

## Study on the Reaction Mechanism for Carbon Dioxide Reforming of Methane over supported Nickel Catalyst

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**Abstract:** The adsorption and dissociation of methane and carbon dioxide for reforming on nickel catalyst were extensively investigated by TPSR and TPD experiments. It showed that the decomposition of methane results in the formation of at least three kinds of surface carbon species on supported nickel catalyst, while CO<sub>2</sub> adsorbed on the catalyst weakly and only existed in one kind of adsorption state. Then the mechanism of interaction between the species dissociated from CH<sub>4</sub> and CO<sub>2</sub> during reforming was proposed.

**Keywords:** Adsorption, dissociation, supported nickel catalyst, methane, carbon dioxide, reforming.

Carbon dioxide reforming of methane is a particularly important reaction which takes place on the metal surface. Despite their potential usefulness in energy industry and environment optimization, the nature of the active carbonaceous species produced by the dissociative adsorption of methane and/or carbon dioxide and the detailed mechanism of the reforming reactions over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst are not yet known. This paper clarifies the stability, reactivity, selectivity and other properties of the carbonaceous species adsorbed on the metal surface.

The Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a conventionally incipient wetness impregnation method, with aqueous solutions of nitrates as metal precursors. Then the catalyst sample (100 mg) was firstly pretreated in O<sub>2</sub> flow of 20 mL/min at 973 K for 30 min, then the O<sub>2</sub> flow was switched to H<sub>2</sub> flow of 30 mL/min and reduced for 1 hr. After the sample was cooled to room temperature in H<sub>2</sub> flow, 30 mL/min He flow was introduced to purge the sample for 30 min. TPSR and TPD experiments were carried out in an apparatus, which consisted of a flow switching system, a heated reactor, and an analysis system<sup>1</sup>.

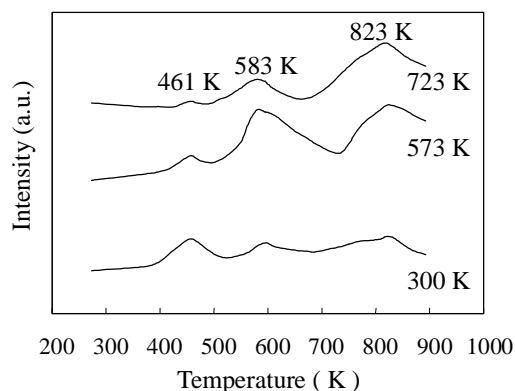
After flushing the reactor with H<sub>2</sub>/He (1:2) flow (following methane decomposition at a certain temperature), the hydrogenation of the surface carbonaceous CH<sub>x(ad)</sub> species was investigated by TPSR technique. **Figure 1** showed that the decomposition of methane could result in the formation of at least three kinds of surface carbon species on supported nickel catalyst. Generally, the carbon deposition is comprised of various forms of carbons, which are different in terms of reactivity. The distribution and

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features of these carbonaceous species depend sensitively on the nature of transition metals and the conditions of methane adsorption. These carbonaceous species can be described as: completely dehydrogenated carbidic  $C_\alpha$  type, partially dehydrogenated  $CH_x$  ( $1 \leq x \leq 3$ ) species, namely  $C_\beta$  type, and carbidic clusters  $C_\gamma$  type formed by the agglomeration and conversion of  $C_\alpha$  and  $C_\beta$  species under certain conditions. A fraction of the surface carbon species, which might be assigned to carbidic  $C_\alpha$  (~461 K), was mainly hydrogenated to form methane even below 500 K. It showed that carbidic  $C_\alpha$  species is rather active and thermally unstable on nickel surface. The carbidic  $C_\alpha$  species was suggested to be responsible for CO formation<sup>2</sup>. The significant amount of surface carbon species was hydrogenated to methane below 600 K and was assigned to partially dehydrogenated  $C_\beta$  (~583 K) species. The majority of the surface carbon was hydrogenated above 800 K and was attributed to carbidic clusters  $C_\gamma$  (~823 K)<sup>2</sup>.

**Figure 1** TPSR spectra of  $CH_4$  in  $H_2$  flow on fresh 8wt% Ni/ $Al_2O_3$  at different adsorption temperatures of 300 K, 573 K, and 723 K



It also indicated that the formation of three kinds of surface carbon species with different structures and properties largely depend on the exposure temperature and duration to methane. When the nickel catalyst was exposed to methane above 723 K, the carbidic  $C_\alpha$  species was not detected, and a significant amount of  $C_\beta$  was transformed into the carbidic clusters  $C_\gamma$ . It showed that the carbidic clusters  $C_\gamma$  species might be the precursor of the surface carbon deposition, which may be produced by the interactions between  $C_\alpha$  and  $C_\beta$  species,  $C_\alpha$  and  $C_\alpha$ , or  $C_\beta$  and  $C_\beta$ .

