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Effect of nanostructured supports on catalytic methane decomposition*

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Abstract: Carbon deposition from catalytic methane decomposition has drawn increasing interest recently. Previously, we have found the carbon formation depends on the crystalline structure of the support, following the trend of Ni/CeO_2 > Ni/CaO > Ni/MgO, because Ni supported on MgO is uniformly dispersed and can stabilize high-x CH_x intermediates. We have also found that the addition of Pt can inhibit the carbon deposition on Co/Al_2O_3 because the alloying between Pt and Co results in the better dispersion of Co on the support. Furthermore, it was revealed that by judging the Ni/Mg molar ratio from 1 to 0.25 we could reduce the diameter of deposited carbon nanotubes from 20 to 12 nm, with substantially smaller production rate. All of these previous studies indicated that better dispersion of the supported metal would benefit the decreasing of carbon deposition. Here we present our recent investigation of the effect of support particle size on the carbon deposition. Three different types of 10 wt% Co/Al_2O_3 catalysts were prepared: Co on commercial Al_2O_3 (Cat 1), Co on sol-gel-processed Al_2O_3 (Cat 2), and sol-gel-made homogeneous Co-in-Al_2O_3 (Cat 3). TEM showed that the diameter of the Co_3O_4 particles in sol-gel Al_2O_3 is only around 6 nm, while it is 20–40 nm in the commercial catalyst. By using XRD and FTIR, Co was identified as crystalline Co_3O_4 in the as-prepared Cat 1 sample, $CoAl_2O_4$ in Cat 2, and amorphous Al_2O_3 in Cat 3, indicating the best dispersion in Cat 3. Methane CO_2 reforming was studied on the three catalysts. Longer lifetime was measured for Cat 3 as compared to those on Cat 1 and Cat 2 (>20 h vs. 1 h). The support size effect is discussed.

Carbon deposition from catalytic methane decomposition has drawn increasing interest recently. The deposited carbon may appear as coke, resulting in the catalyst deactivation or the plugging of reactors [1]. Alternatively, it may form surface carbides that can be converted to more valuable hydrocarbons by the subsequent low-temperature hydrogenation [2,3]. Moreover, we have very recently found that the deposited carbon can occur in the form of nanotubes with open-edged structure and can possess high capacity of hydrogen uptake after alkali-doping [4].

In a comparative study [5], carbon deposition from methane decomposition was found to depend on the crystalline structure of the support. Ni supported on MgO has shown an excellent resistance, much better than that on CeO_2 and CaO, to the coke formation during the partial oxidation of methane to syngas at atmospheric pressure, 750 °C and high methane/oxygen ratios. This is because NiO and MgO can form an ideal solid solution. As a result, Ni is uniformly dispersed in the MgO matrix after its reduction. The highly distributed Ni can favorably stabilize high-x CH_x intermediates and therefore retard the deposition of carbon.

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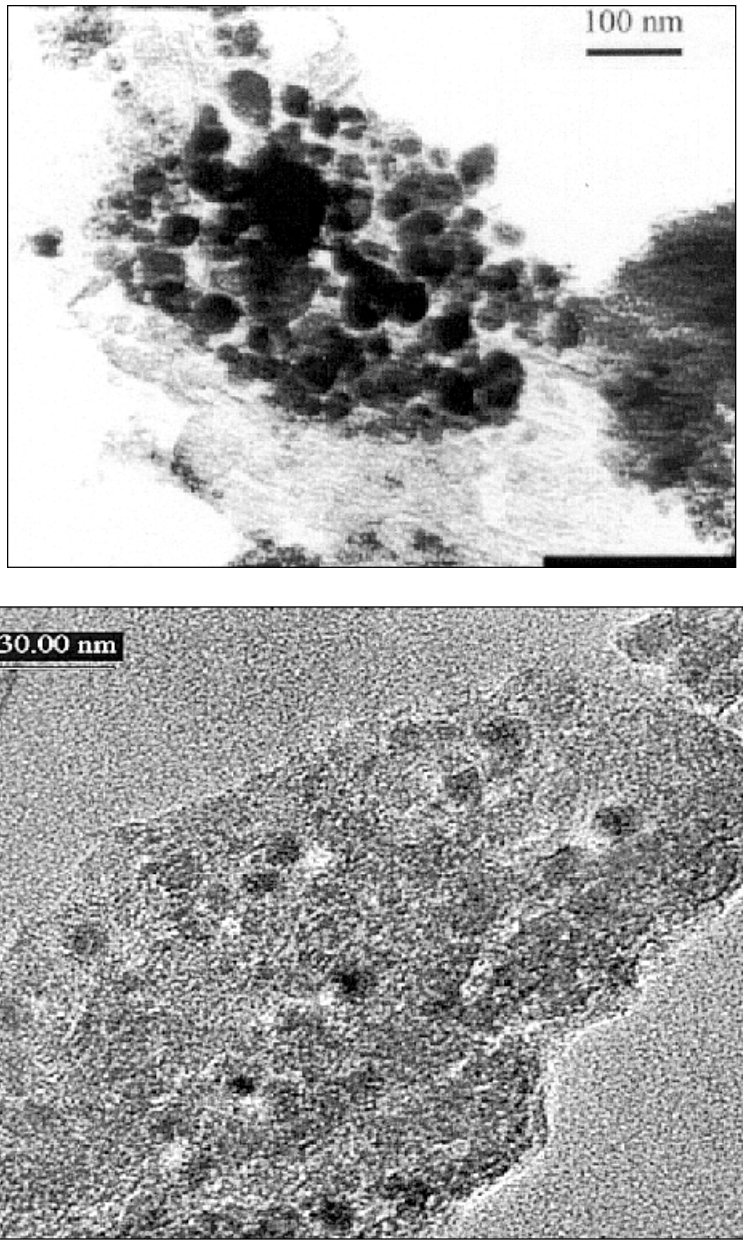

