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# Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

# Hydrogen–deuterium exchange of methane on nickel surface prepared by the reduction of nickel oxide

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## ARTICLE INFO

## ABSTRACT

The hydrogen–deuterium exchange reactions of methane in a deuterium stream were studied by a pulse experiment over a reduced nickel catalyst. The reduced nickel (Ni1373) prepared from nickel oxide calcined at 1373 K had a higher activity than the reduced nickel (Ni773) prepared from the nickel oxide calcined at 773 K. This could be due to the ratio of the Ni(1 0 0) to Ni(1 1 1). As the Ni1373 could have the surface of a higher Ni(1 0 0)/Ni(1 1 1) ratio, Ni1373 had a higher activity than Ni773.

## 1. Introduction

A tartaric acid-modified nickel catalyst is one of the most successful enantio-selective heterogeneous catalysts. For the hydrogenations of prochiral β-ketoesters, an enantioselectivity up to 98% e.e. was attained [1]. The catalyst is simply prepared by immersing an activated nickel catalyst in an aqueous solution of tartaric acid [2]. The enantioselectivity is obtained by the adsorption of the tartaric acid on the nickel surface. The enantio-selective hydrogenation over a tartaric acid-modified nickel catalyst is known to be a structure-sensitive reaction [3,4]. It was reported that the modified catalyst with greater than a 40 nm nickel crystallite size gave a high enantioselectivity [4]. A certain smooth surface area would be necessary for tartaric acid to be adsorbed in the appropriate conformation to interact with a substrate in order to attain a high enantioselectivity. 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) [5]. This could be due to the difference between the surface structure of Ni773 and

that of Ni1373, but no such investigation has been carried out to prove this point.

The hydrogen–deuterium (H/D) exchange reaction of $CH_4$ with $D_2$ over various metals [6,7] and metal oxides [8–10] has been studied for many years. Various types of methods for this exchange reaction have been reported, that is, (i) $D_2$ was pre-adsorbed on the catalyst in the recirculation reactor followed by $CH_4$ circulation [11], (ii) the mixture of dilute $CH_4$ and $D_2$ was passed through the catalyst bed in the flow (or circulation) reactor [10,12], and (iii) the adsorption of $CH_4$ on the catalyst followed by desorption as deuterated methane in the $D_2$ stream [13].

In this study, during the course of the studies for investigating the difference between Ni773 and Ni1373, the hydrogen–deuterium (H/D) exchange reaction of $CH_4$ with $D_2$ was carried out over these reduced nickel catalysts as follows: (i) a catalyst was placed in a fix-bed flow reactor under a flowing mixture of He and $D_2$ and (ii) $CH_4$ was introduced by a pulse and the exchanged methane by a dissociated deuterium on the catalyst was detected by mass spectroscopy. We previously reported a new method of corrections for the fragmentation peaks in order to precisely determine the ratio of the exchanged products by quadrupole mass spectrometry [14]. Methane decomposition is known to be a structure-sensitive reaction and the reactivity is reported as Ni(1 0 0) > Ni(1 1 1) [15]. As the H/D exchange of methane would also be a structure-sensitive reaction, the exchange activity could reveal the surface, which predominantly catalyzes the reaction.

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## 2. Experimental

### 2.1. Materials

CH$_4$ (99.99%), D$_2$ (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 the decomposition and calcination of nickel hydroxide (Wako Pure Chemical Ind., Ltd., Lot ACJ6158) in a mixture of N$_2$ (40 cm$^3$ min$^{-1}$) and O$_2$ (10 cm$^3$ min$^{-1}$). The nickel oxides prepared at 773 K and 1373 K were designated NiO773 and NiO1373, respectively.

