



# Hydrogen–deuterium exchange of methane on nickel and potassium promoted nickel prepared by the reduction of nickel oxide

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## ABSTRACT

The hydrogen–deuterium exchange reactions of methane in a deuterium stream were studied by a pulse experiment over a reduced nickel (Ni1373 prepared from nickel oxide calcined at 1373 K, and Ni773 prepared from nickel oxide calcined at 773 K) and K<sub>2</sub>O promoted reduced nickel (K-Ni1373 and K-Ni773). Ni1373 had a higher exchange activity than Ni773. The effects of the addition of K<sub>2</sub>O resulted in the decrease in the exchange activity due to the inhibition of step defect sites and/or the promotion of the change of nickel crystal structure. High activity of Ni1373 could be due to that the Ni1373 had the surface of a higher Ni(100)/Ni(111) ratio.

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## 1. Introduction

A tartaric acid-modified nickel catalyst is one of the most successful enantio-selective heterogeneous catalysts. For the hydrogenation of prochiral ketones, high enantioselectivity was attained for  $\beta$ -ketoesters (up to 98% e.e.) and 2-alkanones (up to 85% e.e.) [1–3]. The catalyst is simply prepared by immersing an activated nickel catalyst (base nickel catalyst) in a solution of tartaric acid [4]. The enantioselectivity is obtained by the adsorption of the tartaric acid on the nickel surface. For the base nickel catalyst, various types of nickel were used, for example, Raney nickel, supported nickel, reduced nickel (nickel prepared by the reduction of nickel oxide by hydrogen gas), and nickel fine powder. From these studies, it has been revealed that the condition of the nickel surface is one of the important factors for attaining a high enantioselectivity, i.e. the enantio-selective hydrogenation over a tartaric acid-modified nickel catalyst is a structure-sensitive reaction [5,6]. It was reported that the modified catalyst with greater than a 40-nm nickel crystallite size gave a high enantioselectivity [6]. It was also reported that the enantioselectivity of a modified reduced nickel catalyst depended on the preparation temperature of the nickel oxide. The reduced nickel (Ni1373) prepared from the nickel oxide calcined at 1373 K (NiO1373) had a higher enantioselectivity than the reduced nickel (Ni773) prepared from the

nickel oxide calcined at 773 K (NiO773) [7]. This could be due to the difference between the surface structure of Ni1373 and that of Ni773.

The hydrogen–deuterium (H/D) exchange reaction of CH<sub>4</sub> with D<sub>2</sub> over various metals [8–10] and metal oxides [11–13] has been studied for many years. As for the nickel catalysts reported in the literature, they were prepared by the direct reduction of nickel salt precursors at 673 K to 923 K [12,14,15] or prepared through the reduction of nickel oxide, which was calcined at 673 K, on SiO<sub>2</sub> [16]. As the H/D exchange of methane would also be a structure-sensitive reaction (the activity over Ni(100) is higher than Ni(111)) [17,18], the exchange activity reveals which the surface is predominant for the catalytic reaction. In this work, we have drawn attentions on the H/D exchange reactions over Ni773 and Ni1373 in order to reveal the differences of these surfaces. In the previous paper, Ni773 and Ni1373 were prepared at a constant reduction temperature (reduction of nickel oxide to nickel was carried out at 623 K) [18]. We have found the features of the exchange reaction of Ni1373 were much different from those of Ni773 and those reported Ni catalyst in the literature. That is, the preparation of the nickel catalyst through the nickel oxide calcined at high temperature would result in a different nickel surface, when compared to the preparation not through the nickel oxide.

In the present study, the hydrogen–deuterium (H/D) exchange reaction of CH<sub>4</sub> with D<sub>2</sub> was carried out over Ni773 and Ni1373. The effects of the reduction temperature of nickel oxide to nickel and furthermore, the addition of potassium on both the exchange activity and the exchanged species were examined.

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## 2. Experimental

### 2.1. Materials

CH<sub>4</sub> (99.99%), D<sub>2</sub> (99.995%), and He (99.995%) were supplied from the Takachiho Trading Co., Ltd., Japan.

