

PROPERTIES OF THE NI/KIESELGUHR CATALYSTS PREPARED BY PRECIPITATION METHOD

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Abstract—The pore structure of the 40 wt% Ni/kieselguhr catalyst prepared by precipitation of nickel component from a 0.17 M nickel nitrate solution at 90°C changes when the precipitant, 1 M Na₂CO₃ solution, is added to the nickel nitrate solution over different periods. After precipitation for 22 hours, the catalyst experiences narrowing of the pore mouth which leads to appearance of new small pores. However, when the catalyst is prepared by precipitation for 2 hours, the small pores present in the kieselguhr support are blocked by the precipitate particles and only the large pores are remained in the catalyst. The catalyst containing relatively small pores exhibits low reaction rates and changes in the product selectivity in soybean-oil hydrogenation, due to the diffusional resistance of the reactants in the catalyst pores. The effect of the diffusional resistance is not observed with CO hydrogenation, benzene hydrogenation and n-hexane hydrogenolysis, where molecular sizes of the reactants are significantly smaller than the catalyst pores.

INTRODUCTION

In our previous paper [1], we have reported that the properties of the precipitated Ni/kieselguhr catalysts are modified by the precipitation conditions. The size and reducibility of the nickel particles in the catalysts change with the temperature and pH of the nickel-containing solution, the kind and addition rate of the alkaline precipitant, and the aging conditions of the precipitated catalysts [1-3].

The pore structure of the catalysts also changes with the precipitation conditions that determine the amount of nickel silicate produced on the catalyst surface. It has been demonstrated in our previous study [1] that changes in the pore structure modify the apparent reaction rates on the catalysts. This is due to the diffusional resistance of the reactants and the products in the catalyst pores [4].

In this work, we have studied in more detail the nature of the pore structure change with the catalyst preparation conditions and the effect of the catalyst pore structures on the apparent reaction rates of a few test reactions. The test reactions have been selected

among the hydrogenation reactions employing the reactants of different molecular sizes. The catalysts, Ni/kieselguhr, have been prepared so that the average size of the dispersed nickel particles remain constant and only the pore structures are changed.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

Nickel catalysts supported on kieselguhr with the nominal metal loading of 40 wt%, i.e. 40 wt% Ni/kieselguhr, were prepared by the precipitation method. Details of the catalyst preparation procedure were the same as reported earlier [1]. The catalyst samples were different depending on the period that the precipitant, 1 M aqueous solution of Na₂CO₃, was introduced into the 0.17 M nickel nitrate solution. The prepared catalysts were reduced without precalcination at 450°C for 15 hours in a hydrogen stream. The nickel surface area of the reduced catalyst was estimated from the amount of hydrogen chemisorption on the catalyst, which was obtained by extrapolating the hydrogen-desorption isotherm to zero pressure. Before the desorption experiments, the catalyst was cooled in a hydrogen stream from the final reduction temper-

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Table 1. Physical properties of catalyst samples

Catalyst	K2	K8	K22
Precipitation time (hr)	2	8	22
Nickel surface area (m^2/g) ^a	53	51	45
Degree of reduction (%) ^b	62	56	54
Nickel particle diameter ($\text{\AA}$) ^a	53	50	54

a. Measured by H_2 chemisorption. b. Measured by oxygen titration [5].

ature, 450°C , to room temperature. The degree of nickel reduction of the catalysts was measured by the oxygen-titration method, described by Bartholomew and Farrauto [5]. Size distribution of the catalyst pores was measured by a mercury porosimeter (Carloerba, 2000-WS) which measured the pore sizes as small as $39 \text{ \AA}$. In the pore-size estimation, it was assumed that the pores were cylindrical in shape, the surface tension of mercury (99.999%) was 480 dyne/cm , and the contact angle between the catalyst and mercury was 141.3° . The average size of the reduced nickel particles was estimated with an X-ray diffractometer (Rigaku, D/MAXII-A) using $\text{CuK}\alpha$ as the X-ray source.

2. Reaction Tests

The rates of soybean-oil hydrogenation were measured in a slurry-type batch reactor equipped with a pressure regulator to maintain the reactor pressure at a constant level between 3-5 bars. The reaction rate was estimated from the amount of hydrogen supplied into the reactor to maintain the reactor under the isobaric condition. The reactants and the products were analyzed for their compositions with a G.C. after esterification with methanol. Benzene hydrogenation, CO hydrogenation and n-hexane hydrogenolysis were carried out under the atmospheric pressure in a differential gas-phase reactor connected with a syringe pump (Sage Instrument, 341 B) and a vaporizer for introduction of the liquid reactants. Benzene hydrogenation was carried out at 200°C with the H_2 /benzene ratio of 10, CO hydrogenation at 240°C with the H_2 /CO ratio of 3, and n-hexane hydrogenolysis at 280°C with the H_2 /n-hexane ratio of 10.

