Al_2O_3 Modifying Ni/TiO_2 Catalysts over CH_4 Dry Reforming

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Abstract: Addition of aluminum to Ni/TiO_2 improves the stability of the catalyst in CH_4 dry reforming. The resulting $Ni/TiO_2-Al_2O_3$ xerogel after calcinations at 973K for 10 h had a BET surface area in excess of 363 m^2/g contained mesoprores in the range 2.5~2.7 nm. Nitrogen adsorption and X-ray diffraction were used to characterize the function of addition aluminum to Ni/TiO_2 catalyst. The role of aluminum addition promotes the formation of large metallic Ni ensembles increase the dispersion of Ni, suppression of $Ni/TiO_2-Al_2O_3$ catalyst deactivation and carbon deposition.

Key words: CH_4 dry reforming; Nickel catalysis; Al_2O_3 modifying
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1 Introduction

CH_4 dry reforming has been extensively studied for several decades because it produces a more suitable H_2/CO ratio for the Fisher-Tropsch. The CH_4 reforming with CO_2 is also attractive from the environmental viewpoint. The reaction between them is interesting because it can decrease the total emission of greenhouse-effect gases. We have investigated an effect of adding aluminum to Ni/TiO_2 catalysts. The major role of aluminum additive was to improve development of pore structure and inhibit carbon deposition.

2 Experiments

2.1 Preparation of catalysts

The catalysts were prepared by Sol-Gel method. Appropriate amounts of $Al(NO_3)_3 \cdot 9H_2O$ was added into the mixed $Ti(BuO)_4$ and $Ni(NO_3)_2 \cdot 6H_2O$ solution in MeOH to make the gel solutions. A distinct lightly green color of gel was formed where the hydrolysis solution was dropped into the colloidal suspension after 24 h. The gel was dried in air at 453K for 10 h and then calcined at 973K for 10 h with a rate of 1K/min from 298K.

2.2 Catalyst characterization techniques

BET surface area, pore volume and pore size distribution were measured by nitrogen adsorption at a temperature of 77K using Micromeritics ASAP2000 analyzer. Around 0.2 g samples were degassed at 473K during 2 h under 20 μmHg.

XRD was carried out in D-MAX2500 powder diffractometer with Fe radiation at 40 kV, 160 mA.

3 Results and Discussions

3.1 Surface area and pore structure of catalysts

Table 1 BET analysis of 5% $Ni/Ti_{0.5}Al_{0.5}$ calcined at different temperature

Calcination Temperature/K	Surface Area / ($m^2 \cdot g^{-1}$)	Average Pore/nm	Pore Volume / ($cm^3 \cdot g^{-1}$)
453	44.45	2.5	0.03
773	374.2	2.4	0.22
973	363.7	2.7	0.25

Preparation condition: H=5.22; A=0.01; Hydrolysis temp: 298;

The BET surface area of the catalyst is 44.45 m^2/g at 453K. It increased to 374.2 and 363.7 m^2/g as the calcinations temperature increased to 773K and 973K. The average pore diameter increased from 2.5 nm at 453K to 2.7 nm at 973K. It was observed that pore volume decreased from 0.33 to 0.25 as the tem-

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peratures increased from 453 ~ 973K. From the BET surface area, the support modification by the Al_2O_3 addition produces a marked increase of specific surface and pore volume, which were remarkable at 773K. The textural properties of supports influence the catalyic activity in two ways. First, highly dispersed active sites are formed on the supports of large mesopore surface. Second, accessibility of reactant to active sites is high on mesoporous supports and thus results in high reactivity. The aluminum integrated catalyst has a much larger volume per mass since the addition of catalyst. The surface area from mesopores of catalysts is found to show significant effect on CH_4 conversion. Because surface properties play a more important role in this reaction, higher nickel dispersion resulted in higher activity and stability for $Ni/TiO_2-Al_2O_3$. Several researchers have found that the pore structure of catalysts affected catalytic activity in CO_2 reforming[1-2]. Addition of Al_2O_3 promoters could stabilize the surface area and the spinel transition phase of the aluminum support by dispersing well in the Al_2O_3 support.