### 2.2. Preparation of nickel oxide

Nickel oxides were prepared by decomposing and calcining nickel hydroxide (Wako Pure Chemical Ind., Ltd., Lot ACJ6158) in a mixture of N<sub>2</sub> (40 cm<sup>3</sup> min<sup>-1</sup>) and O<sub>2</sub> (10 cm<sup>3</sup> min<sup>-1</sup>) for 3 h. The nickel oxides prepared at 773 K and 1373 K were designated NiO773 and NiO1373, respectively.

### 2.3. Preparation of K<sub>2</sub>O promoted nickel oxide

Potassium carbonate (Wako Pure Chemical Ind., Ltd., Lot LTE 1645, 0.00367 g) was dissolved in distilled water (40 cm<sup>3</sup>). Nickel hydroxide (2.16 g) was added to the potassium carbonate solution and stirred at 353 K for 2 h and dried. The resulting solid was calcined in a mixture of N<sub>2</sub> (40 cm<sup>3</sup> min<sup>-1</sup>) and O<sub>2</sub> (10 cm<sup>3</sup> min<sup>-1</sup>) at 773 K or 1373 K for 3 h. The K<sub>2</sub>O promoted nickel oxides prepared at 773 K and 1373 K were designated K-NiO773 and K-NiO1373, respectively.

### 2.4. Catalytic test

A continuous gas flow fixed bed glass reactor (14 mm id) was used for the catalytic test. The measurement without an exchange reaction was first carried out by a CH<sub>4</sub> pulse (0.6 cm<sup>3</sup>) without a catalyst in a He (50 cm<sup>3</sup> min<sup>-1</sup>) stream. Consequently, NiO773, NiO1373, K-NiO773, or K-NiO1373 (0.127 g) was placed in the reactor and treated with a D<sub>2</sub> stream (mixture of D<sub>2</sub> (3 cm<sup>3</sup> min<sup>-1</sup>) and He (50 cm<sup>3</sup> min<sup>-1</sup>)) at an atmospheric pressure for 1 h. The reduction of nickel oxide was confirmed by XRD (Shimadzu XD-3A) experiments. The resulting reduced nickel catalysts were designated Ni773, Ni1373, K-Ni773, and K-Ni1373 respectively. Reduction was carried out at 573, 623, 673, or 723 K. The resulting catalysts were designated (K-)Ni773-573, (K-)Ni773-623 and so on. The H/D exchange reaction was carried out in the same reactor by a CH<sub>4</sub> pulse (0.6 cm<sup>3</sup>) under a continuous gas flow of a mixture of D<sub>2</sub> (3 cm<sup>3</sup> min<sup>-1</sup>) and He (50 cm<sup>3</sup> min<sup>-1</sup>) at 573 K. The outlet from the reactor was connected to a Q-mass spectrometer (PFEIFFER Vacuum Prisma QMS 200) by a silica capillary tube (0.05 mm id × 2.5 m). The data set of the ion current (*m/z* = 12–20) was collected every 0.7 s. Background corrections to the observed spectra were made (H<sub>2</sub>O at *m/z* = 18). The second exchange reaction was carried out at a 45-min interval to check the stability of the catalyst. From the beginning of the first run to the end of the second run, the gas flow of D<sub>2</sub> and He was maintained. As the results of the first run and the second run were almost the same, the catalysts were considered stable during the experiment and the results of the first run are shown in this paper.

### 2.5. Determination of BET surface area

The BET surface area of the reduced nickel catalysts was measured using a Micromeritics Gemini 2375 by N<sub>2</sub> adsorption at 77 K.

### 2.6. Determination of the exchanged species by the correction of the methane isotopologues

The determination of the isotopologues of methane was carried out by quadrupole mass spectroscopy. The methane isotopologues CH<sub>i</sub>D<sub>4-i</sub> (*i* = 4–0) have shown characteristic fragmentation patterns,

which however, overlap each other. Therefore, to obtain the pure molecular ion peaks of the methane isotopologues, corrections have to be made for the observed ion peaks. In the present study, to determine each of the isotopologues in the pulse experiment, the pulse areas of the ion current were calculated by our newly proposed method. The detailed correction method is described elsewhere [19].