RESULTS AND DISCUSSION

1. Properties of the Dispersed Nickel Particles

Table 1 shows the properties of the nickel particles deposited on the kieselguhr support by precipitation for different periods. The nickel surface area and the degree of nickel reduction decrease as the precipitation periods become longer.

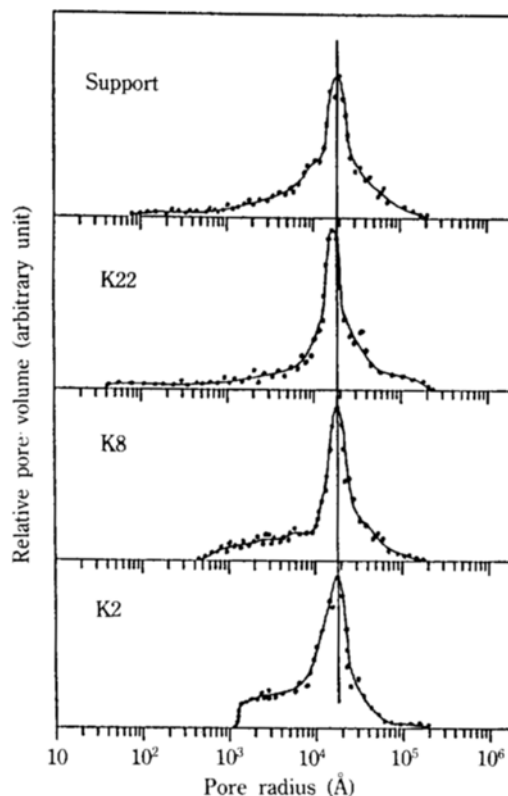


Fig. 1. Pore size distribution of the kieselguhr support and the precipitated catalysts. K2, K8 and K22 are the catalysts prepared by precipitation for 2, 8 and 22 hours, respectively.

The average size of the nickel particles, however, is not affected by the precipitation periods. The particle diameter for K8 is slightly smaller than those for K2 and K22, but an independent estimation from the XRD measurement, which are not shown here, supports that the average diameters are almost the same for the three catalyst samples.

No variation of the nickel particle size with the precipitation period is somewhat contrary to the result obtained by Coenen [6]. However, this may be explained as follows. Previous study [1] has indicated that two major factors determine the nickel particle size: the rate of precipitation and the pH of the precipitating solution. Of the two factors, the pH of the solution is a dominant one particularly when it is high. Since the catalysts of this study have been prepared under the pH as high as 9.0, the nickel particle size has been determined mostly by the pH of the solution than by the precipitation rate, and therefore remains almost the same for the three catalyst samples.

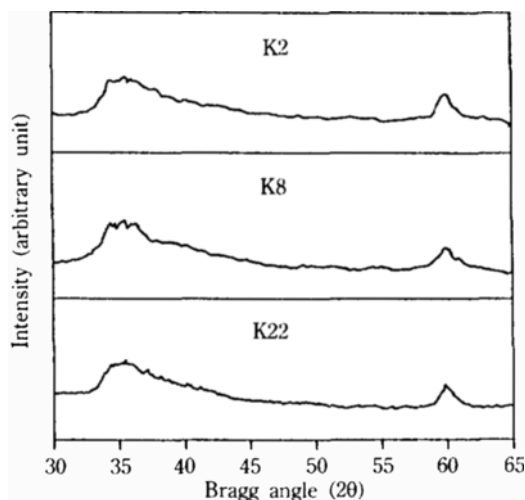


Fig. 2. XRD spectra of precipitated catalysts after drying. K2, K8 and K22 are the catalysts prepared by precipitation for 2, 8 and 22 hours, respectively.

2. Modification of the Catalyst Pore Structure

Fig. 1 shows the changes in the catalyst pore structure when the catalysts have been prepared by precipitation for different periods. The kieselguhr support without any nickel deposition contains the pores distributed between 70 Å and 20 μm (2×10^5 Å) with the most population near 2 μm. The catalyst prepared by precipitation for 22 hours (K22) shows a similar pore structure as for the kieselguhr support except that new small pores appear in the size range below 70 Å. The most populated pores for K22 are smaller than for the kieselguhr support by about 0.5 μm.

The catalysts lose the pores in the micro-pore range when prepared by precipitation for shorter periods. Namely, the catalyst after 8-hour precipitation (K8) has completely lost the pores smaller than 400 Å, and one after 2-hour precipitation (K2) has lost the pores smaller than 1000 Å. For these two catalysts, the most populated pores are centered at 2 μm, same as for the kieselguhr support.

