Promotion in Activity and Stability of Nickel-Magnesia Solid Solution Catalyst by Structural Rearrangement via Hydration for Reforming of CH_4 with CO_2

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It was found that the water treatment of $Ni_{0.03}Mg_{0.97}O$ solid solution catalyst promotes the catalytic activity and stability for CO_2 reforming of CH_4 and that this promoting effect is attributed to the structural rearrangement of solid solution via the formation of nickel and magnesium hydroxides.

Reforming of CH_4 with CO_2 to synthesis gas is an important reaction in terms of the chemical conversion of natural gas to liquid fuels.[1,2] Recently authors found that reduced $Ni_{0.03}Mg_{0.97}O$ solid solution showed promising activity, excellent stability and high resistance to carbon deposition for this reaction.[3,4] However, the low activity and deactivation due to the oxidation of reduced Ni species was observed on this catalyst when the reaction was carried out under low temperature and high space velocity.[5] As well known, the surface structure as well as the activity of the basic oxide MgO supported catalyst is strongly dependent upon the preparation method, starting material and calcination temperature.[6-8] In the case of our NiO-MgO solid solution catalyst, the precursor is a mixed carbonate of nickel and magnesium. In this study, we modified NiO-MgO solid solution catalyst by water treatment, and found a significant promotion in both catalytic activity and stability.

NiO-MgO was prepared by coprecipitating method using $Ni(C_2H_3O_2)_2$, $Mg(NO_3)_2$ and K_2CO_3 as starting materials.[5] After the precipitate was filtered and washed with hot water, it was dried at 393 K overnight, followed by calcining in air at 773, 973 and 1223 K for 10 h respectively. In this paper, we designate these catalysts 773Ni3, 973Ni3 and 1223Ni3, in which the prefix numeral (773, 973 and 1223) represents the calcination temperature and the suffix numeral (3,10) represents the Ni content in the form of Ni/(Ni+Mg) mol%. The modified solid solution catalyst (H_2ONi3) was made by treating 1223Ni3 with distilled water (10 ml-water /g-catalyst) and then drying at 393 K overnight. MgO which was prepared by the same method as 1223Ni3 was impregnated with acetone solution of $Ni(C_5H_7O_2)_2$ in order to obtain a MgO supported Ni metal catalyst (3% Ni/MgO) for comparison. The nickel loading of this supported catalyst was the molar ratio Ni/(Ni+Mg) = 0.03. The CH_4-CO_2 reaction was carried out in a fixed bed flow type reactor made of quartz tube. The catalyst was reduced *in situ* in H_2 flow at 1123 K for 0.5 h. The typical reaction conditions are: reaction temperature 773 or 1023 K, total pressure 0.1 MPa, CH_4/CO_2 = 1/1 or 2/1, W/F = 0.1 gh/mol, weight of catalyst 0.05 g. The number of active Ni site was determined by O_2 chemisorption at room temperature assuming $O_{ad}/Ni_{surf} = 1$. The amount of O_2 adsorption was measured by volumetric method. Bulk phases of catalyst were identified by X-ray diffraction using CuK_α radiation. Temperature-programmed hydrogenation (TPH) was used to evaluate the deposited carbon formed during the CH_4-CO_2 reaction.[9]

It has been known in the previous paper that 1223Ni3 has only NiO-MgO solid solution phase.[4] Whereas, $Ni(OH)_2$ and $Mg(OH)_2$ are formed through water treatment from XRD spectra of H_2ONi3(Figure 1), and thermogravimetric study indicated that about 30 mol% of $Ni_{0.03}Mg_{0.97}O$ solid solution is converted into hydroxides. It is obvious from Figure 1 that 773Ni3 and 973Ni3 exhibit broader peaks than those of 1223Ni3 at almost the same diffraction angles. In addition, the peak width decreases with the calcination temperature. This is due to the poor crystallization by lower temperature calcination. After reduction, no peaks attributed to Ni metal is observed on 1223Ni3, 973Ni3 and H_2ONi3, while they are present on 3% Ni/MgO, 773Ni3 and 1223Ni10 indicating the formation of large Ni metal particles on the latter catalysts. For the reduced H_2ONi3, the similar XRD pattern to that of 1223Ni3 is observed. Clearly, the hydroxides formed during the water treatment are decomposed into NiO-MgO again in the pretreatment procedure.