The composition of the isotopologue P(CH<sub>i</sub>D<sub>4-i</sub>) (*i* = 4–0) after the exchange reaction was calculated using the peak area S(CH<sub>i</sub>D<sub>4-i</sub>) of its corrected intrinsic parent ion (Eq. (1)).

$$\begin{aligned} P(\text{CH}_4) &= 100 \times S(\text{CH}_4)/S_{\text{sum}} \\ P(\text{CH}_3\text{D}) &= 100 \times S(\text{CH}_3\text{D})/S_{\text{sum}} \\ P(\text{CH}_2\text{D}_2) &= 100 \times S(\text{CH}_2\text{D}_2)/S_{\text{sum}} \\ P(\text{CHD}_3) &= 100 \times S(\text{CHD}_3)/S_{\text{sum}} \\ P(\text{CD}_4) &= 100 \times S(\text{CD}_4)/S_{\text{sum}} \\ S_{\text{sum}} &= S(\text{CH}_4) + S(\text{CH}_3\text{D}) + S(\text{CH}_2\text{D}_2) + S(\text{CHD}_3) + S(\text{CD}_4) \end{aligned} \quad (1)$$

## 3. Results and discussion

### 3.1. The H/D exchange activity over the reduced nickel catalyst and the K<sub>2</sub>O promoted reduced nickel catalyst

Table 1 shows the H/D exchange activities of Ni773 and Ni1373 prepared at reduction temperatures from 573 K to 723 K. The exchange activity of Ni1373 has turned out to be much higher than that of Ni773 at all the reduction temperatures. Taking into account that the exchange activity of Ni(1 0 0) would be higher than Ni(1 1 1) [17,18], the surface of Ni1373 could have a higher Ni(1 0 0)/Ni(1 1 1) ratio. This idea would also be supported by the following reasons. (i) It was reported that NiO(1 0 0) can be reduced to Ni(1 0 0) by hydrogen at 623 K [20]. (ii) As nickel oxide is a crystal like NaCl, the NiO(1 0 0) face has the lowest surface energy density ( $\gamma$ ). It is reasonable to infer the equilibrium form of the crystal is a hexahedron, which mainly consists of (1 0 0) faces. When  $\gamma(1 1 1)$  is smaller than  $\sqrt{3}\gamma(1 0 0)$ , however (1 1 1) may appear on the surface of the crystal [21]. As the NiO1373 was calcined at high temperature, it is reasonable to assume that the crystal would be relatively stable and have a high NiO(1 0 0)/NiO(1 1 1) ratio. (iii) As the crystallinity of Ni1373 was higher than that of Ni773 (nickel crystallite size, Ni1373: 68 nm, Ni773: 28 nm) [22], the Ni1373 would have a larger terrace without disorder than Ni773. Table 1 also indicates the exchange activity of Ni773 and Ni1373 decreased with the increase in the reduction temperature of nickel oxide. As the increase of the reduction temperature caused the sintering and decrease in the BET surface area, the specific exchange activity is also shown in Table 1. The specific activity over Ni773 decreased with the increase in the reduction temperature, while that over Ni1373 increased with the increase in the reduction temperature.

**Table 1**

Exchange activity of Ni773 and Ni1373 prepared at various reduction temperatures.

| Catalyst <sup>a</sup> | Exchange activity/% | BET surface area/m <sup>2</sup> g <sup>-1</sup> | Specific exchange activity <sup>b</sup> /% |
|-----------------------|---------------------|---|--|
| Ni773-573             | 29                  | 7.0   | 4.1  |
| Ni773-623             | 5.6                 | 4.1   | 1.4  |
| Ni773-673             | 1.5                 | 2.4   | 0.63                                       |
| Ni773-723             | 1.3                 | 2.1   | 0.62                                       |
| Ni1373-573            | 48                  | 4.2   | 12   |
| Ni1373-623            | 43                  | 3.3   | 13   |
| Ni1373-673            | 41                  | 2.4   | 18   |
| Ni1373-723            | 37                  | 1.9   | 20   |

<sup>a</sup> Ni773-\*\*\*, Ni1373-\*\*\*; \*\*\* indicates the reduction temperature of nickel oxide.

