D}_c$ of Ni between the catalysts obtained from different precursors seems to be due to the difference in the crystallinity of nickel oxides which exist as intermediate products in the course of the reduction process.

Figure 3 shows that $\bar{D}_c$ of Ni in the hydrogen-reduced catalysts increases with an increase in the proportion of $NiCO_3$ in the precursors in accord with the decrease in metal surface area. On the other hand, the increase in the proportion of $NiCO_3$ means the decrease in $Ni(OH)_2$ loading on SiO_2 which will bring about a progressive decrease in the size of relatively small crystallites originating from $Ni(OH)_2$. Accordingly, a large proportion of $NiCO_3$ in the precursor will lead to a broad or a bimodal distribution of Ni crystallites in the reduced catalyst. The findings shown in Fig. 4 support this change in

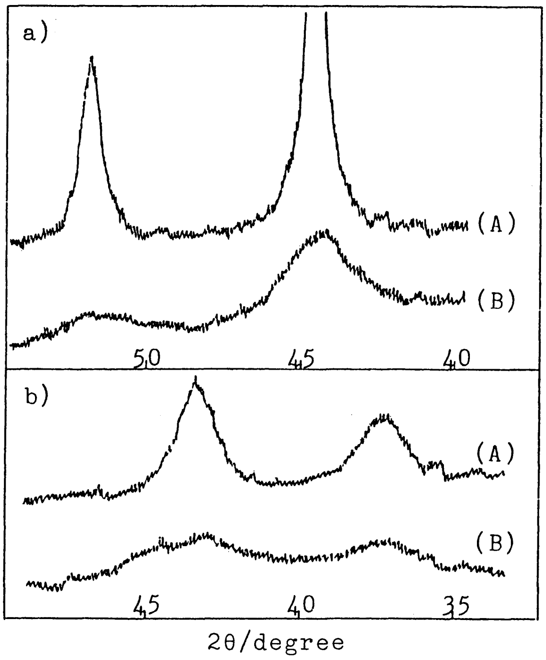

Fig. 2. XRD patterns for a) $Ni-SiO_2$ and b) NiO_x-SiO_2 obtained from (A) $NiCO_3$ rich and (B) $Ni(OH)_2$ rich precursors.

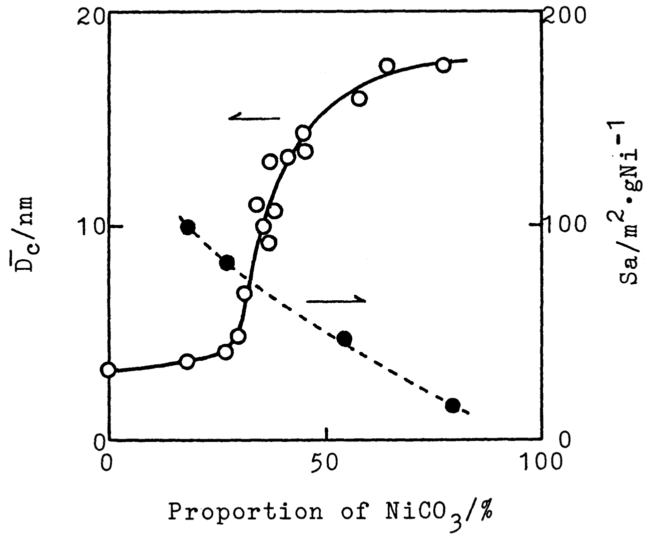

Fig. 3. Dependence of the mean crystallite size(○) and the surface area(●) of Ni metal on the composition of catalyst precursors.

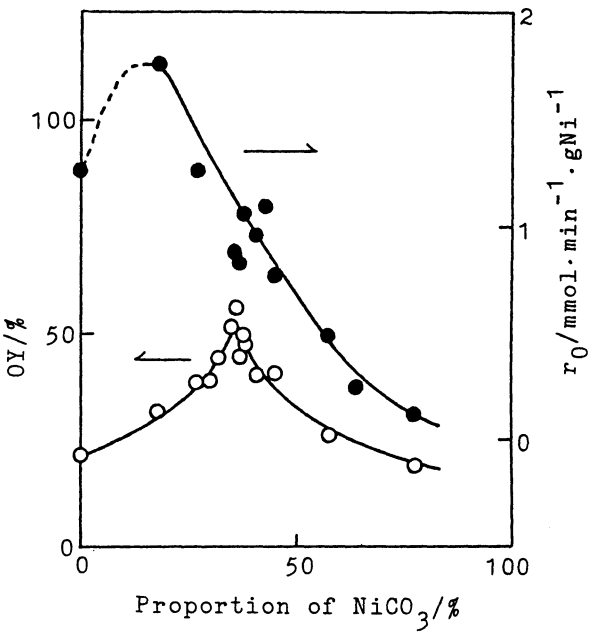

Fig. 4. Dependence of the activity(●) and the enantioselectivity(○) of modified Ni-SiO_2 catalysts on the composition of catalyst precursors.

CSD. The selectivity(OY) of modified Ni-SiO_2 catalysts in enantioselective hydrogenation of MAA decreased with increasing percentage of $NiCO_3$ beyond ca. 40% in spite of the increase in $\bar{D}_c$ and the decrease in the initial hydrogenation rate (r_0). This decrease in OY can be explained by the decrease in the activity of larger crystallites with high selectivity as well as the increase in the contribution of smaller crystallites with low selectivity to overall hydrogenation; the selectivity primarily depends on the crystallite size of Ni as reported previously.[1,5)]

Thus, the composition of the precursors, which depends on the preparation conditions, not only alters $\bar{D}_c$ but also appears to affect the CSD of Ni in the reduced catalysts and hence influence the activity and selectivity in the structure-sensitive reactions such as the enantioselective hydrogenation. Further studies concerning the CSD of Ni in these catalysts are now in progress.

References

1) Y. Nitta, F. Sekine, T. Imanaka, and S. Teranishi, J. Catal., 74, 382(1982).
2) Y. Izumi, T. Harada, T. Tanabe, and K. Okuda, Bull. Chem. Soc. Jpn., 44, 1418 (1971).
3) Y. Shimomura, I. Tsubokawa, and M. Kojima, J. Phys. Soc. Jpn., 9, 521(1954).
4) R. M. Mallya and A. R. V. Murthy, J. Indian Inst. Sci., 43, 65(1961).
5) Y. Nitta, F. Sekine, T. Imanaka, and S. Teranishi, Bull. Chem. Soc. Jpn., 54, 980(1981).

(Received May 14, 1984)