Studies of the Activation and Homologation of Methane on Supported Metal Catalysts

Lin-Hua Song, Zi-Feng Yan, Shi-Kong Shen

Department of Chemical Engineering, University of Petroleum, Dongying 257062, Shandong, P. R. China

Introduction

One of the intriguing problems in heterogeneous catalysis is the activation and direct conversion of methane into liquid fuel and useful chemicals[1]. Methane activation is very difficult because methane is a thermodynamically stable product with a noble gas-like configuration. The very strong tetrahedral C-H bonds (435kJ/mol) offer no functional groups, magnetic moments, or polar distortions to facilitate chemical attack. Of interests are the recent works reported by Belgued[2] and Koerts[3] who achieved the conversion of methane by two-step reaction occurred under the moderate temperatures to form C_2-C_6 alkanes. Here we report the results of activation and homologation of methane to form C_2 to C_6 alkanes at moderate conditions in a two-step route in which methane is first thermally activated. Of special is that the two-step reactions were performed at the same temperature and that the method of transient evaluation of the catalysts was systematically suggested.

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. The surface carbon created from methane was characterized by a temperature programmed surface reaction (TPSR) in a flow of 20ml/min of hydrogen. The procedure of the evaluation of homologation of methane is described as follows:

$$\underset{20\text{ml/min}}{\overset{3\text{mins}}{H_2 \longrightarrow}} \; \underset{10\text{ml/min}}{\overset{4\text{mins}}{CH_4 \longrightarrow}} \; \underset{20\text{ml/min}}{\overset{10\text{mins}}{H_2 \longrightarrow}} \; \underset{20\text{ml/min}}{\overset{8\text{mins}}{He \longrightarrow}} \; \underset{20\text{ml/min}}{\overset{5\text{mins}}{H_2 \longrightarrow}} \; \underset{20\text{ml/min}}{\overset{5\text{mins}}{He \longrightarrow}} \; He$$

Product analysis was performed on line with an ion-trap detector (Finnigan-MAT 700).

The presence of surface carbon formed by the decomposition of methane was well manifested by its reaction with hydrogen. After flushing of the reactor with pure helium flow (following methane dissociation at a certain temperature for 5mins and cooling quickly to room temperature) and switching to a hydrogen flow, the desorbed species from the metal surface along with the temperature programmed process were simultaneously testified by the above on-line ion-trap detector.

Results and Discussion

The homologation of methane is thermodynamically not allowed in one reaction step, due to the positive change in Gibbs free energy (+16.8 kcal/mol at 500K). A tentative approach is to split the overall reaction into two reaction steps occurring under different conditions.

$$CH_4 + CH_4 \rightarrow C_2H_6 \qquad (1)$$

$$CH_4 \rightarrow CHx + (4\text{-}x)\,H \qquad (2)$$

$$CHx + CHx + (6\text{-}2x)\,H \rightarrow C_2H_6 \qquad (3)$$

In such a two-step route the thermodynamic limitation might be overcome. The decomposition of methane (2) is endothermal $\triangle H > O$ (For gas phase reaction under standard conditions, $\triangle H^0_s = +96.08$kcal/mol) while the change in entropy is positive $\triangle S > O$ ($\triangle S^0_s = +29.25$cal/mol). The hydrogenation of CHx (x=0-3) species to form higher hydrocarbons (3) is exothermic $\triangle H < 0$ (For gas phase reaction under standard conditions, $\triangle H^0_s = -89.84$ kcal/mol) and the change in entropy is negative $\triangle S < 0$ ($\triangle S^0_s = -15.94$ cal/mol). It means that the changes in Gibbs free energy of the reaction steps (2) and (3) might be both negative under different conditions. Therefore, the overall reaction could be occurred under a certain moderate temperature, hence $\triangle G_T < 0$. Table 1 shows that the two-step reaction method is effective for the homologation of methane and that the conversion of methane depends decisively on the nature of transition metals. It also indicates that the two steps can be performed at the same temperature. Platinum and cobalt exhibit favorable catalytic performance.