Table 1 illustrates the properties of various catalysts. BET surface area of reduced H_2ONi3 was found to be 39 m^2/g nearly twice as much as that of 1223Ni3 (19 m^2 / g). This indicates that a structural rearrangement of 1223Ni3 solid solution takes place via hydration. It can be seen that the low calcination temperature and the increased Ni loading promoted the

Table 1. Catalytic properties of various nickel-magnesia catalysts for CH_4-CO_2 reforming

Catalyst	r_i[a] /μmolg^{-1}s^{-1}	r_t[b]/r_i	S[c] /m^{2}g^{-1}	$O_{2\,(298\,K)}$[d] /μmolg^{-1}	$O_{2\,(873\,K)}$[e] /μmolg^{-1}	$O_{2\,(298\,K)}/O_{2\,(873\,K)}$	D_{red}[f] /%	TOF[g] /s^{-1}
1223Ni3	40	0.83	19	5.0	10.5	0.48	3	4.0
H_2ONi3	200	0.99	39	11.2	54.5	0.21	15	8.9
3% Ni/MgO	160	0.86	16	8.8	226.5	0.04	62	9.1
973Ni3	160	0.99	42	23.6	146.7	0.16	40	3.4
773Ni3	258	0.93	53	24.3	212.2	0.11	59	5.3
1223Ni10	160	0.97	30	30.3	130.4	0.23	11	2.6

[a]Initial CO formation rate. [b]CO formation rate after 1 h on stream. [c]BET surface area measured by N_2 adsorption at 77 K after reduction at 1123 K for 0.5 h. [d]Amount of O_2 adsorption at room temperature. [e]Amount of O_2 adsorption at 873 K. [f]Reduction degree estimated by O_2 up-take at 873 K according to Ni^0/Ni_{total} ($Ni^0 + 1/2O_2 \rightarrow NiO$). [g]On the basis of O_2 up-take at 298 K, assuming $O_{ad}/Ni_{surf} = 1$.

reducibility. This tendency is in agreement with our XRD results and those reported formerly.[10] The increase in reduction degree from 3 to 15% by hydration allows us to propose that 1223Ni3 and H_2ONi3 may have different structures. It has been suggested that significant structural change accompanying the transformation of the hexagonal brucite $Mg(OH)_2$ to the cubic MgO may allow entry of Ni^{2+} ions at defects or imperfections formed at the moving phase boundary during dehydration.[11]

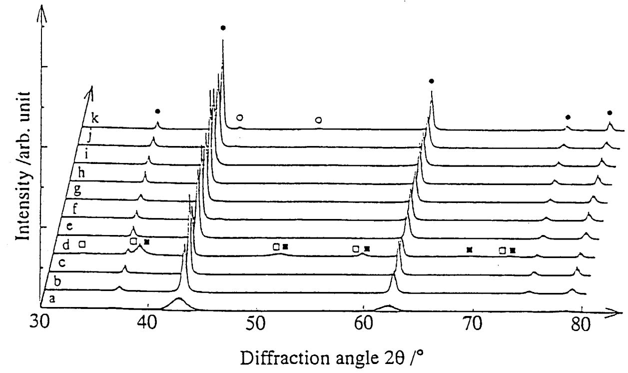

Figure 1. X-ray diffraction patterns of various nickel-magnesia catalysts after calcination and reduction.
Before reduction: (a) 773Ni3, (b) 973Ni3, (c) 1223Ni3, (d) H_2ONi3, (e) 1123Ni10.
After reduction: (f) 773Ni3, (g) 973Ni3, (h) 1223Ni3, (i) H_2ONi3, (j) 1123Ni10, (k) 3% Ni/MgO.
Reduction pretreatment: H_2 100%, 50 ml/min, 1123 K, 0.5 h.
● NiO/MgO solid solution, ○ Ni, □ $Ni(OH)_2$, ■ $Mg(OH)_2$.

