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Influence of the phase composition of titania on catalytic behavior of Co/TiO_2 for the dry reforming of methane

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The phase transfer of TiO_2 from anatase to rutile for a 10wt% Co/TiO_2 catalyst during the reduction causes serious disappearance of activity at 0.1 MPa during CH_4/CO_2 reforming, whereas the transfer for 0.5wt% Co/TiO_2 brings about relatively stable activity at 2 MPa.

The CH_4/CO_2 reforming reaction ($CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$) is attractive for generating synthesis gas and is related to the generation of fuel for fuel cells and GTL (gas to liquid) technology. The major drawback for the CH_4/CO_2 reforming is catalytic deactivation due to coke deposition (mainly emphasized in earlier reports) and sintering of metal. In order to overcome the problem and to develop effective catalysts with high durability, a number of transition metal catalysts supported on various oxides have been examined (see ref. 1 for a recent review). It has been found that the nature of the supports affects the catalytic behavior strongly, and TiO_2[2] and ZrO_2[3] which show strong interaction with metal, have been reported as effective supports. The interaction may be dependent on the H_2 reduction temperature, which would affect the nature of metal and support. However, the effects on the catalytic behavior have not been discussed extensively. In this contribution, the influence of reduction temperature on the catalytic behavior of Co/TiO_2 was investigated at 0.1 and 2 MPa (industrial condition for GTL).

The Co/TiO_2 catalysts were prepared by an incipient wetness method by using TiO_2 (Ishihara Sangyo, A-100, 100% Anatase form) and an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$. Cobalt loading was set to 0.5–10 wt%. The samples were dried at room temperature and 373 K, followed by calcination at 673 K in air to remove the NO_3^- from the cobalt precursor. 500 mg of the catalyst was loaded into a tubular inconel reactor passivated with an aluminum diffusion coating. After the catalysts were reduced with H_2 at 973–1173 K for 1 h at 0.1 MPa, the temperature was adjusted in He to 1023 K. Subsequently, the pressure was adjusted to the reaction pressure (0.1 or 2 MPa) and He was switched to the reactant gas ($CH_4/CO_2 = 1$, total flow rate of 50 ml min^{-1}). The reaction products were analyzed by a gas chromatograph with TCDs. The amounts of coking on the catalysts were quantified by TPO (temperature programmed oxidation) with O_2/He.

Fig. 1 shows time on stream of CO_2 conversions and H_2 yields for 10wt% Co/TiO_2 at 0.1 MPa reduced at different temperatures. The catalysts reduced below 1023 K retained relatively stable activity for 24 h, while the catalysts reduced above 1123 K did not show any activity. After the reaction for 24 h, the amounts of coking were measured (Table 1). No coke was detected (<0.01 wt%) for all the catalysts indicating that the low activities for the catalysts reduced above 1123 K is not attributable to coking. The results of XRD measurements for 10wt% Co/TiO_2 after H_2 reduction at 1023 and 1123 K and after the following CH_4/CO_2 reforming at 0.1 MPa are shown in Fig. 2. Metallic Co was observed on both catalysts after the H_2 reduction. The average particle size of metallic Co evaluated from the results of XRD was approximately same for these catalysts (26 nm; reduced at 1023 K, 33 nm; reduced at 1123 K), indicating that the difference of the catalytic behavior is not correlated to the initial particle size of metallic Co. Phase transfer of TiO_2 from anatase to rutile was observed during the reduction at higher temperature (1123 K) and the formation of inactive complex, *i.e.* $CoTiO_3$ was visible after the reaction on the catalysts. On the other hand, the formation of rutile and $CoTiO_3$ were not visible after the reaction following to the reduction at lower temperature (1023 K). These results demonstrated that the low activities of the catalysts reduced above 1123 K are mainly due to the oxidation of the metallic Co to $CoTiO_3$ by CO_2 in the initial period of the reaction. The deactivation caused by the metal oxidation during the CH_4/CO_2 reforming has also been reported for NiMgO solid solution[4] and molybdenum carbide catalysts.[5] The different oxidation behavior of the metallic Co was dependent on the nature of the TiO_2 phase, *i.e.* metallic Co on rutile was easily oxidized under the reaction conditions and the catalysts showed rather low activity. By contrast, metallic Co on anatase was not easily oxidized under the same conditions and the catalysts showed relatively stable activity.

