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Comparative study on hydrogen-assisted “one-step” methane conversion over Pd–Co/SiO_2 and Pt–Co/NaY catalysts

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Abstract

In our laboratory, methane conversion to higher hydrocarbons in “one-step” process under non-oxidative condition at low temperature was first introduced and investigated over Pd–Co/SiO_2 prepared by sol/gel method [Guczi et al., Catal. Lett. 54 (1998) 33] and over Pt–Co/NaY [Guczi et al., Stud. Surf. Sci. Catal. 119 (1998) 295] bimetallic catalysts. It was found that methane conversion in one-step process is at least 2.5 times higher than that measured in “two-step” process on the same catalysts. In the present work, the two-step and one-step processes are compared. It has been established that in one-step process when methane dissociation occurs in the presence of hydrogen containing helium, not only the production of higher hydrocarbons increases but also the selectivity is shifted towards larger molecules. Palladium–cobalt system proved to be more efficient than the corresponding platinum–cobalt catalysts. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of the two-step reaction in the non-oxidative low temperature methane conversion over metal catalysts (e.g. Pt, Co and Ru), it has been fully accepted that in the first step methane is chemisorbed to produce CH_x surface species followed by hydrogenation of the CH_x species to form hydrocarbons by homologation [3–5]. The yield, i.e. the fraction of the surface CH_x species converted into higher hydrocarbons, depends on the metal itself [5], the structure and morphology of the metal particles [6] and the support [7,8]. The conversion, i.e. the fraction of methane introduced and converted into larger hydrocarbons is normally low. However, in the oxidative methane coupling carried out in a recirculation reactor, the yield of ethylene amounts to as high as 80%, when a membrane contractor has been used to facilitate complexation of olefins with Ag^+ ions [9]. Similar efficiency was achieved by continuous removal of C_{2+} olefins [10].

One of the major drawbacks in the two-step process is that at high temperature and on large metal particles methane undergoes deep dissociation to form highly hydrogen-deficient carbon on the surface. Moreover, due to the exothermicity of hydrogen chemisorption, the higher the temperature, the more hydrogen is desorbed giving way to further C–H bond rupture. This may result in the formation of inactive carbon on the surface, which cannot be removed by subsequent hydrogenation. For instance, in a static system after an abrupt increase in the amount of chemisorbed methane on nickel no further increase was observed [11].

In order to diminish this side effect, first we changed the metal particle size using Pt–Co/NaY [12] and Ru–Co/NaY [13] catalysts. It was established that nanoscale bimetallic particles encapsulated into the

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zeolite supercages revealed high activity in the C–H bond rupture in methane. The platinum and ruthenium in the bimetallic particles facilitated dissociation of the hydrogen molecules active in removing the surface species. In mechanistic studies a correlation was found between the hydrogen content of the surface CH_x species (the optimum value for x being around 2) and the chain length of the hydrocarbons produced in the second step. The C_{2+} selectivity was found to be in the range 80–90%.

To overcome the difficulties caused by "deep dissociation" of methane, one-step methane conversion was suggested in which methane pulses were flushed over Pd–Co/SiO_2 and Pt–Co/NaY catalysts in the presence of H_2/He mixture under non-oxidative conditions at low temperature [1,2]. When a certain amount of hydrogen (1.3 vol.%) was admixed to helium and methane pulses were introduced, the conversion based upon the amount of methane converted into higher hydrocarbons, increased compared to that measured in a two-step process. Similar phenomenon was observed on nickel catalysts: during steam reforming trace amount hydrogen in the methane stream hampered deactivation of the catalyst [14]. Moreover, on Pt/Al_2O_3 catalyst the hydrogen pressure determines the location of carbon (coke) [15].

In the present paper, we wish to compare by a mechanistic study the one-step and two-step methane conversions over Pt–Co/NaY and Pd–Co/SiO_2 samples. Details about the scenario of the surface processes will be given, i.e. we wish to know whether CH_x species start polymerizing during methane chemisorption and the hydrogen helps only in removing the hydrogen-deficient carbon species, or the CH_x species starts polymerizing only during hydrogenation. Methane chemisorption is principally an endothermic process [16] and the quasi-equilibrium is shifted toward more and more hydrogen-deficient surface CH_x species as, e.g. the hydrogen flow rate is altered or the temperature increases. Beyond a threshold value in the number of hydrogen atoms of the surface CH_x species (the optimum value in x is about 2), CH_x becomes inactive in the surface chain growing process. Since the hydrogen is continuously removed from the surface during the methane flow, the system is starving in hydrogen. The x value in the CH_x species is ensured to be higher than without hydrogen, making it more capable for polymerization. This is the idea of the one-step process and under this condition we assume that surface polymerization of the C_1 units starts already during chemisorption.