<sup>b</sup> Exchange activity/BET surface area.

As the crystallinity of NiO773 was low, the increase in the reduction temperature resulted in the change of the crystal structure, i.e. the structure with moderately high Ni(1 0 0) ratio to that with high Ni(1 1 1) ratio that is the stable face of fcc crystal. The ratio of even higher index facets would also decrease by the sintering, resulting in low exchange activities. This idea is supported by DFT studies that decomposition of methane on nickel was higher on Ni(2 1 1) than Ni(1 1 1) [23]. On the other hand, as the crystallinity of Ni1373 was high, the crystal structure was not changed easily and the decrease of the proportion of Ni(100) would be small. The increase of the specific activity with the increase in the reduction temperature could be attributed to the decrease of the high-index facets by the sintering. The H/D exchange activity could be higher on Ni(1 0 0) than on the high-index facets.

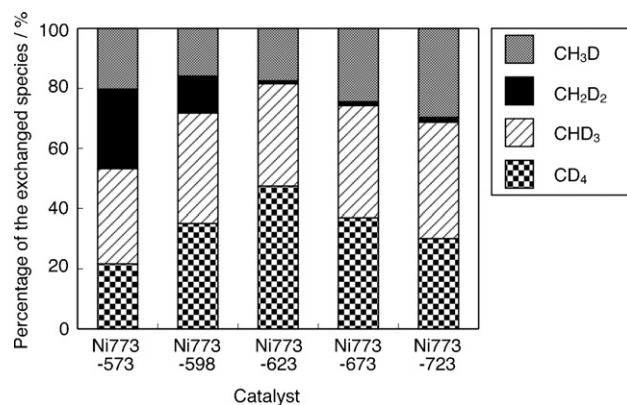
In order to investigate the activity on the high-index facets of the crystal, K<sub>2</sub>O promoted nickel was used for the H/D exchange reaction. It is reported that when nickel was promoted by K<sub>2</sub>O, K<sub>2</sub>O was localized on the step defect sites and it inhibited these sites [24]. It is also expected that the addition of K<sub>2</sub>O to the nickel crystal would result in the decrease of the crystallinity and accelerate the change of crystal structure. Table 2 shows the H/D exchange activity, BET surface area, and the specific activity of K<sub>2</sub>O promoted nickel (K-Ni773 and K-Ni1373) prepared at reduction temperatures from 573 K to 723 K. Comparing the specific activity of K-Ni773 and that of Ni773 (Table 1), the activity of K-Ni773-573 and K-Ni773-623 were lower than that of the corresponding Ni773. This could be due to that Ni773-573 and Ni773-623 had the step defect sites that were inhibited by K<sub>2</sub>O and/or the addition of potassium facilitated the structural change of nickel crystal. The inhibition of exchange reaction by potassium could be explained by the increase of the dissociation barrier of methane. DTF study indicated that increase of the barrier was given by the interaction between the induced dipole moment in the transition state of the dissociating methane and the electrostatic field induced by the potassium adatoms [25]. On the other hand, the activity of K-Ni773-673 and K-Ni773-723 were as low as that of Ni773-673 and Ni773-723. It could be when the reduction temperature was as high as 673 K and 723 K, the change to Ni(1 1 1) from Ni(1 0 0) takes place irrespective of the presence of potassium and the predominance of Ni(1 1 1) lowered the activity. As for K-Ni1373 and Ni1373, the specific activity of K-Ni1373-573 and Ni1373-573 were almost the same. Taking into account that they had similar BET surface area, the results would indicate that Ni1373 did not have sites that were inhibited by K<sub>2</sub>O and that the promotion of structural change by the addition of potassium did not observed at the reduction of 573 K. However, for the nickel prepared by the reduction over 623 K, the specific activity significantly decreased by the addition of potassium, probably because of the decrease in the proportion of Ni(1 0 0) by the structural change promoted by potassium.

