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Thermogravimetric Study of Carbonaceous Deposits on Nickel Catalysts Physically Mixed with an Unreducible Oxide

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NiO physically mixed with an unreducible oxide such as MgO, SiO_2 and α-Al_2O_3 showed high activity in the formation of carbonaceous deposits after the reduction of NiO in a CH_4 stream. When the stream was switched to CO_2, the entire Ni was oxidized again to NiO after the removal of the deposits, though the entire Ni involved in a pure NiO or in a supported Ni/MgO was not oxidized. The size of Ni particles formed in these mixtures was less than 10 nm in diameter.

The Ni supported on MgO (Ni/MgO) was a good performing catalyst for the CO_2 reforming reaction of CH_4 to give H_2 and CO.[1] Unfortunately the lifetime of Ni/MgO was not long enough.[2,3] The short lifetime seemed to be responsible for the formation of carbonaceous deposits. In this study amounts of carbonaceous deposits were observed in different gas streams by a thermogravimetric analyzer (TGA).

The catalysts used in this study were physical mixtures of NiO with an unreducible oxide such as MgO, SiO_2, and α-Al_2O_3. Also Ni/MgO and pure NiO were tested as references. Nickel oxide was prepared from the calcination of $Ni(NO_3)_2 \cdot 6H_2O$ (Extra pure, Wako Chemical Industries, Ltd.) at 300 °C. The MgO, 99.98% pure, was ultrafine single crystal MgO, #100, furnished by Ube Industries Ltd. The SiO_2 was prepared by calcination at 800 °C of the colloidal silica, Snowtex-N, provided by Nissan Chemical Industries, Ltd. The α-Al_2O_3 was prepared from γ-Al_2O_3 (Showadenko K.K.) by calcination in air at 1200 ℃ for 3 h. The Ni-acetylacetonate (Ni-AA) was furnished by Dojindo Laboratories.

Each of the physical mixtures, NiO+MgO, NiO+SiO_2, and NiO+αAl_2O_3, were obtained by mixing two materials in an agate mortar and pestle. The supported catalyst, Ni/MgO, was prepared by decomposing Ni-AA which had been mixed physically with MgO without any solvent.[3,4] The mixed ratio, N_{Ni}/N_{Mg}, N_{Ni}/N_{Si}, N_{Ni}/N_{Al}, was 1/2 in atomic ratio. The mixture was made into a pressed pellet, a small portion of which, 30-50 mg, was placed in a quartz TGA-cell. At first, the specimen was calcined at a programmed temperature in a stream of Ar (30mL/min) in the TGA system. Ni-AA decomposed in this process. The system used was Shimadzu TGA-50, which weighs to a precision of about 0.001mg. The gas-streams used were (a) CH_4(20 mL/min)+Ar(20), (b) CO_2(20)+Ar(20), and (c) CH_4(20)+CO_2(20)+Ar(20), where each gas was controlled by a Mass flow controller (Stec Inc.). As to the programmed temperature, the temperature was elevated from 100 °C to 800 °C at a rate of 20 °C/min, and then maintained at 800 °C. If it was necessary, the gas stream was switched to another after the temperature was lowered below 100 °C.

The experimental results obtained are summarized in Fig. 1. As to the pure NiO (See the uppermost row in Fig. 1.), it is obvious in the figures that the pure NiO was reduced to Ni by CH_4 and also by

CH_4+CO_2. The weights of NiO and of reduced Ni were in fair agreement with the calculated values which are shown by dotted lines in the figures. The weight of Ni neither increased nor decreased after the reduction of the entire NiO and even after the exposure to a switched stream of CO_2. Its BET area after the exposure of CO_2 was 0.9 m^2 g^{-1}, which corresponds to particles of 0.8 μm in diameter under the assumption of spherical Ni particles, where only the surface of the particles would be oxidized by CO_2.