### 2.3. Catalytic test

A continuous gas-flow fixed bed glass reactor (14 mm i.d.) was used for the catalytic test. The measurement without an exchange reaction was first carried out by a CH$_4$ pulse (0.6 cm$^3$) without a catalyst in a He (50 cm$^3$ min$^{-1}$) stream. The NiO773 or NiO1373 (0.127 g) was placed in the reactor and treated with a D$_2$ stream (mixture of D$_2$ (3 cm$^3$ min$^{-1}$) and He (50 cm$^3$ min$^{-1}$)) at an atmospheric pressure for 1 h at 623 K. The reduction of NiO773 and NiO1373 was confirmed by XRD (Shimadzu XD-3A) experiments. The resulting reduced nickel catalysts were designated Ni773 and Ni1373, respectively. The H/D exchange reaction was carried out in the same reactor by a CH$_4$ pulse (0.6 cm$^3$) under a continuous gas flow of a mixture of D$_2$ (3 cm$^3$ min$^{-1}$) and He (50 cm$^3$ min$^{-1}$) at 573 K or 613 K. A small amount of the outlet flow was leaked continuously through a silica capillary tube (0.05 mm i.d. × 2.5 m) into a Q-mass spectrometer (PFEIFFER Vacuum Prisma QMS 200) for isotopic analysis. 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$_2$O at m/z = 18). The second exchange reaction was carried out at a 45 min interval for checking the stability of the catalyst. From the beginning of the first run to the end of the second run, the gas flow of D$_2$ and He was maintained. As the results of the first run and the second run were almost the same, the catalysts were stable during the experiment and the results of the first run are shown in this paper.

### 2.4. Determination of BET surface area

The BET surface area of the reduced nickel catalysts was measured using a Micromeritics Gemini 2375 by N$_2$ adsorption at 77 K.

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

When the determination of the isotopologues of methane was carried out by quadrupole mass spectroscopy, the methane isotopologues CH$_i$D$_{4-i}$ ($i$ = 4–0) have their own characteristic fragmentation patterns, which 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 this 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 [14].

The composition of the isotopologue $P$(CH$_i$D$_{4-i}$) ($i$ = 4–0) after the exchange reaction was calculated using the peak area
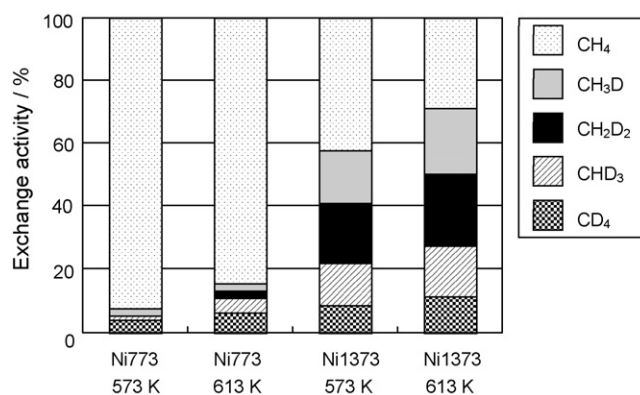


**Fig. 1.** H/D exchange activity over the reduced Ni catalysts.

$S$(CH$_i$D$_{4-i}$) of its corrected intrinsic parent ion (Eq. (1))

$$P(CH_4) = 100 \times S(CH_4)/S_{sum}$$
$$P(CH_3D) = 100 \times S(CH_3D)/S_{sum}$$
$$P(CH_2D_2) = 100 \times S(CH_2D_2)/S_{sum}$$
$$P(CHD_3) = 100 \times S(CHD_3)/S_{sum}$$
$$P(CD_4) = 100 \times S(CD_4)/S_{sum}$$
$$S_{sum} = S(CH_4) + S(CH_3D) + S(CH_2D_2) + S(CHD_3) + S(CD_4)$$

(1)

## 3. Results and discussion

### 3.1. The H/D exchange activity and the composition of the exchanged species over the reduced nickel catalyst

Fig. 1 shows the H/D exchange activity over Ni773 and Ni1373 at 573 K and 613 K. The exchange activity ($P$(CH$_3$D) + $P$(CH$_2$D$_2$) + $P$(CHD$_3$) + $P$(CD$_4$)) of Ni1373 was much higher than that of Ni773. Considering the surface areas of Ni773 (5.8 m$^2$ g$^{-1}$) and Ni1373 (4.0 m$^2$ g$^{-1}$), the activity per Ni surface area of Ni1373 was 11.0 times that of Ni773 at 573 K, and 6.6 times at 613 K. Fig. 2 shows the percentage of each exchanged species in all the exchanged species over Ni773 and Ni1373 at 573 K and 613K. For the reaction over Ni773, the percentage of CH$_2$D$_2$ was small compared to the other isotopologues. At 613 K, the percentage of CH$_3$D and CD$_4$ decreased and that of CH$_2$D$_2$ and CHD$_3$ increased compared to the results at 573 K. On the other hand, for the reaction over Ni1373, the composition of CH$_2$D$_2$ was much greater than the reaction over Ni773. The composition of each methane isotopologue was almost not changed by the increase in the reaction temperature from 573 K to 613 K.
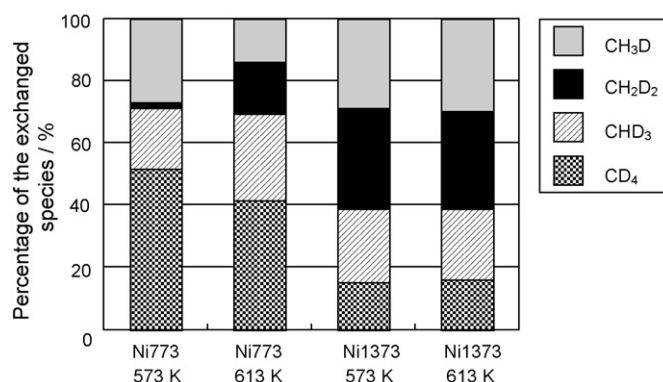


