Isolation of intermediate compounds of catalytic reactions on single crystal surfaces

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A key intermediate of the methanation reaction on nickel catalyst is a carbidic carbon. Accumulated carbidic intermediates on Ni(100) gives a p(2×2) p4g structure, whereas that on Ni(111) is too complex to be solved. A single domain carbide layer accidentally on Ni(111) allowed us to solve the structure explicitly. Comparison of the carbide layer on Ni(100) and that on Ni(111) showed that the carbon atoms are arranged by forming the same ordered structure. The carbide layers prepared on Ni(100), Ni(111) and Ni(110) have almost equal decomposition temperatures. Consequently, we can conclude that the same overlayer compound is formed on the three surfaces. Furthermore, the hydrogenation of the p4g carbide on Ni(100) occurs at almost equal rate to the turnover frequency of the catalytic methanation reaction. The structure insensitive methanation reaction on Ni(100), Ni(111) and Ni(110) is responsible for the same intermediate compound on these surfaces.

The same strategy was applied to the reaction of NO with H_2 on Pd(100), Rh(100) and Pt-Rh(100) surfaces, and a $c(2\times2)$-N overlayer was isolated on each of these. The hydrogenation of the isolated $c(2\times2)$-N produced predominantly NH species, which indicates slow NH species hydrogenation.

Keywords: Surface carbide; surface nitride; intermediates; $NO+H_2$ reaction; methanation reaction; catalysis on single crystal

1. Introduction

A catalytic reaction is in general composed of several elementary steps as described by $R \rightarrow X_1 \rightarrow X_2 \rightarrow X_i \rightarrow P$, where the reaction intermediates (X_i) are formed steadily on surface during catalysis. A final goal of the mechanismistic study of the catalysis is to elucidate the structure and reactivity of the key intermediates. For this purpose, single crystal surface is suitable for the structural identification of intermediates because the accumulated intermediates will make an ordered arrangement. When one step is markedly slow compared to the others, accumulation of the key intermediates will be attained on the surface. As a result we can clarify the structure and reactivity of the isolated intermediates.

A good example is the methanation reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$, on Ni catalyst, where the key intermediate is carbidic carbon. When the hydrogenation of carbidic carbon is rather slow compared to the deposition of carbidic intermediate, the surface will be covered with a carbide layer. The same strategy was applied to the reaction of NO with H_2, $NO + H_2 \rightarrow N + H_2O$, on Pd(100), Rh(100) and Pt-Rh(100) surfaces. It is well known that Pd, Pt and Rh are not only inert for the dissociative adsorption of N_2 but also make no bulk nitrides. However, these metals are active for the reaction of NO with H_2 which may proceed through N intermediates. Accordingly, when the removing processes of N intermediates are slow compared to the deposition of N, the N intermediates will be accumulated on the surface, and the structure and reactivity of the intermediate can be clarified.

2. Results and discussion

1. STRUCTURE AND REACTIVITY OF CARBIDIC INTERMEDIATES ON Ni(100), Ni(111) AND Ni(110) SURFACES

Methanation reaction on nickel catalyst, $CO + 3H_2 \rightarrow CH_4 + H_2O$, occurs via carbidic intermediates [1,2], where the amount of carbidic intermediates on the surface is controlled by a dynamical balance of the deposition and the hydrogenation of carbidic intermediate [3,4]. Consequently, the amount of carbidic carbon on the catalyst will increase as the hydrogen pressure is decreasing, and the disproportionation reaction of CO, $CO + CO \rightarrow C + CO_2$, may correspond to a limit of the zero pressure of H_2. Fig. 1(a) and (b) show the LEED patterns of the carbidic carbon overlayer formed on Ni(100) and Ni(111), respectively. The LEED pattern (a) on Ni(100) is a typical $p(2 \times 2)$ p4g structure with characteristic missing spots [5]. Compared to this, pattern (b) on Ni(111) is very complex. The methanation reaction, however, takes place in almost equal rate on either Ni(100) and Ni(111). If the carbidic overlayer on these two surfaces would correspond to the intermediates accumulated on the catalysts, a question may arise why is the methanation reaction structure insensitive although the LEED patterns are so different for the two surfaces. To solve this question, it is indispensable to elucidate the structure and the reactivity of carbidic carbon overlayer on Ni(100) and Ni(111). For this purpose, we prepared one monolayer carbide on Ni(100) and Ni(111) surfaces by annealing the single crystal Ni disks in UHV chamber. It was confirmed that the carbide layer prepared by the segregation has the same structure as that obtained by the disproportionation reaction. Furthermore, the carbide overlayer on Ni(100) undergoes the hydrogenation reaction in almost equal rate to the turn-over frequency of the methanation reaction. This fact may prove that the carbide overlayer corresponds to the carbidic intermediates accumulated on the surface.

