Studies of Direct Carbonylation of Methane on Silica-Supported Transition Metal Catalysts

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Introduction

A considerable effort has been made in the past decade to convert the cheap raw materials ---- methane into more valuable compounds[1,2]. Methane is thermodynamically stable and its activation and transformation pose a great challenge to homogeneous and heterogeneous catalysis. Among various processes the oxidative coupling of methane is of considerable interest because it can produce C_2 compounds in one step. Direct carbonylation of methane to form ethanal and ethanol is a very attractive route for the effective utilization of methane. This reaction is also thermodynamically not allowed in one reaction step, due to the positive change in Gibbs free energy (+18.90 kcal/mol at 500K). This thermodynamic limitation makes it impractical till now. Here we report the new method to achieve the direct carbonylation of methane on silica-supported transition metals.

Experimental

The catalysts were prepared by ion-exchanging the silica support with solutions of transiition metals to yield a nominal 5 wt% metal. The following solution of salts of transition metals were used: $[Fe(NH_3)_6^{3+}$、$Co(NH_3)_6^{3+}$、$Ni(NH_3)_4^{2+}$、$Pd(NH_3)_4^{2+}$ and $Pt(NH_3)_4^{2+}]$.

For each experiment 300mg of the catalyst were placed in the micro-reactor and was reduced in - situ at 723K. Methane decomposition was performed from a flow of 10ml/min of methane. Each of pulses of 0.3ml of CO syn-gas (95% CO + 5% H_2) in a flow of 20ml/min of helium at temperature programmed conditions and at constant temperature conditions was given at each of temperature interval (50K) and at each of time interval (10mins) respectively. Product analysis was performed on line with an ion-trap detector (Finnigan - MAT 700).

Results and Discussion

The direct carbonylation of methane is thermodynamically not allowed in one reaction step, due to the positive change in Gibbs free energy (+18.90 kcal/mol at 500K). A important approach is to split the overall reaction into two reaction steps occurring under different conditions.

$$CH_4 + CO \rightarrow CH_3CHO \quad (1)$$
$$CH_4 \rightarrow CHx + (4\text{-}x)\,H \quad (2)$$
$$CHx + CO + (4\text{-}x)\,H \rightarrow CH_3CHO \quad (3)$$

In such a two-step route the thermodynamic limitation might be overcome. The decomposition of methane (2) is endothermal $\triangle H > O$ $\triangle H^0_s = +96.08$kcal/mol) while the change in entropy is positive $\triangle S > O$ ($\triangle S^0_s = +29.25$cal/mol). The direct carbonylation of CHx (x = 0-3) species to form ethanal and ethanol (3) is exothermic $\triangle H < 0$ (For gas phase reaction under standard conditions, $\triangle H^0_s = -100.26$ kcal/mol) and the change in entropy is negative $\triangle S < 0$ ($\triangle S^0_s = -57.92$ cal/mol). Therefore, the overall reaction could be occurred under certain moderate temperature, where $\triangle G_T < 0$. Practically, the activation of methane[3] and H_2-D_2 exchange reaction[4] of methane on metal surface indicate that the reaction (2) can occur under moderate temperatures. The reaction (3) was extensively studied in the formation of aldehyde and alcohol in the Fischer-Tropsch reaction[5].

Figure 1. CO pulses at different temperature on saturately adsorbed methane on 5wt% Pd/SiO_2 catalyst at 423K

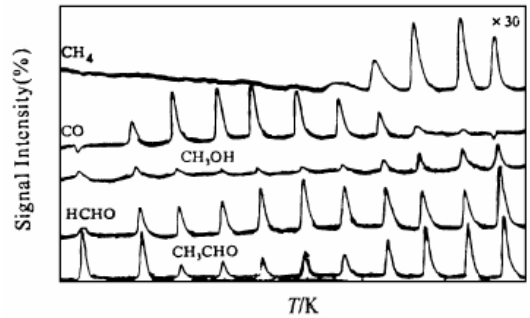


Fig.1 shows that the optimum temperature of carbonylation of CHx(ad) (x < 3) species lies in the range of 523-723K on cobalt. It is interesting that this temperature range is coincident with the range of dissociative adsorption of methane. It means that the two step reactions of the direct carbonylation of methane can be performed at the same temperature. Platinum (Fig.2) exhibits the similar behavior with cobalt, but less activity than cobalt.