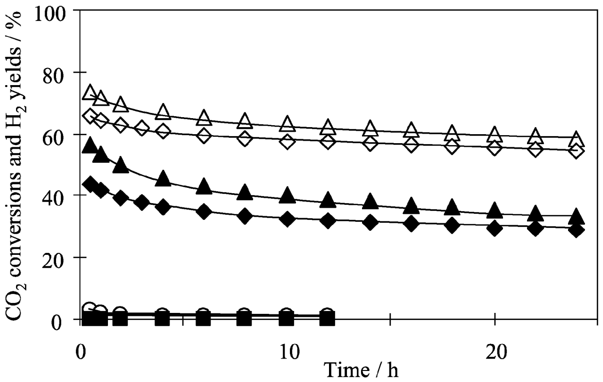

Fig. 1 CO_2 conversions (open symbols) and H_2 yields (closed symbols) *vs.* time on stream for 10wt% Co/TiO_2 catalysts at 1023 K and 0.1 MPa reduced at different temperatures (reduction temperature: (△, ▲) 973 K; (◇, ◆) 1023 K; (□, ■) 1123 K; (○, ●) 1173 K).

Methane is preserved at high pressures in natural gas fields, and most Fischer–Tropsch synthesis and methanol synthesis from H_2/CO are performed at high pressures in the GTL process. Hence, from an economical point of view, the CH_4/

Table 1 The amounts of coking on Co/TiO_2 catalysts after reaction for 24 h at 0.1 or 2 MPa (the catalysts were reduced at different temperatures)

Co loading (wt%)	Reaction pressure/MPa	Reduction temperature/K	Coke amount (wt%)
10	0.1	973	n.d.
		1023	n.d.
		1123	n.d.
		1173	n.d.
0.5	2	973	2.90
		1023	3.41
		1123	0.02
		1173	0.25

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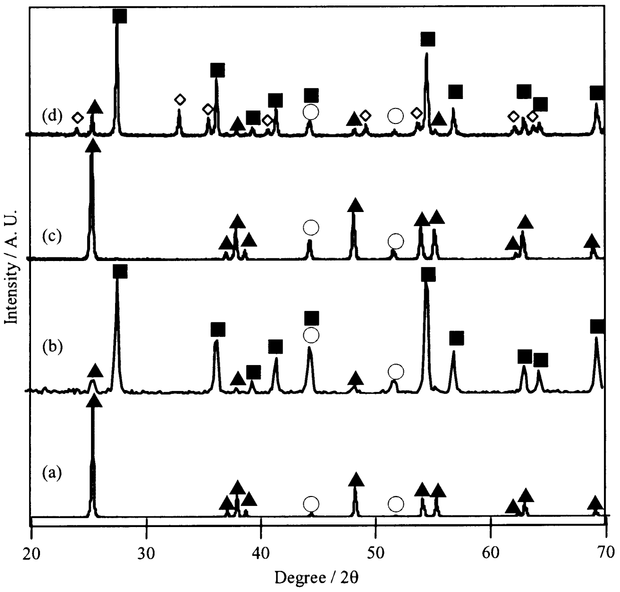

Fig. 2 XRD results for 10wt% Co/TiO_2 after H_2 reduction ((a) and (b)) and after subsequent reaction at 0.1 MPa for 24 h (c) and 12 h (d). Reduction temperature: (a) and (c), 1023 K; (b) and (d), 1123 K: (▲) TiO_2-anatase; (■) TiO_2-rutile; (○) metallic Co; (◇) $CoTiO_3$.