**Table 2**  
Exchange activity of K-Ni773 and K-Ni1373 prepared at various reduction temperatures.

| Catalyst <sup>a</sup> | Exchange activity/% | BET surface area/m <sup>2</sup> g <sup>-1</sup> | Specific exchange activity <sup>b</sup> /% |
|-----------------------|---------------------|---|--|
| K-Ni773-573           | 6.9                 | 8.3   | 0.84                                       |
| K-Ni773-623           | 2.4                 | 5.3   | 0.45                                       |
| K-Ni773-673           | 1.8                 | 2.8   | 0.65                                       |
| K-Ni773-723           | 1.7                 | 2.5   | 0.69                                       |
| K-Ni1373-573          | 45                  | 4.0   | 11   |
| K-Ni1373-623          | 30                  | 4.1   | 7.1  |
| K-Ni1373-673          | 17                  | 2.5   | 6.9  |
| K-Ni1373-723          | 9.1                 | 1.7   | 5.5  |

<sup>a</sup> K-Ni773-\*\*\*, K-Ni1373-\*\*\*: \*\*\* indicates the reduction temperature of nickel oxide.

<sup>b</sup> Exchange activity/BET surface area.



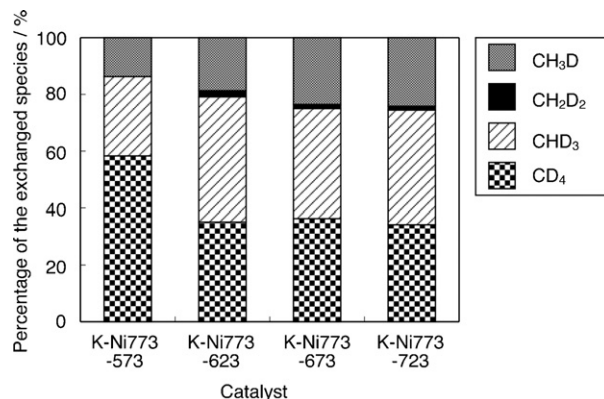
**Fig. 1.** Percentage of the exchanged species over Ni773 at various reduction temperatures.

### 3.2. The exchanged species over the reduced nickel catalyst and the K<sub>2</sub>O promoted reduced nickel catalyst

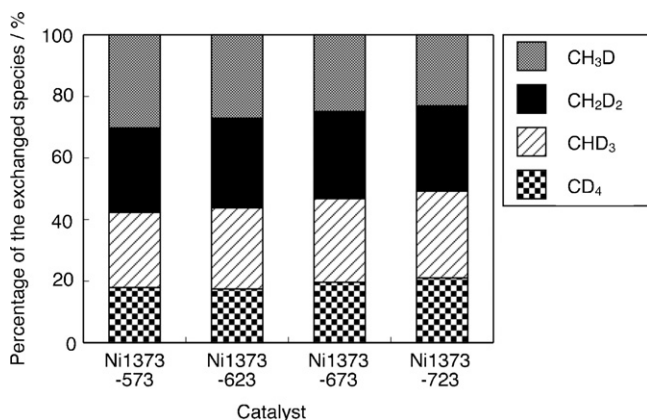
Figs. 1 and 2 show the percentages of all the exchanged species over Ni773 and K-Ni773, respectively. For the reactions over Ni773, CH<sub>2</sub>D<sub>2</sub> was observed for the Ni773-573 that had relatively high exchange activity. However, the percentage of CH<sub>2</sub>D<sub>2</sub> decreased with increases in the reduction temperatures and little CH<sub>2</sub>D<sub>2</sub> was observed over Ni773-623, -673, and -723. As for K-Ni773, low percentage of CH<sub>2</sub>D<sub>2</sub> was observed for all the reduction temperatures.