Figure 1. Effect of metal loadings on methane homologation at 523K on Co/SiO_2 catalysts

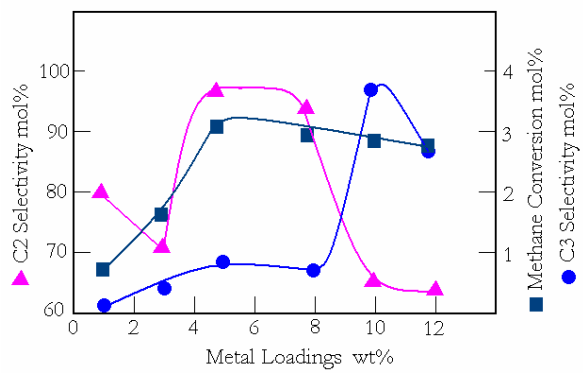


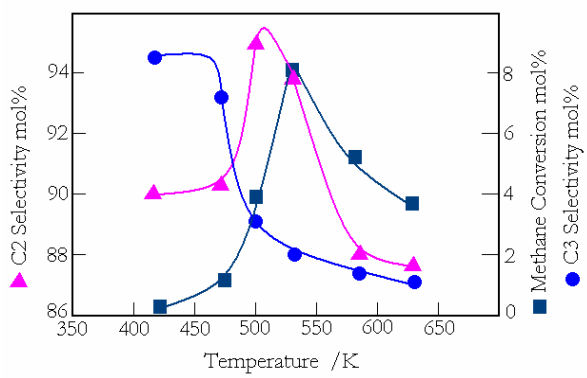
Table 1 Catalytic Performance of Different Transition Metal Catalyst on Methane Homologation at 523K

Catalyst	Metal Load. (wt.%)	CH_4 Conversion (mol%)	Selectivity to (mol%)		
			C_2	C_3	Total
Pt/SiO_2	5.0	9.91	90.13	6.13	96.26
Pd/SiO_2	5.0	0.62	98.06	----	98.06
Co/SiO_2	5.0	2.65	99.06	0.83	99.89
Ni/SiO_2	5.0	0.02	8.03	1.61	9.64
Fe/SiO_2	5.0	0.01	0.55	0.02	0.57

Fig. 1 demonstrates that the optimum transition-metal loading is 5wt%. Fig. 2 illustrates that between the two reactions exists a temperature gap between the optimum adsorption of methane and the subsequently optimum hydrogenation even though the two steps can be performed at the same temperature range. It means that the reactive intermediates of methane homologation are not just only the carbidic species formed by the decomposition of methane firstly suggested by Koerts. The other factors, such as bimetal alloy, metal additives and supports, were also investigated. The results indicate that bimetal and metal additive catalysts show negative effects for methane homologation and that the silica is the most effective support. EDAX data shows that the non-noble metal in bimetal catalysts and the metal additive in additive catalysts largely enriched on the surface of the

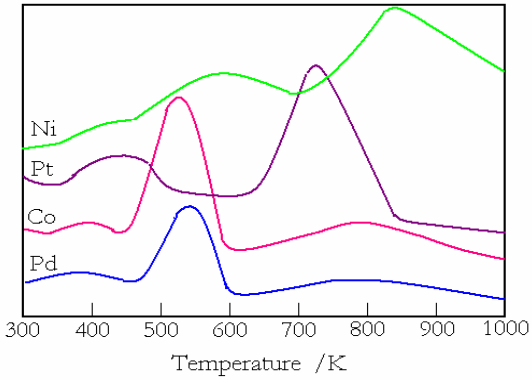
catalysts. It means that the transition metals enriched on the catalyst surface act as the unique role of the activation and homologation of methane. Further experiments indicated that the catalytic performance and product distribution sensitively depend on the nature of transition metals and the variance of the conditions of the reactions. This means that the optimization of the homologation of methane on supported transition metals could result in an attractive route for the utilization of methane.