**Fig. 2.** Composition of the exchanged species over the reduced Ni catalysts.

As methane decomposition is known to be a structure-sensitive reaction and the reactivity was reported as Ni(1 0 0) > Ni(1 1 1) [15], the H/D exchange of methane would also be a structure-sensitive reaction and the reactivity would be Ni(1 0 0) > Ni(1 1 1). The present results indicate that the ratio, Ni(1 0 0)/Ni(1 1 1), on Ni1373 would be greater than that on Ni773, if one could assume that the surface was composed of low index planes, i.e. (1 0 0) and (1 1 1). As the nickel crystallite size of Ni773 was smaller than that of Ni1373 (Ni773: 28 nm, Ni1373: 68 nm) [16], the crystallinity of Ni773 was lower than that of Ni1373, therefore, the Ni773 would have a greater lattice disorder than Ni1373. The studies of the effects of lattice disorder and/or step sites necessary for the more precise evaluation of the exchange activity are currently underway. However, if the contribution of the lattice disorder and/or step sites for the H/D exchange reaction were significant, the activity of Ni773 seemed to be greater than that of Ni1373. In this study, as Ni1373 had a higher exchange activity than Ni773, the Ni(1 0 0)/Ni(1 1 1) ratio rather than the step sites would mainly control the exchange activity on Ni1373 and Ni773.

On the other hand, it was reported that NiO(1 0 0) was reduced to Ni(1 0 0) by hydrogen at 623 K [17]. As Ni1373, which would have a higher Ni(1 0 0)/Ni(1 1 1) ratio, was prepared by the reduction of NiO1373 by hydrogen at 623 K, NiO1373 could also predominantly have the NiO(1 0 0) face. As nickel oxide is a crystal like NaCl, the Ni(1 0 0) face has the lowest surface energy density ($\gamma$). Based on the first approximation, the equilibrium form of the crystal is a hexahedron, which consists of (1 0 0) faces. When $\gamma$(1 1 1) is smaller than $\sqrt{3}\gamma$(1 0 0), (1 1 1) appears on the surface of the crystal [18]. As the NiO1373 was calcined at high temperature, it is reasonable to assume that the crystal would be relatively stable and have a high Ni(1 0 0)/Ni(1 1 1) ratio.

For the already reported H/D exchange reaction over the Ni catalyst [7,19], the initial distributions of the exchanged species were almost the same as the results obtained with Ni773 in the present study, that is, the composition of $CH_2D_2$ was low, while those of $CH_3D$ and $CD_4$ were high. The nickel catalysts reported in the literature were prepared by the direct reduction of nickel salt precursors at 673 K to 923 K [9,20,21] or prepared through the reduction of nickel oxide, which was calcined at 673 K, on $SiO_2$ [12]. It is assumed that the nickel catalysts in the literature and Ni773 could predominantly contain Ni(1 1 1), which is the most stable plane for the fcc crystal. The features of the exchanged species like Ni1373 in this study were much different from the already reported results over the Ni catalyst. 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. Based on the results of the present study, the surface of the Ni catalyst, Ni(1 0 0)/Ni(1 1 1), could be controlled by the calcination temperature of the NiO precursor.

### 3.2. Time course of the exchanged species in the pulse experiment

Fig. 3 shows the change in the ion current of each isotopologue over Ni773. Fig. 4 shows that over Ni1373. Both results were obtained by the reaction at 573 K. As for the reaction over Ni773, the $CH_3D$ signal first reached a peak, and those of the other isotopologues were delayed. On the other hand, as for Ni1373, the signals of $CH_3D$ and $CH_2D_2$ simultaneously reached peaks, while the signals of $CHD_3$ and $CD_4$ were broad, and particularly, the signal of $CD_4$ had two peaks.