CO_2 reforming should also be carried out under high pressures ($\geqslant$ 2 MPa) in such a process. However, most of the researches were performed at atmospheric pressure, and only a few studies were conducted at high pressures.[5–8] As it is well known that higher pressures favor coking,[6–8] researches of the reforming reaction under high pressures are required. Thus, the reaction pressure was increased to 2 MPa. Since 10wt% Co/TiO_2 showed serious coking at this pressure and the reactor was plugged after reaction for 6 h, the loading of the cobalt was decreased step by step until, finally, 0.5wt% Co/TiO_2 showed relatively stable activity with only trace amounts of coke. Fig. 3 shows CO_2 conversions and H_2 yields *vs.* time on stream at 2 MPa for 0.5wt% Co/TiO_2 reduced at different temperatures and the amounts of coking during the reaction for 24 h are also summarized in Table 1. In contrast to the results at 0.1 MPa, the catalysts reduced above 1123 K retained relatively stable activity for 24 h while the catalysts reduced below 1023 K showed rather low activity. Lower amounts of coking were observed on the catalysts with high activity (reduced above 1123 K), while large amounts of coking were detected on the catalysts with less activity (reduced below 1023 K). The results of TEM observation for the catalyst reduced below 1023 K showed the formation of whisker and pyrolytic carbon encapsulating the surface of the catalysts during the reaction. Rostrup-Nielsen[9] reported that the latter deactivated the catalysts for the reforming reaction. Further, TPR revealed that all of the Co_3O_4 in 0.5wt% Co/TiO_2 was reduced to metallic state by H_2 reduction above 1023 K. From these results, the rather low activities for the catalysts would be attributed to the coking on the active sites. The results of XRD indicated that phase transfer of TiO_2 from anatase to rutile occurred during the reduction at higher temperature (1123 K) and the following reaction, coinciding with the results at 0.1 MPa (Fig. 2). These results demonstrate that weaker interaction between cobalt and anatase for 0.5wt% Co/TiO_2, which for 10wt% Co/TiO_2 induced relatively stable activity at 0.1 MPa, causes serious coking and the catalysts lose activity at 2 MPa. Note that increasing pressure increases the opportunity for coking as shown in this contribution and in refs 6–8. On the other hand, stronger interaction between cobalt and rutile for the 0.5wt% Co/TiO_2, which for the 10wt% Co/TiO_2 led to $CoTiO_3$ and brought about rather low activity at 0.1 MPa, prevents coking at 2 MPa and gives the catalysts relatively stable activity. As a result, the effects of reduction temperature on the activity of the two Co/TiO_2 catalysts were reversed. The rutile form of TiO_2, which was obtaned by transformation of anatase by calcination at 1373 K, was also employed for preparing catalysts. Even if the catalysts were reduced at 973 K, trends of activities were same as those of catalysts reduced above 1123 K, *i.e.* no activity for 10wt% Co/TiO_2 at 0.1 MPa, yet relatively stable activity for 0.5wt% Co/TiO_2 at 2 MPa. The results will be presented in subsequent full papers.

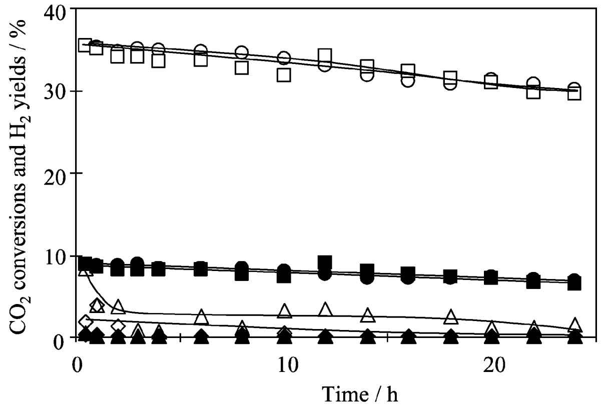

Fig. 3 CO_2 conversions (open symbols) and H_2 yields (closed symbols) *vs.* time on stream for 0.5wt% Co/TiO_2 catalysts at 1023 K and 2 MPa reduced at different temperatures (reduction temperature: (△, ▲) 973 K; (◇, ◆) 1023 K; (□, ■) 1123 K; (○, ●) 1173 K).

We have revealed that the type of the TiO_2 for the Co/TiO_2 in the CH_4/CO_2 reforming should be optimized for obtaining high performance of the catalyst and that the loading of the Co is also a important factor and the resultant catalysts have been dependent on the reaction condition. Although the activities of Co/TiO_2 were very low as catalysts for the CH_4/CO_2 reforming,[1] the optimized catalysts in this contribution showed extremely high resistance to coking at 0.1 and 2 MPa. The knowledge obtained in this research can be applied to design TiO_2 supported metal catalysts for the reforming reactions of hydrocarbons not only with CO_2, but also with steam, air, and oxygen.

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