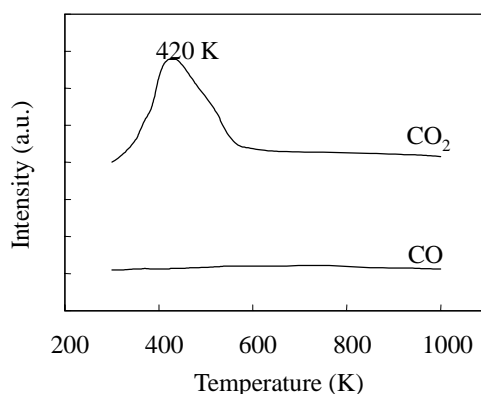
**Figure 2** showed  $CO_2$  TPD on fresh 8wt% Ni/ $Al_2O_3$  catalyst after pretreatment  $CO_2$  was adsorbed on the catalyst at room temperature (300 K). A broad  $CO_2$  desorption peak appeared at 420 K on the  $CO_2$  TPD profiles and CO desorption was not detected. This exhibited that  $CO_2$  weakly adsorbed on the catalyst and only one kind of adsorption state formed. From the thermodynamic point of view, dissociated adsorption of  $CO_2$  is impossible on the reduced nickel catalyst. Hereby, it was reasonable that no  $CO_2$  dissociation was observed from TPD profiles.

The CO TPD profiles over the fresh Ni/ $Al_2O_3$  catalyst were obtained following CO adsorption at 300 K (**Figure 3**). The response of  $CO_2$  formation was recorded to monitor the occurrence of CO disproportionation during the process of temperature programming. It was observed that two apparent  $CO_2$  desorption peaks appeared at 410

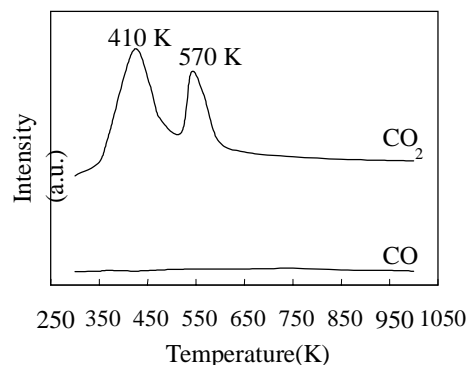
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K and 570 K, but the intensity of CO remained almost unchanged. The CO<sub>2</sub> desorption peak at 410 K was similar to the CO<sub>2</sub> peak on the CO<sub>2</sub> TPD profiles, which desorbed at 420 K. It indicated that CO disproportionation reaction occurred at room temperature and weakly adsorbed CO<sub>2</sub> was formed. The CO<sub>2</sub> desorption at 570 K may be derived from disproportionation of strongly adsorbed CO on the catalyst.

**Figure 2** CO<sub>2</sub> TPD over fresh 8wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst



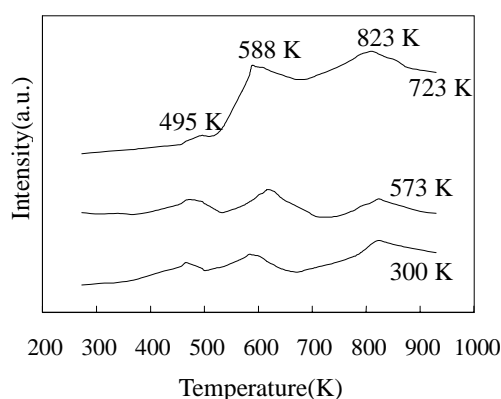
**Figure 3** CO TPD over fresh 8wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst



As shown in **Figure 4**, TPD spectra of methane on fresh Ni/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited that three correspondent peaks of CO<sub>2</sub> were observed. It means that methane decomposition on the transition metals truly takes place and the reactivity of the surface carbon species depends sensitively on the varieties of the adsorptions.

For TPSR spectra in the flow of hydrogen, desorbed product is mainly methane (**Figure 1**). But for TPD spectra in the flow of helium, desorbed species were mainly CO<sub>2</sub> and some amount of CO, which means that the TPD process was actually a process of temperature-programmed oxidation (TPO), in which the surface carbon was oxidized to form CO and CO<sub>2</sub>. The surface oxygen species, which resulted in the oxidation of surface carbon, might be the residual or remaining surface bonded oxygen (M-O) on transition metals. The oxygen atoms in subsurface and bulk phase of the metal cannot migrate to the surface below 1000 K<sup>1</sup>.

**Figure 4** TPD spectra of CH<sub>4</sub> decomposition into CO<sub>2</sub> in He flow on fresh 8wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at different adsorption temperatures of 300 K, 573 K, and 723 K



During the TPD process, the surface carbon produced by the decomposition of methane might migrate to the sites of bonded oxygen and interact with them to form carbon oxides. It means that peak temperature gaps ( $\Delta T$ ) of correspondent surface carbon species between TPD and TPSR might be the parameters of characterizing the mobility of the different surface carbon (**Figure 1** and **4**). An examination of the peak temperature gap indicated that the mobility of different surface carbon species on nickel catalyst is consistent with the order of  $C_\gamma > C_\beta > C_\alpha$ , with the  $\Delta T$  value of 0, 5, and 34K, respectively. This indicated that the carbonaceous species formed by the decomposition of methane are mobile enough and interact with the partial metal oxide to form CO<sub>2</sub>. In the meantime, from **Figure 4** another conclusion can be drawn that  $C_\alpha$  and  $C_\beta$  species could be transformed into  $C_\gamma$  species and the transformation could be accelerated with the increasing adsorption temperature, similar to those exhibited in TPSR studies (**Figure 1**).

Based on all the above studies, the possible reaction processes of carbon dioxide reforming of methane can be inferred as follows: methane is firstly decomposed into hydrogen and different surface carbon species — carbidic  $C_\alpha$ , carbonaceous  $C_\beta$  and carbidic clusters  $C_\gamma$ , then the absorbed CO<sub>2</sub> reacts with  $C_\beta$  (or  $C_\alpha$ , less possibly) to form CO.  $C_\gamma$  species might be the precursor of carbon deposition on nickel catalyst surface.

## References

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