3.2 The role of aluminum on $Ni/TiO_2-Al_2O_3$ catalysts

The reasons for deactivation of Ni-based catalysts can be described to carbon deposition on the Nickel crystallites and the sintering of nickel particles.

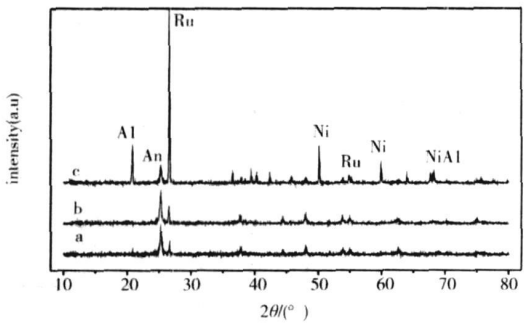

Fig. 1 X-ray diffraction patterns for 5 wt% $Ni/TiO_2-Al_2O_3$ catalyst
(a) Reduced at 973 for 2 h
(b) after 5 h reaction at 973K
(c) after 120 h reaction at 973K
An: Anatase; Ru: Rutile; NiAl: $NiAl_2O_4$

The XRD measurements of fresh reduced catalysts and the used catalysts were performed and the patterns are shown in Figure 1, in which (a) is taken on the fresh catalyst while (b) and (c) are kaken on the used catalyst. The phase of rutile, anatase and $NiAl_2O_4$ is the main phase in the samples. The crystalline phase of Ni can also be identified. It was reported that, brookite, anatase, and rutile can coexist in the temperatures from 673 ~ 973K[3] and TiO_2 transforms to rutile between 903K and 973K[4]. These results are in agreement with what the XRD presents. Rutile is more stable and final phase of titania, and anatase transforms into rutile at 973K. However, the extension of the co-existence of rutile and anatase may be due to the integration of aluminum. The existence of anatase may also contribute to the higher performance.

The metallic Ni in the reduced samples preferentially forms small crystallites, and the dispersion of Ni increases by adding Al_2O_3. Several research groups[5-6] have reported that the migration of Ni from the bulk to the surface of the catalyst may migrate to the surface during the reaction. For the XRD result (Fig. 1) Al_2O_3 can react with the reduced NiO to form $NiAl_2O_4$. This process may promote the migration of Ni. The interaction among components can affect the distribution of components and the structrue of the catalyst and in addition, thus affect the activity of the catalyst. Chen and Ren[7] showed that carbon deposition is markedly suppressed if $NiAl_2O_4$ is formed during the pretreatment step of an $NiAl_2O_4$. It showed no carbon deposition in XRD on $Ni/TiO_2-Al_2O_3$ catalyst after reaction for 120 h. The strong interaction of the NiO bond in the $NiAl_2O_4$ results in the formation of small crystallites on the catalyst surface, which are relatively stable toward sintering and carbon deposition[8].

4 Conclusion

The Ni-based catalysts modified by Al_2O_3 are adequate for the CH_4 reforming with CO_2. When Al_2O_3 is added to the support, the formation of $NiAl_2O_4$ depressed the carbon deposition over $Ni/TiO_2-Al_2O_3$. This resulted in the catalyst exhibiting stable activity during the CH_4 dry reforming. On the other hand, the presence of Ni aluminate spine decreases the carbon deposition in the $Ni/TiO_2-Al_2O_3$ catalysts.

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Al_2O_3 修饰 Ni/TiO_2 催化剂上甲烷干重整反应

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摘　要：通过 Al_2O_3 修饰的 $Ni-TiO_2-Al_2O_3$ 干凝胶催化剂，该催化剂在 973K条件下焙烧 10 h后比表面积为 363m^2/g，孔分布介于 2.5~2.7 nm之间。采用 BET和 X—射线衍射考察了 Al_2O_3 组份对 Ni/TiO_2 催化剂的影响。结果表明，Al_2O_3 的加入使催化剂颗粒度变小，镍的分散度提高，抑制了 Ni/TiO_2 催化剂的积碳，从而明显的提高了 $Ni—TiO_2—Al_2O_3$ 催化剂上甲烷和二氧化碳重整反应的活性和稳定性。

关键词：甲烷重整；N基催化剂；Al_2O_3修饰

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