Figure 2. TPSR speat ra of methane in H_2 st reem on freah 6w t% Pd/SiO_2 catalyst at different adsorption temperature of methane
a) T = 300K (b) T = 423K (c) T = 523K; (d) T = 673K;

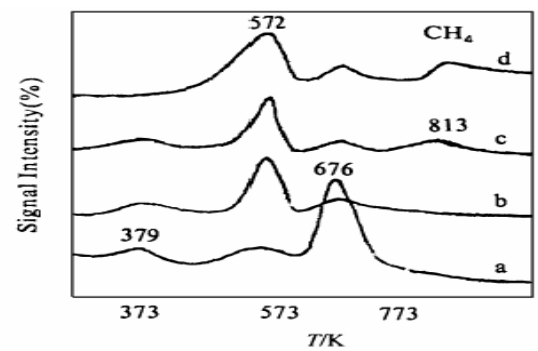


Fig.1 to Fig.3 shows that the catalytic performance and product distribution depends sensitively on the nature of metals and the variance of the reaction conditions, especially the temperature of carbonylation. The result of blank experiment illustrates that no ethanal and ethanol were formed on the silica support under the same reaction conditions. In contrast to cobalt, Fig. 3 illustrates that optimum temperature range of the carbonylation of CHx(ad) species on palladium is enlarged to 823K and that the conversion of the carbonylation is reversely increased along with the increasing of the temperature. TPSR results of adsorbed methane on palladium and Fig.3 show that the hydrogenation to methane and carbonylation of CHx(ad) species formed by the decomposition of methane are the competitive reactions, especially on the H(ad)-enriched metal surface. The interaction of H(ad) with adsorbed surface species results in the formation of hydrogenated products (such as CH_4, CH_3CH_2OH and CH_3OH). Large amounts of H(ad) may be originated from the migration of H(ad) in the subsurface and

bulk phase to surface with the increasing of the temperature. Similar TPPR results of carbonylation of methane on other metals indicated that palladium and nickel catalysts favor the direct carbonylation of methane.

Figure 3. CO pulses at different temperature on saturatelv CH_4 adsorbed 5wt% Pd/SiO_2 catalyst at 573K.

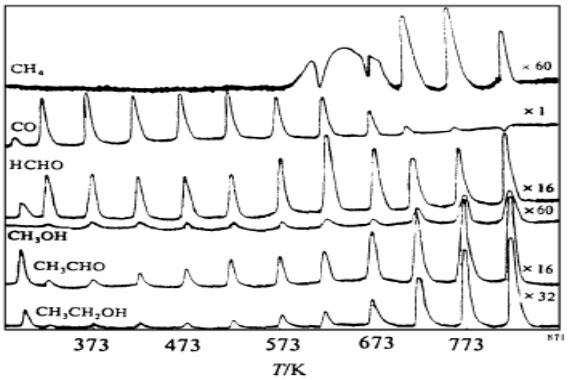
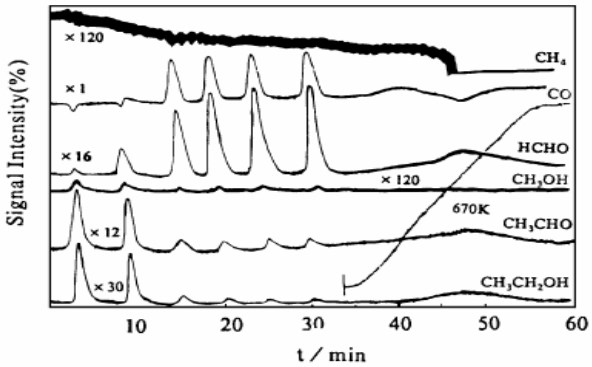


Fig.4 shows that the involvement of H(ad) acts as an important role in the formation of HCHO and ethanol and that adsorbed CO is also the resource of surface carbon species, which can decompose and interact with surface H(ad) to form CHx(ad) species at higher temperature. The comparative experiment of syn-gas on fresh metal catalyst illustrates that surface carbon species formed by the decomposition of carbon monoxide is actually one of the source of surface carbon for carbonylation.