Coenen [6] has reported that the nickel compounds such as nickel hydroxide, nickel carbonate, and nickel silicate are produced on the catalyst surface after the precipitation step. Particularly, when the pH of the precipitating solution is relatively high as in this study, nickel silicate is the most dominant species and its amount is dependent mostly on the pH of the solution than on the precipitation rate. Such a phenomenon has been confirmed in this study by an XRD observation (Fig. 2) which shows only the peaks corresponding to nickel silicate on the catalysts.

Table 2. Initial composition of soybean oil

Fatty acid	Composition (mol%)
Palmitic acid	10.7
Stearic acid	3.6
Oleic acid	22.0
Linoleic acid	55.7
Linolenic acid	8.0

The precipitation rate, however, seems to determine the size of the silicate particles deposited on the catalyst. This interpretation is derived from the results of Fig. 1. Namely, relatively small silicate particles are deposited on the inner wall of the kieselguhr pores, particularly in case of K22, so that the pore size of the catalyst after precipitation becomes smaller than that of kieselguhr. When the precipitation rate increases, the silicate particles become larger and block the mouth of the relatively small pores. Finally, when the precipitation rate becomes as fast as for K2, the catalyst pores are blocked up to the size of 1000 Å as observed in Fig. 1.

We have attempted to verify the above interpretation by an independent XRD observation of the prepared catalysts, but have failed due to the broad nature of the silicate XRD peaks. Regardless of the interpretation, it is an important result that the catalyst of different pore structures have been obtained by different precipitation rates.

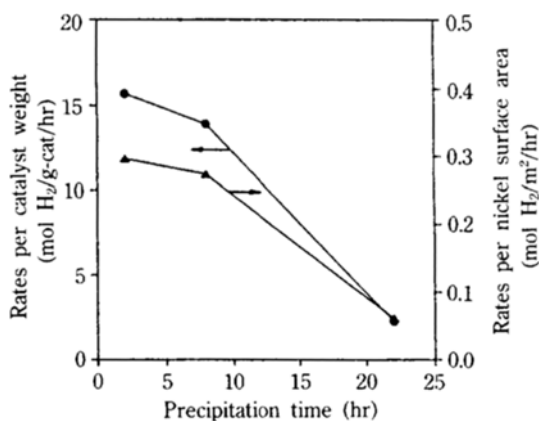
3. Apparent Reaction Rates on the Catalysts

3-1. CO Hydrogenation

It is well-known [7] that the activity of the supported metal catalyst is modified by two major factors: the metal crystallite size and the metal-support interaction. The crystallite size effect is not observed in this study because the catalyst samples have the same size distribution of the nickel particles as shown in Table 1. Instead, the metal-support interaction may be significant in this study because the catalysts have been reduced to different extents. Changes in the catalytic activity due to the different degrees of metal reduction has been demonstrated for the cobalt catalysts in CO hydrogenation [8, 9]. Catalyst samples of this study in CO hydrogenation have been tested to investigate the possible effect of the metal-support interaction. Since the molecular size of CO, 3.7 Å [10], is much smaller than the size of the catalyst pores, CO should not experience the diffusional resistance in the catalyst pores. The kinetic results in Table 3 show almost constant reaction rates and product distribution for the three catalyst samples. Accordingly, the electronic modification of the catalyst activity by the nickel-kieselguhr or the nickel-nickel oxide interaction is not

Table 3. Rates and product distribution in CO hydrogenation

Catalysts	Reaction rates (s ⁻¹)	Product distribution (mol%)		
		C ₁	C ₂	C ₃
K2	0.011	92.5	6.35	1.15
K8	0.011	92.0	6.40	1.68
K22	0.009	92.6	5.79	1.66

**Fig. 3. Rates of soybean-oil hydrogenation.**

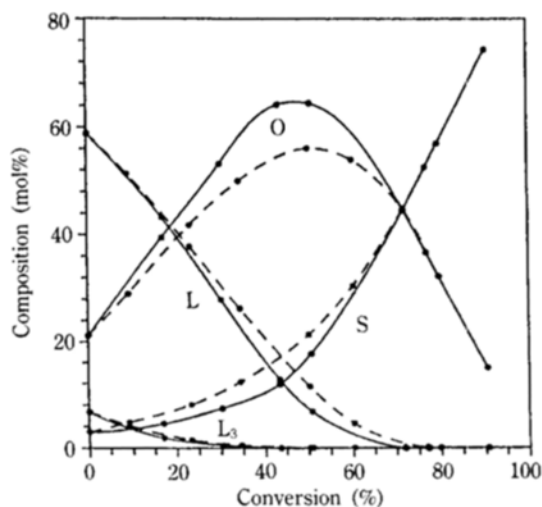
● : Rates per catalyst weight, ▲ : Rates per nickel surface area.

observed with the catalyst samples of this study.