Two mechanisms for the H/D exchange reaction of $CH_4$ were proposed, that is, a stepwise exchange and a multiple exchange [9]. For the stepwise exchange, one hydrogen atom in methane is exchanged at each residence on the surface. For the
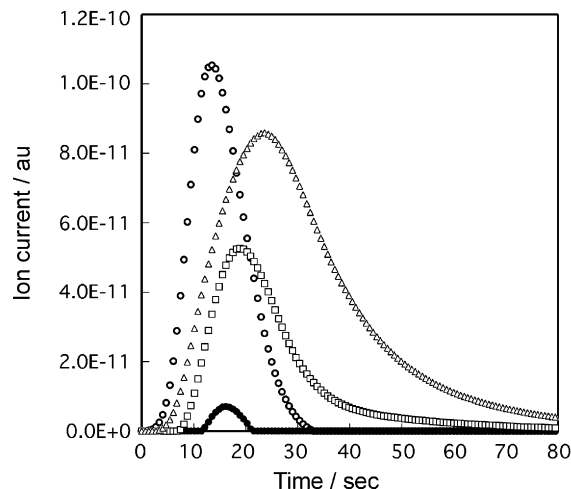


**Fig. 3.** Change in the ion current of each isotopologue over Ni773: (○) $CH_3D$; (●) $CH_2D_2$; (□) $CHD_3$; and (△): $CD_4$.

multiple exchange, more than one hydrogen atoms in methane are exchanged in one residence. Considering the features of the exchanged species over Ni773 as mentioned in Section 3.1 (composition of $CH_2D_2$ was small), the exchange reaction over Ni773 would proceed with the same mechanism as reported in the literature [9]. As $CH_3D$ is obtained by a single step (stepwise exchange), the signal of the ion current would first reach a peak. The $CH_2D_2$, $CHD_3$, and $CD_4$ would be obtained by the multiple exchange, and the desorption of these isotopologues would be delayed compared to that of $CH_3D$. On the other hand, for the exchange reaction over Ni1373, $CH_3D$, $CH_2D_2$, $CHD_3$, and $CD_4$ began to be produced at almost the same time. These features were quite different from the results obtained on Ni773. As Ni1373 has a high exchange activity, these results could be due to the repetition of the stepwise exchange, that is, readsorption and further exchange of the partly deuterated species. For the $CD_4$ signal, the peaks observed at about 20 s from the injection of the pulse could be due to the contribution of the multiple exchange. Based on the results in Figs. 3 and 4, it is suggested that the exchange reaction would proceed via a different mechanism on Ni773 and Ni1373.
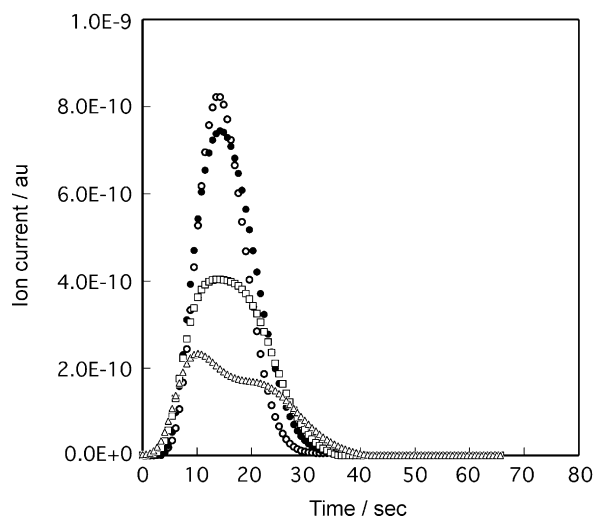


**Fig. 4.** Change in the ion current of each isotopologue over Ni1373: (○) $CH_3D$; (●) $CH_2D_2$; (□) $CHD_3$; and (△) $CD_4$.

## 4. Conclusion

The H/D exchange reactions of methane in a deuterium stream in a fixed bed flow reactor were studied over the reduced nickel catalyst. The Ni1373, prepared from the nickel oxide calcined at 1373 K, has a higher activity than the Ni773 prepared from the nickel oxide calcined at 773 K. This could be attributed to the ratio of the Ni(1 0 0) to Ni(1 1 1). As the Ni1373 could have a higher Ni(1 0 0)/Ni(1 1 1) ratio, Ni1373 had a higher activity than Ni773.

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