Figure 4. CO Pulses at 423K on Saturately CH_4 adsorbed 5wt% Pd/SiO_2 catalyst



On the methane adsorbed metal surface, the decomposition of CO was very weak and its influence on carbonylation of methane was also very weak. The partial decomposition and hydrogenation of carbon monoxide at higher temperature results in the increasing of the formation of ethanal at 673K with the increasing of the pulse numbers of syn-gas. The comparative experiments indicate that the carbonylation of CHx(ad) species formed by the decomposition of surface probe molecules CH_3I mostly results in the formation of ethanal. It means that the formation of HCHO mainly comes from the direct gas phase reaction of CO and H_2. Optimization of the direct carbonylation of methane might results in the novel process for the effective utilization of methane.

Figure 5. CO pulses at 673K on saturately CH_4 adsorbed 5wt% Pd/SiO_2 catalyst at 673K.

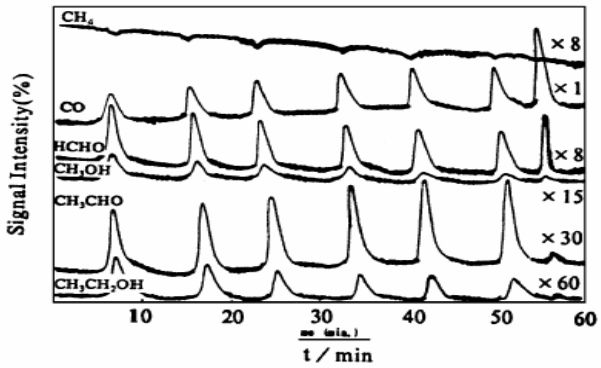
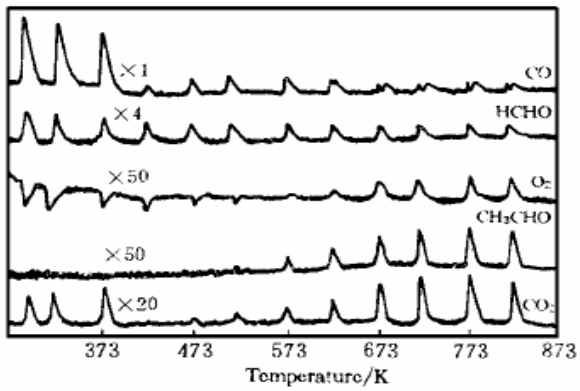


Figure 6. CO pulses at different temperatures on fresh 5 wt % Pt/SiO_2 catalyst



Conclusions

The direct carbonylation of methane on supported transition metal catalysts was extensively investigated by using the temperature programmed pulse reaction (TPPR) and constant temperature pulse reaction (CTPR). An important approach is to split the overall reaction into two reaction steps occurring under moderate conditions. Methane is firstly decomposed by a reduced transition metal catalyst into adsorbed surface carbonaceous species, then carbonylation of surface carbonaceous species was employed at different conditions. In such a two-step route the thermodynamic limitations can be overcome and the homologation of methane may be practically achieved. The catalytic performance and product distribution of direct carbonylation of methane sensitively depend on the nature of transition metals and the variance of the reaction conditions. Carbonaceous species formed by the decomposition of methane on metal surface may be the active intermediate which are responsible for the lengthening of carbon-carbon chain on catalyst surface. Optimization of the direct carbonylation of methane might results in the novel process for the effective utilization of methane.

References

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