Fig. 1 TEM image of (a) 10 wt% Co supported on commercial γ-Al_2O_3; (b) sol-gel-processed 10 wt% Co-in-Al_2O_3.

In the experiments of preparing carbon nanotubes from the methane decomposition over Ni/MgO catalysts, we have observed that by judging the Ni/Mg molar ratio from 1 to 0.25, the Ni particles, and hence the deposited carbon nanotubes, reduce their diameter from 20 to 12 nm. The carbon deposition rate is also substantially decreased [6].

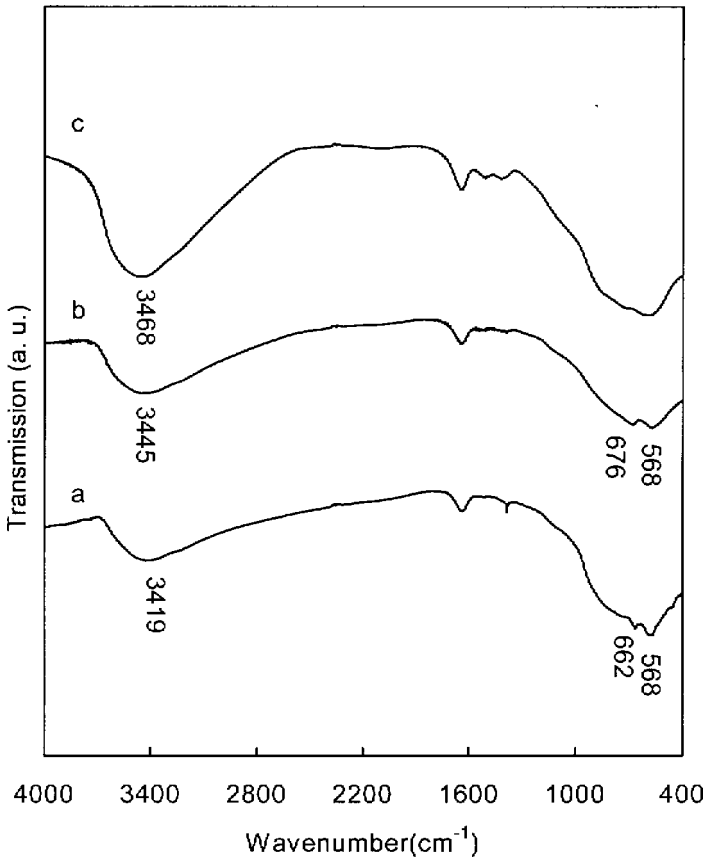

Fig. 2 FTIR spectra for the as-prepared catalysts: (a) Co/commercial γ-Al_2O_3; (b) Co/sol-gel Al_2O_3, (c) sol-gel-processed homogeneous Co-in-Al_2O_3.

We have also found that alloying can greatly enhance the distribution of Co metal in the Al_2O_3-supported catalysts, hence increasing its resistance to the carbon deposition during partial oxidation of methane to syngas. By using CO as a molecular probe, our IR study has exhibited that the addition of Pt has enhanced the Co distribution and inhibited the carbon deposition on Co/Al_2O_3 [1]. All of these previous studies indicate that better dispersion of the supported metal would benefit the decreasing of carbon deposition.