Figure 2 Temperature effect for methane homologation on Pt/SiO_2 catalyst



Methane decomposition on transition-metal surface is a thermally activated process. Fig. 3 reveals that methane was initially produced at higher rates on almost all catalysts and higher hydrocarbons was detected only in traces. The result indicate that three kinds of carbonaceous species with different structures and properties are formed by the decomposition of methane on catalyst surface, which are tentatively assigned as follows: Cα (379K), carbidic species; Cβ (572K), carbonaceous CHx (x<3) species and Cγ (813K), graphitic carbon species respectively.

Figure 3 TPSR spectra of adsorbed methane on different metals at 523K.



Further experiments showed that the distribution and the features of these different carbonaceous species depend sensitively on the nature of transition metals and the different conditions of methane adsorption. The results of adsorbed methane at different exposure duration at 573K indicate that the adsorbed methane is initially decomposed into high hydrogen-deficient carbidic Cα and carbonaceous Cβ species. The formation of carbidic Cα species was greatly decreased along with the lengthening of methane exposure time. It may be caused by the increasing of the surface carbon coverage. Further experiments even indicated that the formation of Cα is seriously inhibited and the transformation of Cα into Cβ and Cγ species is greatly accelerated with the increasing of carbon coverage and the adsorption temperature of methane. TPSR results of adsorbed methane and results of surface reaction of probe molecules CH_3I showed that the carbidic Cα and carbonaceous Cβ species are the surface intermediates of the homologation of methane and that the presence of reactive Cα species is the origin of the temperature gap between the methane adsorption and subsequent hydrogenation.

Table 2. Catalytic Performance of Transition Metal Catalysts on Various Supports for Methane Homologation at 523K

Catalyst	Support	Metal Loadings (wt%)	CH_4 Conversion (mol%)	Selectivity to (mol%)	
				C_2	C_3
PtS	SiO_2	3.0	1.31	92.91	5.18
PtA	Al_2O_3	3.0	0.66	92.79	3.20
PtT	TiO_2	3.0	----	-----	----
PdS	SiO_2	5.0	0.62	98.06	----
PdA	Al_2O_3	5.0	0.57	97.70	0.73
PdT	TiO_2	5.0	0.52	95.38	1.29
CoS	SiO_2	5.0	2.65	99.06	0.83
CoA	Al_2O_3	5.0	0.01	86.78	6.08
CoT	TiO_2	5.0	0.01	90.00	----
FeS	SiO_2	5.0	0.01	0.55	0.02
FeA	Al_2O_3	5.0	0.01	30.45	----
FeT	TiO_2	5.0	----	-----	----

Each figure should have a number and caption, formatted as follows below the figure:

Conclusions

The homologation of methane on supported transition metal catalysts was extensively investigated by using the transientresponse technique (TRT). The different factors which greatly affect the reaction were also extensively studied. An important approach is to split the overall reaction into two reaction steps occurring under moderate temperatures. In such a two-step route the thermodynamic limitations can be overcome and the homologation of methane may be practically achieved. The optimum conversion of methane on 5wt% Pt/SiO_2 catalyst in the homologation of methane is 9.91% reached at 523K.

The activation of methane on silica-supported transition metals was well investigated by TPSR spectroscopy, which revealed that a large variance of carbon reactivity and their distribution of surface carbons were greatly influenced with the conditions of formation of surface carbon and with the nature of the transition metals. Carbidic Cα and carbonaceous Cβ species formed by the decomposition of methane on metal surface may be the active intermediates which are responsible for the lengthening of carbon-carbon chain on catalyst surface.

References

[1] D. M. Golden, S. W. Benson, *Chem. Rev.*, **1969**, 69,125.
[2] T. Koerts, R. A. van Santen, *J. Catal.*, **1992,** 138,101.
[3] M.Belgued, J. Saint-Just, *Catal. Today*, **1992**, 13, 437.