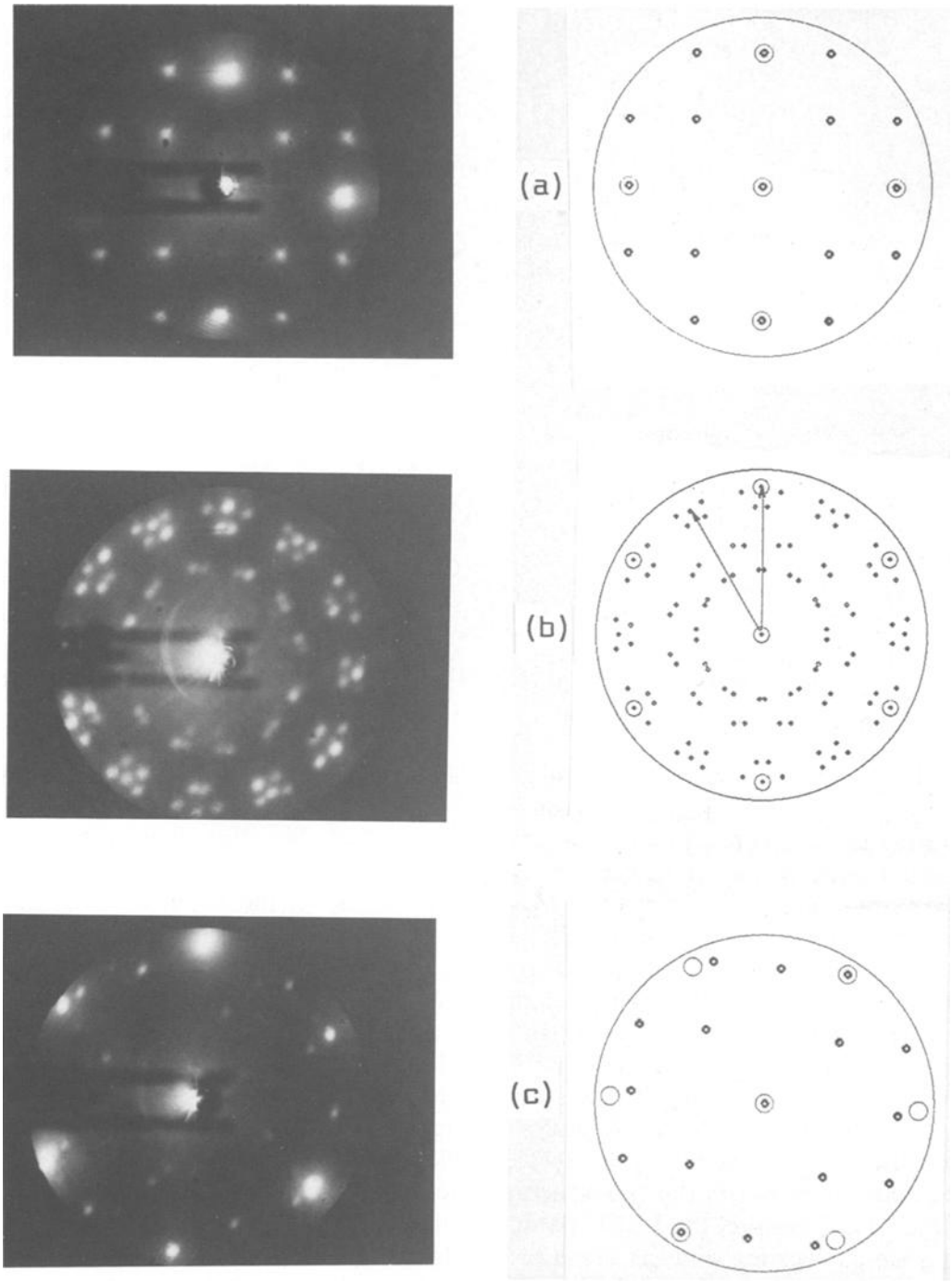

Fig. 1. LEED patterns of carbide overlayer. (a) p4g carbide layer on Ni(100); (b) full domain carbide layer on Ni(111); (c) a single domain carbide layer on Ni(111).

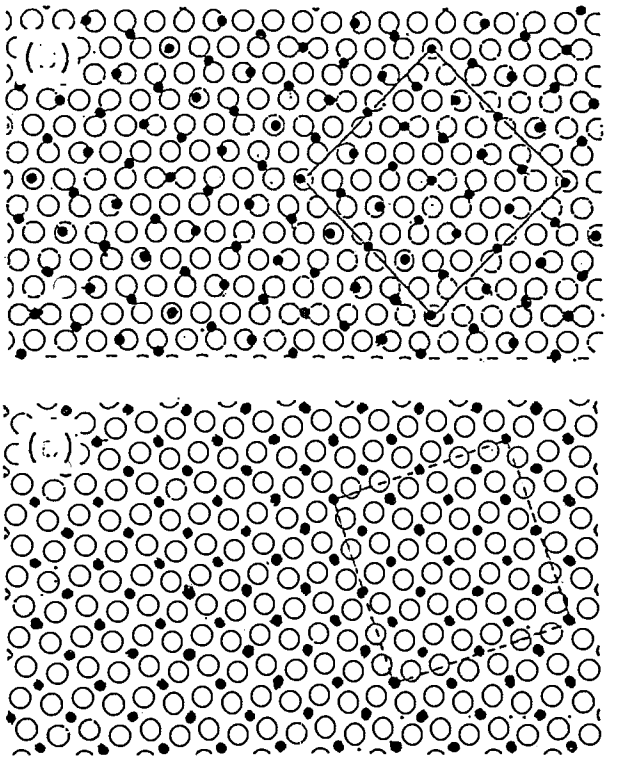

Fig. 2. (a) C atoms of carbide layer on Ni(111); (b) p(2×2) p4g carbide on Ni(100).

The LEED pattern of the carbide on Ni(111) is too complex to be solved, but we accidentally found the formation of a single domain carbide layer on Ni(111) during the segregation of carbon at 520 K in UHV. Fig. 1(c) shows a typical LEED pattern. As a result, the structure of the carbide layer on Ni(111) was explicitly solved [6], which was found to be equal to the (/39 × /39)R16.1 structure given by McCarroll [7] by the computer simulation. By computer simulation, however, it is difficult to give a suitable C/Ni ratio for this model. Therefore, we carefully compared the C/Ni ratio for one monolayer carbide prepared on Ni(100) and Ni(111) surfaces and found that the C_{KVV}/Ni_{LMM} has almost equal value for Ni(100) and Ni(111) surfaces. Based on these results, a new model shown in fig. 2(a) was derived, where the ratio of C/Ni = 20/40 = 0.444. In this figure, the Ni atoms are tentatively described at the original position. If this new model on Ni(111) is piled upon the p(2 × 2) p4g carbide on Ni(100) shown in (b), the two structures are almost completely overlapped each other. Furthermore, the LEED pattern of the single domain carbide on Ni(111) has similar missing spots as the p(2 × 2) p4g carbide on Ni(100) shows.