As to the physical mixtures of NiO+MgO, NiO+SiO_2, and NiO+αAl_2O_3, as soon as NiO was entirely reduced to Ni in a stream of CH_4, each specimen rapidly and greatly increased their weights. It is possible to attribute the increases to the formation of carbonaceous deposits, because the weights increased far beyond the weight of NiO. Atomic ratios of carbon to Ni, N_C/N_{Ni}, for NiO+MgO, NiO+SiO_2, and NiO+αAl_2O_3 were 14-13, 12-10 and 9-6, respectively, at 100 min after the reduction of the entire NiO, where the ratio was calculated under the assumption that the increase in weight was attributed only to carbon. That is, the activities for the carbonaceous deposits formations are in the sequence of NiO+MgO > NiO+SiO_2 > NiO+αAl_2O_3, in which the activity is defined as N_C/N_{Ni}. In a switched stream of CO_2, the carbonaceous deposits disappeared at above 650-680 °C at a faster speed than that of formation.(See Fig. 1a) As soon as the entire carbonaceous deposits disappeared, each specimen increased their weights to a limit value suggesting the formation of NiO. In Fig. 1b, it is obvious that the NiO involved in the mixtures was reduced also in the stream of CH_4+CO_2. However, the amounts of deposit were 1/10 greater than those formed in a CH_4 stream. It was of interest to see if the carbonaceous deposits formed in a stream of CH_4 would disappear in a stream of CH_4+CO_2. Fig. 1c shows the results of the tests. Both of NiO+MgO and NiO+αAl_2O_3 increased the additional deposits, but unexpectedly NiO+SiO_2 decreased them. In addition, surface areas of Ni particles and their diameters obtained by the adsorption of H_2 at 0 °C were 72 m^2 g^{-1} (Ni) [5 nm], 77 m^2g^{-1}(Ni) [4.5 nm], 45 m^2g^{-1}(Ni)[7 nm], for NiO+MgO, NiO+SiO_2, and NiO+αAl_2O_3, respectively, after the mixed NiO was reduced by CH_4, oxidized by CO_2, moved into an adsorption apparatus, reduced by H_2, and then evacuated at 300 °C for 2 h.

The results of Ni/MgO are shown in the lowermost row of Fig. 1. It was recognized from the weight that the chemical form of nickel involved in Ni/MgO was a reduced Ni after the thermal decomposition of Ni-AA in a stream of Ar. It is obvious in Fig. 1a that the amount of carbonaceous deposits is N_C/N_{Ni}=1.7, which is 1/10 greater than those of the mixtures described above. The deposits disappeared in a stream of CO_2 similarly to the case of the mixtures. However, even after the disappearance of carbonaceous deposits, the specimen weight did not increase to the weight of NiO. Figs. 1b and 1c of Ni/MgO show similar results to those of NiO+MgO.

As described above, the NiO mixed with an unreducible oxide showed very different results from those of the pure NiO and the supported Ni/MgO. The activities for the carbonaceous deposit formations are in the sequence of NiO+an unreducible oxide >> Ni/MgO >> pure Ni. The reason for the result is not clear. However, the experimental results are highly reproducible except for the temperatures. The difference among the experimental results described above are possibly attributed to the particle size variation of reduced Ni. When the size of Ni particles is as large as μm in diameter, the bulk of the particles would be hard to oxidize entirely to NiO. The pure NiO would fall under this category. On the contrary, the NiO mixed with an unreducible oxide showed oxidation of the entire reduced Ni in the stream of CO_2 after reduction of the NiO. This finding shows that the Ni particles were so small as to be oxidized entirely.

Each type of specimen showed a very different value in the amount of carbonaceous deposits. It is known that whiskerlike carbon was formed by the decomposition of CH_4 on a nickel catalyst at 500 °C,

