# High Catalytic Activity of Ion-Exchanged Nickel on Carboxymethylated Wood Char in Methanation of Carbon Monoxide

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Catalytic behavior of ion-exchanged nickel on carboxymethylated wood char in methanation of carbon monoxide was examined at 300-500 °C. Its activity was higher than those of nickel/activated carbon and nickel/Y-zeolite. The result demonstrated that carboxymethylation of wood is an effective modification for high dispersion of metallic nickel particles on the char.

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Techniques for achieving good dispersion of metal particles on carbonaceous materials are important for the preparation of highly functional carbon-metal composites, including high performance carbon supported metal catalyst.[1] Several methods for this purpose have been developed with various types of carbon and metal.[2,3] However, there is no report to use wood in stead of charcoal or activated carbon as the support or the matrix. Recently, the first author Suzuki found extremely high reactivity of carboxymethylated wood char with ion-exchange nickel and iron in the hydrogasification.[4] This will be a valuable piece of information that good dispersion of metal particles on carbon can be realized through carboxymethylation of wood as the modification pretreatment. The present work describes high catalytic activity of such a nickel-loaded wood char in the titled reaction on account of the high dispersion of metallic nickel particles.

Powdered birch (*Betula ermanii Cham*, 0.25-0.50 mm in diameter) having carboxyl content of 7 mmol/100 g was carboxymethylated with $ClCH_2COOH$ and NaOH in 80% EtOH at 60 °C for 2 h, according to the procedure by Nakano et al.[5] In this reaction, OH groups of cellulose, a major component of wood, are converted into $OCH_2COOH$, so that the modified wood possesses a .large amount of carboxyl group as cation-exchangeable site. Two carboxymethylated woods with carboxyl contents of 280 and 140 mmol/100 g, abbreviated as $CM_H$ and $CM_L$, respectively, were prepared. After washing them with 1N HCl followed by deionized water, ion-exchange nickel was introduced by percolation using a solution of $(CH_3COO)_2Ni•4H_2O$, as previously described.[4] The amount of nickel was adjusted to about 7wt % in char. For comparison, the nickel salt was also loaded on to activated carbon (AC, Wako Pure Chemicals) and NaY zeolite (Toyo Soda) with equal size to the wood powder by wet impregnation and the same ion-exchange method as above, respectively. The nickel-loaded $CM_H$, $CM_L$, and AC were heat-treated in a flow of nitrogen at 600 °C for 1 h to prepare chars (designated N-$CM_H$, -$CM_L$, and -AC). NiY zeolite (NiY-Z) obtained was calcined at 400 °C for 16 h and then *in situ* reduced in a hydrogen flow at 450 °C for 16 h, as described by Bajpai et al.[6] The reduction treatment was also made for N-$CM_H$, -$CM_L$, and -AC, and the resulting chars were denoted by the prefix "H-". All these samples were characterized by the average crystallite size of metallic nickel ($L_{Ni}$) and specific surface area ($S_A$), as given elsewhere.[3,7] For chars, the CHO composition also was determined by ultimate analysis. Methanation of carbon monoxide was all conducted in a fixed-bed downflow reaction apparatus, where a Pyrex-tube reactor (8mm i.d.) was charged with an equal volume (1.8 cm in height) of each catalyst vacuum dried overnight at 50 °C. The weight packed was about 0.12 g for chars and 0.50 g for NiY-Z. A mixture of hydrogen (99.99% purity) and carbon monoxide (99.95% purity) in the volume ratio of 3:1 as the reactant gas was fed at the total flow of 120ml (STP) $min^{-1}$ to the reactor being held at 150 °C. The reactor was then raised at the rate of $10°Cmin^{-1}$ up to 500 °C for evaluation of the catalytic activity by temperature-programmed method. The product stream, after removal of water condensed in a cold trap, was withdrawn at regular intervals to determine the concentration of methane as the only product detected by gas chromatography using a flame ionization detector and a column of Porapak Q. Blank runs were carried out with a hydrogen flow of 90 $mlmin^{-1}$ to check the methane evolution from catalyst. All runs were duplicated to examine the reproducibility. The average value of any data point was ± 10% or less, and thus, it was adopted as reliable data.

Figure 1 compares the catalytic behavior in the temperature range of 300-500 °C among all the catalysts. Table 1 summarizes their properties and weight losses after the activity measurement. The conversion profile for four CM chars was obtained by subtracting small methane evolved in the blank test from the measured methane production curve with the reactant gas. For N- and H-AC, as well as NiY-Z, correction was not made because no methane was produced in their blank runs.

N-AC had a negligibly small catalytic ability, although no other species than nickel metal was detected by X-ray diffraction (XRD). This was also the case with H-AC. Such extraordinarily low activities of both AC would be attributable to the large amount of nondissociative carbon monoxide adsorbed on metallic nickel[8] rather than the poor dispersion of the catalyst indicated by their large $L_{Ni}$. As would be expected, N-$CM_L$ and -$CM_H$ with much smaller $L_{Ni}$ compared to N- and H-AC exhibited substantially catalytic activities. Only about 2% weight loss for either N-CM confirmed no great methane formation from the solid part. It was furthermore evident that the activity of N-CM was not handicapped by the smaller $S_A$ than those of AC. Although wood impregnated with nickel acetate and nickel nitrate also can produce nickel metal dominantly by the action of hydrogen and carbon monoxide evolving during the pyrolysis,[4,7] the formation of the fine particles is characteristic of carboxymethylated wood with ion-exchanged nickel.[4] Highly dispersed metallic nickel on N-CM thus formed would have the ability to dissociate carbon monoxide adsorbed and, therefore, act as the active site for the reaction. N-$CM_H$ surpassed N-$CM_L$ in the activity regardless of their equal $L_{Ni}$. This can be explained by their different amounts of surface nickel; larger ion-exchangeability of wood will be favorable for more abundant production of finer metal particles[4], most of which would not be detected by XRD. $L_{Ni}$ for both N-CM was unchanged before and after the activity test, but the catalytic activity would raise by increasing surface nickel during the methanation reaction. This