Here we present our recent investigation of the effect of support particle size on the carbon deposition. Three different types of Co/Al_2O_3 catalysts were prepared with the same Co loading (10%), including Co supported on commercial Al_2O_3 (Cat 1), Co supported on sol-gel-processed Al_2O_3 (Cat 2) and sol-gel-made homogeneous Co-in-Al_2O_3 (Cat 3). Cat 3 was prepared by sol-gel processing in the following procedure: 10 mmol of aluminum tri-sec-butoxide (ASB, ACTOS 97%) was dissolved in 150 mmol of isopropanol (Fisher Scientific 99.9%), and then 5 mmol acetylacetone (Merck 99.5+%) was added as chelating agent by refluxing the solution under nitrogen atmosphere. The precursor solution was vigorously stirred at room temperature for 30 min. Nickel nitrate dissolved in about 60 mmol of deionzed water was added drop by drop under mild stirring. The sample gelated in a few minutes. The resulting transparent and green gel was aged for 5 days at room temperature and dried at 333 K for 5 days. Then it was calcined at 873 K for 5 h. Cat 1 and Cat 2 were prepared by incipient wetness

impregnation. Cat 1 employed commercial g-Al_2O_3 (Merck) as its support. The g-Al_2O_3 support of Cat 2 was synthesized following the above sol-gel procedure (for Cat 3), but only 60 mmol of deionzed water without cobal nitrate was added during the sol-gel processing. The samples were calcined at 873 K for 5 h. The loading of nickel was 10 wt% for all three catalysts.

The high-resolution TEM images in Fig.1 show that the size of the cobalt particles supported on commercial g-Al_2O_3 (Cat 1) is in the range of 20–40 nm while that on sol-gel-processed Co/Al_2O_3 (Cat 3) is rather small, < 6 nm only. By using XRD and FTIR (see Fig. 2), Co was identified as crystalline Co_3O_4 in the as-prepared Cat 1 sample, $CoAl_2O_4$ in Cat 2 and amorphous Co/Al_2O_3 in Cat 3, also indicating the best dispersion in Cat 3. The strong doublet i.r. bands at 663 and 568 cm^{-1} in Fig. 2a are typical Co–O vibration in the cubic spinel structured Co_3O_4 [7], while the doublet peaks at 676 and 568 cm^{-1} in Fig. 2b are characteristic of $CoAl_2O_4$ [8], in a good agreement with XRD results (not shown).

The specific surface area measured by BET method decreases in the order of Cat 3 > Cat 2 >> Cat 1. The catalysts, which were obtained from sol-gel processing, had very high surface area, 183.2 m^2g^{-1}, while the surface area of the catalyst on traditional Al_2O_3 support (Cat 1) was only 90.9 m^2g^{-1}, about half of the former.

The catalytic activity and stability were evaluated on a quartz microreactor (I.D. 4 mm) packed with 100 mg of catalysts (35–50 mesh size). The catalysts were reduced in a flow of H_2 (30 ml/min) at 873 K for 1 h before a premixed feedstock (19.8% CH_4/17.5% CO_2/Ar) was introduced into the catalyst bed. The outlet gas composition was measured by gas chromatography. The amount of coke deposited on the reacted catalysts was measured in situ by mass spectrometry as previously described in detail [5]. The catalytic activity of the three samples (Cats 1, 2, and 3) was approximately the same as each other. However, there was a large difference in their resistance to coke. Cat 3 showed good coke resistivity and could last for longer than 20 h of reaction. A little coke was observed on Cat 2, whereas a large amount of coke was deposited on Cat 1. It plugged the reactor completely within 1 h of reaction. This may suggest that the nanoscaled structure of the support is beneficial for the inhibition of coke formation. It is reasonable that high surface area can enhance the dispersion of active components, like cobalt on the sol-gel Al_2O_3, and thus prevent the segregation of cobalt on the surfaces. This reduces the number of sufficiently large ensembles of Co atoms, which are responsible for coke deposition [9]. Therefore, the outstanding performance and excellent coking resistance of the sol-gel-processed Co/Al_2O_3 catalyst for CO_2 reforming of methane may be greatly related to its nanostructure of the support, high BET surface area, and high distribution of cobalt. Recently, we have found that a sol-gel-processed Ni/Al_2O_3 catalyst prepared by the same procedure has an excellent coking resistivity during the methane CO_2 reforming. It could last more than 80 h of reaction with little coke deposition, whereas the Ni catalyst supported on commercial g-Al_2O_3 only lasted 3 h, owing to complete shattering of catalyst. This further supports the above views.

In summary, the metal distribution in supported catalysts can be controlled by the crystalline structure of the support, the metal/support ratio, the alloying, and the preparation procedures of the support. By sol-gel processing, nanostructured Co can be made, showing excellent activity and stability for the methane CO_2 reforming.

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