2. Experimental

2.1. Catalyst preparation

The Pt–Co/NaY catalyst is denoted by $Pt_{12}Co_{88}$/NaY, was prepared by successive ion exchange method detailed in Ref. [17]. The Pt^{2+} ions using $Pt(NH_3)_4(NO_3)_2$ complex were exchanged first into NaY zeolite, then the platinum complex decomposed by heat treatment in air using a temperature ramp of $3^\circ C\,min^{-1}$. Then, cobalt in the form of $Co(NO_3)_2\cdot 6H_2O$ as Co^{2+} ions was introduced into the sample. The total metal loading was 5.9 wt.%, Pt and Co contents being 12 and 88 at.%, respectively, determined by X-ray fluorescence method. The hydrogen uptake measured in pulse mode at 100°C, was 110 $\mu mol/g_{cat}$ after reduction, which corresponds to high metal dispersion. For preliminary experiments (hydrogen and temperature dependence), a $Pt_{77}Co_{23}$/NaY sample was employed which had been prepared in the same way.

The palladium–cobalt bimetallic sample denoted by $Pd_{67}Co_{33}/SiO_2$, was prepared by sol/gel method using $Pd(NO_2)_2(NH_3)_2$ and $Co(NO_3)_2\cdot 6H_2O$ dissolved in ethyleneglycol and tetraethylorthosilicate, $Si(OC_2H_5)_4$ was used for the gelation process [1]. The total metal loading is 5 wt.%. The characterization of the samples was carried out by means of XRD.

2.2. Catalyst characterization

X-ray photoelectron spectroscopy (XPS) of the samples were performed on the reduced catalyst samples using an XSAM-800 cpi photoelectron spectrometer manufactured by KRATOS. Al Kα and Mg Kα characteristic X-ray lines were applied using an 80 eV pass energy for measuring cobalt and palladium spectra, respectively [18].

2.3. Catalytic reaction

The reaction for methane conversion was investigated in a flow system detailed elsewhere [12] using

100 mg catalyst in the temperature range between 150 and 250°C. For comparison of one-step and two-step processes at 250°C, one 0.5 cm^3 (22.3 μmol) methane pulse was introduced into a stream of 1.3 vol.% H_2/He mixture with a total flow rate of 100 $cm^3\,min^{-1}$ (one-step). The reaction products were collected in a trap at liquid nitrogen temperature. After having warmed up, the sample was analyzed by means of a gas chromatograph type CHROMPACK CP 9002 using a 50 m long plot fused silica column (0.53 mm ID) with a stationary phase of CP-Al_2O_3/KCl with a temperature-programmed mode. As a second option, methane pulse was introduced into pure helium (two-step(1)) followed by hydrogenation at the same temperature (two-step(2)). After having the samples analyzed, the hydrogenation was continued in a stream of hydrogen/helium mixture at 400°C for 1 h (two-step(3)) and the products were again collected in a cold trap and were analyzed as previously. The unconverted methane was not trapped at liquid nitrogen temperature because no zeolite filling was used. The reaction was characterized by the amount of C_{2+} products in micromoles (in methane equivalents) and related the amount of catalyst, or the rate was calculated (in $\mu mol\,s^{-1}\,g_{cat}{}^{-1}$) by calculating the contact time from the flow rate and the volume of the methane pulse. Selectivity was calculated by $\left(C_i/\sum_i C_i\right) \times 100$ for $i = 2$–8.

3. Results and discussion

3.1. Effect of hydrogen concentration and temperature on methane conversion

In a previous paper [1], we have reported the hydrogen dependence on methane conversion measured over $Pd_{67}Co_{33}/SiO_2$ sample. The effect of hydrogen partial pressure in H_2/He mixture (from 0 to 80 vol.%) with a total flow rate of 100 $cm^3\,min^{-1}$ was measured at 250°C. Both the product formation and the selectivity of C_2 fraction showed a maximum at 1.3 vol.% H_2/He. The scenario was explained by the fact that neither too low nor too high hydrogen concentration in the gas stream yields appropriate CH_x surface species for optimum performance. Temperature-programmed reaction also indicated that on Pd–Co/SiO_2 and Pt–Co/NaY ethane and propane already formed during methane chemisorption when the reaction was performed in hydrogen containing inert gas [1,2].