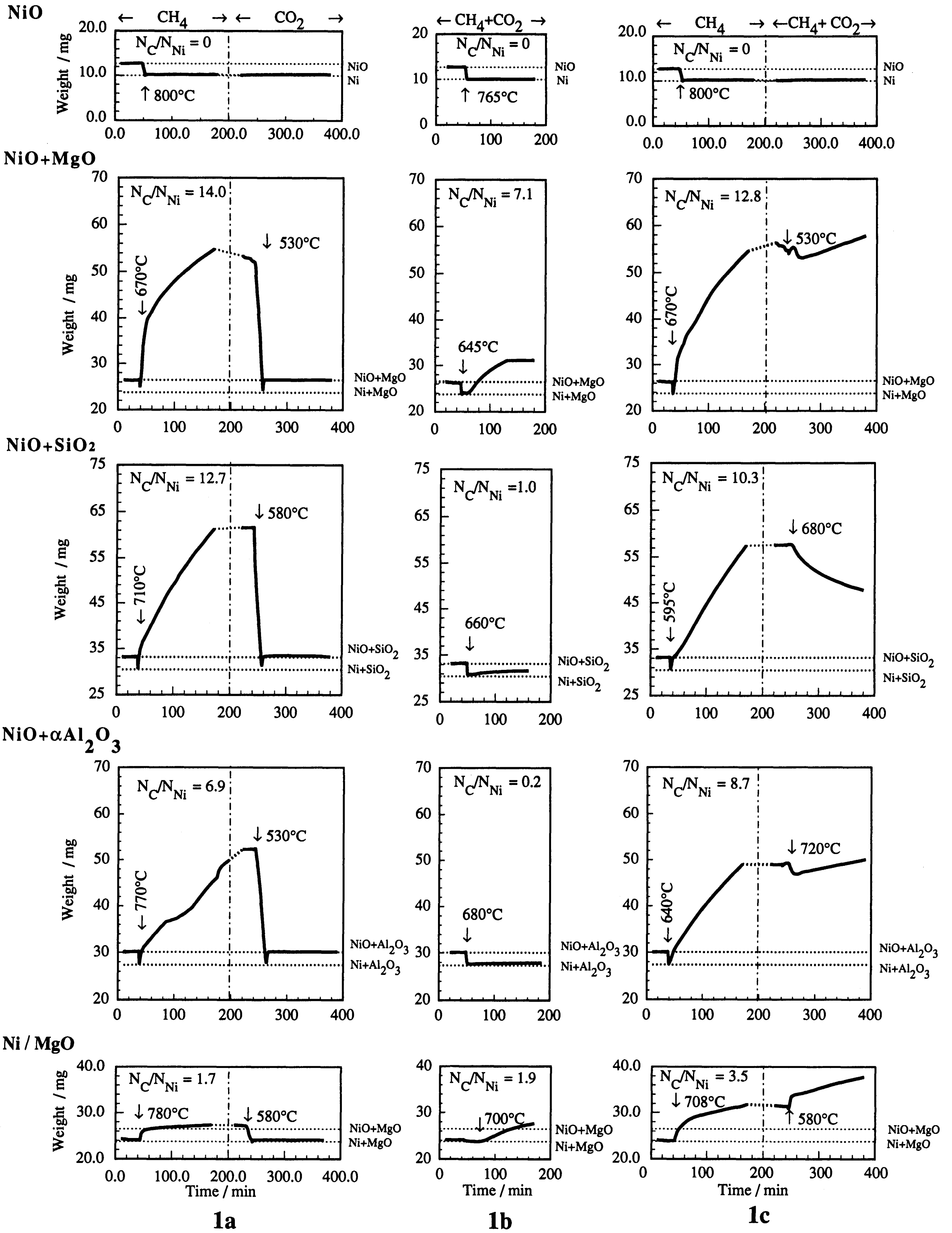

Fig. 1. Results of TGA-tests in various gas-streams. Weight of reduced Ni is normalized to be 10 mg. Atomic ratio, N_C/N_{Ni}, shows the value at 100 min after the reduction of entire NiO to Ni.

that each whisker had a nickel cluster at the end, and that the diameter of the whisker was very close to that of nickel crystal.5) Moreover, there is general acceptance for a growth model of whisker in which diffusion of CHx through Ni particle is involved.6,7) Large amounts of carbonaceous deposits were formed over the reduced nickel of the mixed NiO than that of the pure NiO. This finding shows that clusterlike Ni particles are more active than μm-sized Ni particles. Massaro reported that the surface diffusion of carbon on nickel foil was negligibly small in the range 350-700 °C.8) Anyway, it is very interesting that the mixture of NiO with an unreducible oxide gives clusterlike small Ni particles in CH_4 stream, in which the Ni small particles are formed in the process of carbonaceous deposit formations during the course of NiO reduction. The similar small Ni particles in the mixtures were also obtained in a CO stream. On the other hand, nickel involved in Ni/MgO showed features between those of the pure NiO and of the mixed NiO. This finding shows that the size of Ni particles involved in Ni/MgO is in the range between those of the two. We had reported that the size of Ni involved in different Ni/MgO samples was in the range of less than 100 nm.9)

The values of N_C/N_{Ni} and of Ni surface area give atomic ratios of carbon to surface Ni, $N_C/N_{Ni\text{-surface}}$, such as 117, 110, 114, 34, and 0 for NiO+MgO, NiO+SiO_2, NiO+αAl_2O_3, Ni/MgO, and pure Ni, respectively. The values in the NiO mixtures are almost the same and a significant difference among them could not be found. This finding reveals that the different unreducible oxides in the NiO mixtures behave equally for the formation of carbonaceous deposits which are formed on Ni particles, though the reduction temperature of NiO was greatly influenced by the coexisting unreducible oxide.

The results of the NiO mixtures in a stream of CH_4+CO_2 shown in Fig 1c suggest that the amount of carbonaceous deposits would be controlled in the balance of the following two reactions: (R1): $CH_4 \rightarrow CH_x+(4-x)/2H_2$, and (R2): $CH_x+CO_2 \rightarrow 2CO+x/2H_2$ or $C+CO_2 \rightarrow 2CO$, where CHx denotes carbonaceous deposits, and that the rates of the two reactions would be in the following relation: R1 > R2, R1 < R2, and R1 = R2 for the mixtures of NiO+MgO, NiO+SiO_2, NiO+αAl_2O_3, respectively, because the amounts of deposit increase under the condition of R1 > R2 and decrease under R1 < R2.

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