Two mechanisms for the H/D exchange reaction of CH<sub>4</sub> were proposed, that is, a stepwise exchange and a multiple exchange [12]. For the stepwise exchange, one hydrogen atom in methane is exchanged at each residence on the surface. For the multiple exchange, more than one hydrogen atoms in methane are exchanged in one residence. It was reported that the activation energy of CH<sub>2</sub>(adsorbed) to CH(adsorbed) in the multiple exchange was lower than that of the other dissociation steps on the surface and that further exchanges rather than the desorption to the gas phase of CH<sub>2</sub>D<sub>2</sub> occurred [9]. In this study, on the surfaces of Ni773-623, -673, -723, and all the K-Ni773, CH<sub>2</sub>D<sub>2</sub> was not observed. As mentioned in 3.1, the H/D exchange reaction would occur mainly on Ni(1 1 1) for these catalysts. The Ni(1 1 1) had low exchange activity and the multiple exchange would have occurred on this surface. As Ni773-573 would have much Ni(1 0 0) and/or high-index facets than Ni773-623, -673, -723, stepwise exchange would occur and CH<sub>2</sub>D<sub>2</sub> was observed.

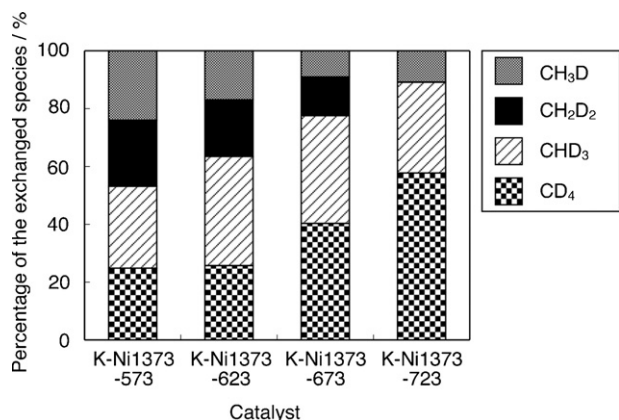
Figs. 3 and 4 show the percentage of each exchanged species over Ni1373 and K-Ni1373, respectively. Over Ni1373, CH<sub>2</sub>D<sub>2</sub> was observed at similar percentage to the other isotopologues at all the



**Fig. 2.** Percentage of the exchanged species over K-Ni773 at various reduction temperatures.



**Fig. 3.** Percentage of the exchanged species over Ni1373 at various reduction temperatures.



**Fig. 4.** Percentage of the exchanged species over K-Ni1373 at various reduction temperatures.

examined reduction temperatures. This could be also due to that Ni1373 had more Ni(100) sites where stepwise exchange occurred. On the other hand, as for the reaction over K-Ni1373, the percentage of CH<sub>2</sub>D<sub>2</sub> decreased with increases in the reduction temperatures, because addition of potassium would promote the change of crystal structure to decrease the proportion of Ni(100).

#### 4. Conclusion

H/D exchange reactions of methane in a deuterium stream in a fixed bed flow reactor were studied over the reduced nickel catalyst. We found Ni1373 had a higher exchange activity than Ni773. And the promotion by potassium resulted in a significant decrease in the exchange activity. This could be caused by the inhibition

of the step defect sites by potassium and/or the promotion of the change of the nickel crystal structure. The present results support the idea that Ni1373 with higher exchange activity than Ni773 could be attributed to a higher Ni(100)/Ni(111) ratio on the surface for the former.

This study analyzed the exchanged species by the pulse of methane in a D<sub>2</sub> stream. Although the pulse technique is not a steady-state reaction, the results of this study could be similar to the results obtained in the early stage of the steady-state reaction, because the analyses of each isotopologue in this study were carried out by the integration of each peak. This would be supported by the fact that the results obtained by Ni773-673 (the ratio of CH<sub>2</sub>D<sub>2</sub> was low and those of CH<sub>3</sub>D and CD<sub>4</sub> were high) were similar to those reported using a conventional closed gas circulation system [12,16]. However, the pulse experiment would be a good technique for analyzing the structure of a fresh catalyst surface, because it can observe the fresh surface of the catalyst not adsorbed and covered by the reactant.

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