The activity of CH_4 -CO_2 reaction under CH_4/CO_2 = 1/1 and 773 K at initial stage and after 1 h versus amount of deposited carbon estimated from the peaks above 873 K in the TPH profiles is plotted in Figure 2. The result gives the activity order per g-catalyst: 773Ni3 > H_2ONi3 > 3% Ni/MgO ≈ 973Ni3 ≈ 1223Ni10 > 1223Ni3. Although the clear relation of carbon deposition with catalytic activity and stability was not established at all, it was found that H_2ONi3 had considerably high activity and stability with high resistance to carbon deposition. Comparing the characteristic data listed in Table 1, we found that larger amount of carbon and lower stability were observed on the catalysts (3% Ni/MgO, 773Ni3) which have higher reduction degree and lower dispersion ($O_{2(298\ K)}/O_{2(873\ K)}$). It is suggested that appropriately strong metal-support interaction and small Ni particles are favorable to get a desirable catalyst for CH_4-CO_2 reaction. Figure 3 shows the alteration of activity as a function of time on stream over H_2ONi3, 3% Ni/MgO and 1223Ni3 catalysts under the severe condition of $CH_4/CO_2/N_2$ = 2 /1 /1 and 1023 K. It is noted that in this case, deactivation occurred on each catalyst. Nevertheless, H_2ONi3 is still the most active and stable one among them. The deactivation on 1223Ni3 has been reported to be induced by the oxidation of Ni metal with CO_2 and/or H_2O.[5] TPH and XRD results confirm that the reason for deactivation on H_2ONi3 can also not be ascribed to the carbon deposition regarding the small amount and no XRD peaks of carbon. The further study is needed to elucidate the deactivation cause.

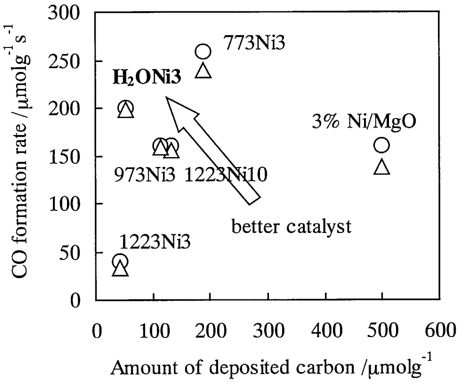

Figure 2. Amount of deposited carbon after 1 h on stream versus CO formation rate at 2 min and 1 h on various catalysts. (○) at 2 min, (△) at 1 h. Reaction condition: CH_4/CO_2 = 1/1, 773 K, W/F = 0.1 gh/mol, 0.05 g catalyst.

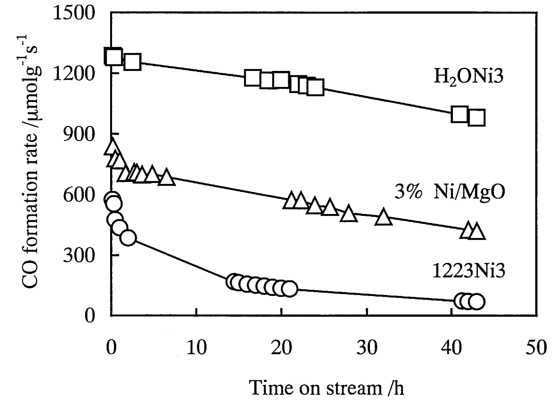

Figure 3. Activity as a function of time on stream over H_2ONi3, 3% Ni/MgO and 1223Ni3 catalysts.
Reaction condition: $CH_4/CO_2/N_2$ = 2/1/1, 1023 K, W/F = 0.1 gh/mol, 0.05 g catalyst.

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