**Table 1.** Properties and weight loss after the activity test for various nickel-loaded catalysts

| Sample[a] | Ni content (wt %) | $L_{Ni}$ [b] (Å) | $S_A$ [c] ($m^2g^{-1}$) | C (wt %) | H (wt %) | Ash[d] (wt %) | O[e] (wt %) | Weight loss (%) |
|---|---|---|---|---|---|---|---|---|
| N-$CM_H$ | 7.0 | 50 | 440 | 85.6 | 2.4 | < 0.1 | 5.0 | 2.0 |
| N-$CM_L$ | 6.6 | 50 | 450 | 83.0 | 3.1 | < 0.1 | 7.2 | 2.2 |
| N-AC | 7.0 | 160 | 710 | 87.5 | 1.8 | 0.1 | 3.7 | 1.5 |
| NiY-Z | 7.0 | < 40 | 460 | – | – | – | – | 9.8 |
| H-$CM_H$ | 7.2 | 40 | 400 | 85.8 | 2.6 | < 0.1 | 4.4 | 4.1 |
| H-$CM_L$ | 6.8 | 40 | 440 | 84.3 | 2.8 | < 0.1 | 6.1 | 4.2 |
| H-AC | 7.2 | 150 | 690 | 87.7 | 1.5 | 0.1 | 3.6 | 2.5 |

[a] See the text. [b] Calculated from the linewidth of the X-ray diffraction at 2θ = about 45°.
[c] By the BET method using $CO_2$ as an adsorbent at −78°C.
[d] Incombustible residue at 600°C, except catalyst. [e] By difference.

was due to the incomplete reduction into metallic nickel by the carbonization of CM in nitrogen. A rapidly increased conversion at temperatures above 450 °C for N-$CM_L$ would be a good indication of the new appearance of active nickel metal. N-$CM_H$ gave lower conversions than NiY-Z in the whole temperature range, probably because of the above-mentioned insufficient reduction and the larger $L_{Ni}$ of the former. However, the difference in the conversion observed between the two catalysts was not so much as would predict from their different amounts of nickel (the amount of nickel for NiY-Z was about 4 times those for N-CM char at the equal packed volume). N-$CM_H$ was thus not inferior to NiY-Z in the activity per unit nickel weight.

Both H-CM excelled NiY-Z in the conversion at around 370-450 °C, as the result of the hydrogen-treatment. The weight loss of 4 % for both H-CM was clearly too small to be responsible for the markedly promoted methane production. H-$CM_H$ exhibited larger activity than H-$CM_L$ at below 400 °C to reconfirm the advantage of larger cation-exchange capacity. However, the conversion of potential surface nickel on N-CM into real surface nickel on H-CM would not be the only effect of the reduction. The reduction caused about 4% weight decrease of each N-CM to produce the corresponding H-CM with a little higher nickel content and smaller $L_{Ni}$. This would reflect the emergence of finer nickel particles from inside the char grain of N-CM by scraping the outer surface. Such an additional increment of surface nickel for H-CM would be also significant for enhancing the catalytic activity. $L_{Ni}$ of either H-CM was almost equal before and after the activity test, indicating stable surface nickel without serious agglomeration. Thus, the chief reason for the gradual drop of conversion observed at above 400 °C would be not the loss of activity but carbon deposition on surface nickel from adsorbed reactant or product, or both. The latter phenomenon relating to the thermodynamic limitation of the methanation reaction should be inevitable when the conversion attains to a high level like the present case did. The character of H-CM with finely dispersed, thermostable metallic nickel particles leading to the high catalytic activity will demonstrate that carboxymethylation of wood followed by introduction of ion-exchangeable metal is a promising method for the preparation of metal-carbon complex materials.

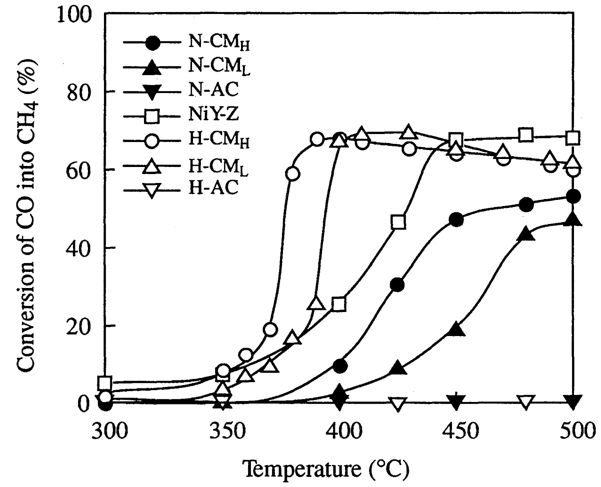

**Figure 1.** Catalytic activity for various nickel-loaded catalysts.

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