Consequently, we conclude that the carbide overlayer on Ni(111) is the same compound as the p(2 × 2) p4g carbide on Ni(100). This conclusion was proved

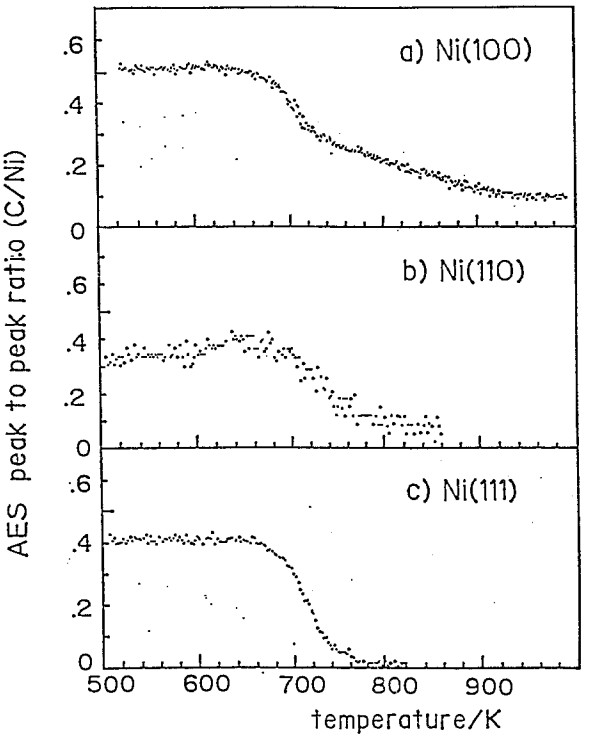

Fig. 3. Thermal decomposition of carbide layer on Ni(100), Ni(111) and Ni(110).

by measuring the decomposition temperature of the carbide layers prepared on Ni(100) and Ni(111). As shown in fig. 3, not only the carbide layer on Ni(100) and Ni(111) but also that on Ni(110) undergoes the decomposition at the same temperature of 685 K, where the carbon atoms formed by the decomposition are rapidly diffused into the bulk of Ni and a clean surface is recovered. From these results, we conclude that the methanation reaction on Ni catalyst occurs via the same intermediate compound, which is the reason why Ni(100), Ni(111) and Ni(110) give an equal activity for the methanation reaction.

2. STRUCTURE AND REACTIVITY OF N-INTERMEDIATES ON Pd(100), Rh(100) AND Pd-Rh(100)

The same strategy was applied to the reaction of NO with H_2 which may proceed via N intermediates, $NO + H_2 \rightarrow N + H_2O$. In fact, the accumulation of N intermediates was attained on Pd(100), Rh(100) and Pt-Rh(100) [8,9,10], but not on Pt(100) [11]. An interesting fact was that the N atoms on Pt-Rh(100) surface give a $c(2 \times 2)$ structure although no accumulation of N atoms occurs on Pt(100), that is, the Pt and Rh atoms have similar affinity to N atoms [12]. When the $c(2 \times 2)$-N overlayer is heated in H_2, the hydrogenation reaction takes

place. Provided that the hydrogenation of N undergoes consecutively, $N \rightarrow NH \rightarrow NH_2 \rightarrow NH_3$, either NH or NH_2 species would be predominantly formed depending on the slow step of the hydrogenation reaction. When the $c(2 \times 2)$-N surface is exposed to H_2 at 400 K, an intense energy loss peak appeared at 3190–3200 cm^{-1}. The formation of NH_x species was proved to be reversible at around 400 K [9,13], and the value of x was deduced to be unity from the pressure dependence of the peak intensity, that is, the following preequilibration is established during the hydrogenation reaction [13].

$$N + H_2 \overset{\text{fast}}{=} NH \xrightarrow{\text{slow}} NH_2 \rightarrow NH_3.$$

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