3-2. Soybean-Oil Hydrogenation

Soybean oil is composed of triglycerides of various fatty acids whose compositions are given in Table 2. The Ni/kieselguhr catalyst is commonly used for the soybean-oil hydrogenation, the adjust the melting point of the final product. Since the molecular size of the triglycerides are relatively large, 14.6 Å in diameter [11], the reactants should experience the diffusional resistance when the catalyst pores are small [12].

We have tested the catalysts of this study in the soybean-oil hydrogenation to observe the effect of the diffusional resistance on the apparent reaction rates. Fig. 3 shows that the reaction rate per the nickel surface area decreases when the catalysts contain many small pores as in the case of the K22 catalyst. The rates are higher on K2 than on K22 because the reactants are accessible to most of the nickel particles in K2. In fact, the trend agrees with one observed by Coenen [2] who showed that the rate of soybean-oil hydrogenation is severely limited by the diffusional resistance when the nickel particles are located in the pores smaller than 25 Å. They reported that the reaction rates per the nickel surface area were remained

**Fig. 4. Changes in the soybean-oil composition with the overall conversion.**

Solid line is for the 2-hour precipitated catalyst (K2) and broken line for the 22-hour precipitated catalyst (K22). S: Stearic acid, O: Oleic acid, L: Linoleic acid, L₃: Linolenic acid.

almost constant when the metal surface area was obtained only from the nickel particles located in the pores larger than 25 Å.

The catalyst pore structure changes not only the apparent overall reaction rate but also the product selectivity in soybean-oil hydrogenation. Fig. 4 shows that the selectivity for oleic acid is lower and one for stearic acid is higher on the K22 catalyst than on K2. This is because the reaction intermediates stay in the catalyst pores for longer periods in K22 than in K2. Since the hydrogenation step proceeds in series to yield the fatty acids of different saturation, longer stay of the reactant intermediates in the catalyst pores allows more production of stearic acid than oleic acid.

3-3. Benzene Hydrogenation and n-Hexane Hydrogenolysis

To study further the effect of the catalyst pore structure on the reaction rates, we have tested the catalyst samples for other hydrogenation reactions such as benzene hydrogenation and n-hexane hydrogenolysis. The molecular sizes of benzene and n-hexane are 6.6 Å and 4.9 Å respectively [10], and therefore the reactants should not experience a significant diffusional resistance in the catalysts. Indeed, Fig. 5 shows that the rates remain almost constant independent of the catalyst samples. The results of Fig. 5, together with those of Fig. 3 and Fig. 4, clearly indicate that the catalytic behavior is modified by the reactant diffusional

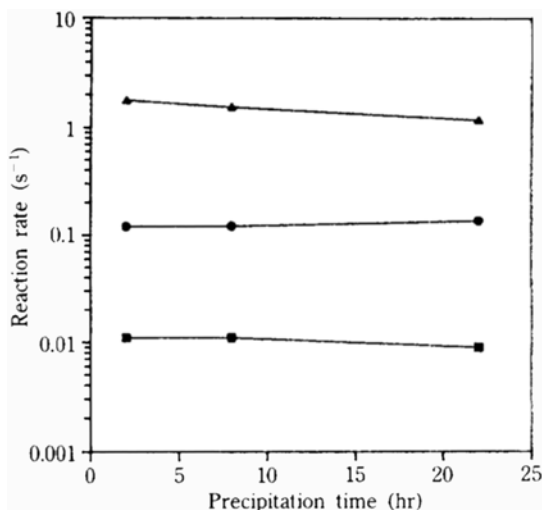


Fig. 5. Rates of various hydrogenation processes on the catalysts precipitated for different periods.

▲ : n-Hexane hydrogenolysis, ● : Benzene hydrogenation, ■ : CO hydrogenation.

resistance only when the reactant molecular sizes are comparable to the sizes of the catalyst pores, as observed in the case of soybean-oil hydrogenation on the K22 catalyst.

CONCLUSION

Modification of the catalyst pore structure has been observed with the Ni/kieselguhr catalysts prepared by precipitation at different rates. The initial pores of the kieselguhr support are either narrowed or blocked depending on the precipitation rates, which is due to the formation of the nickel silicate particles of different sizes. The pore structure change modifies the apparent reaction rates on the catalysts depending on the relative sizes of the reactants and the catalyst pores. In this study, we have demonstrated a clear kinetic evidence of the reactant diffusional resistance in the catalyst by testing the catalyst samples in four

hydrogenation reactions. The rates on the catalysts are modified only in the soybean-oil hydrogenation whose reactant size is comparable to the size of the catalyst small pores

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