Table 1
Effect of hydrogen concentration in He on the product formation on 100 mg catalyst at 250°C over $Pt_{77}Co_{23}$/NaY sample using 10 pulses

H_2 in helium (%)	Products (μmol)	C_2 selectivity (%)	C_{3+} selectivity (%)
0	0.1	90	10
4.8	0.25	77.6	22.4
80	0.05	51.9	48.1

Over $Pt_{77}Co_{23}$/NaY sample, methane (22.3 μmol each and 10 pulses) was introduced at 250°C into a gas flow containing 80, 4.8 and 0 vol.% hydrogen. The amount of products (μmol/100 mg catalyst), the values of C_2 and C_{3+} selectivity are presented in Table 1. At zero hydrogen content mainly ethane was formed and with increasing hydrogen content the amount of C_{3+} increased. In a second set of experiments the temperature dependence of the methane conversion was studied at 50, 150 and 250°C in 80 vol.% H_2/He mixture (Table 2). The high selectivity in the C_6 and C_7 formation at 150°C is supposed to be due to an optimum surface coverage of the hydrogen atoms, which controls dissociation of the CH_4 to surface CH_x species with not too high hydrogen deficiency. On the other hand, at low coverage of surface hydrogen the chain growth of the CH_x species is facilitated at the expense of the hydrogenation and a dedicated balance is set between chain growth leading to C_{2+} hydrocarbons and the desorption of small hydrocarbons.

3.2. One-step methane conversion to larger hydrocarbons over $Pt_{12}Co_{88}$/NaY

As was indicated [1], during 10 successive methane pulses the catalyst was slowly deactivated,

Table 2
Effect of temperature on the product formation and selectivity over 100 mg $Pt_{77}Co_{23}$/NaY catalyst using 10 pulses and 80% H_2/He mixture

Temperature (°C)	Products (μmol)	C_2 selectivity (%)	C_{3+} selectivity (%)
50	0.05	38.9	61.1
150	0.23	11.6	88.4
250	0.05	51.9	48.1

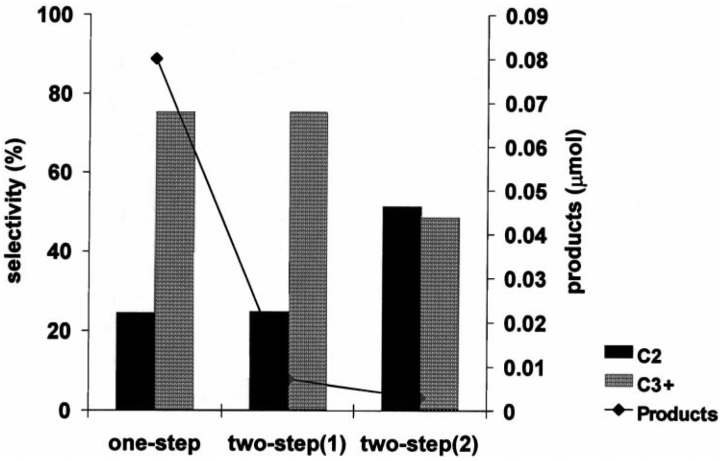

Fig. 1. Comparison of one-step and two-step processes. Amount of products (in μmol/100 mg sample), C_2 and C_{3+} selectivities (%) measured over $Pt_{12}Co_{88}$/NaY catalyst using 22.3 μmol methane pulsed into 1.3% H_2/He mixture (one-step), or 22.3 μmol methane is pulsed into He (two-step(1)) followed by hydrogenation at 250°C (two-step(2)).

therefore, in the further experiments single methane pulse (22.3 μmol) was applied. The result for $Pt_{12}Co_{88}$/NaY is presented in Fig. 1. From these results we can conclude that the one-step process performed over NaY-supported bimetallic catalysts is superior to those measured on the same catalysts in a two-step process. In the former case the conversion of methane is about 5% referred to 1 g of catalyst, whereas in the two-step process it is about eight times less. In the case of the $Pt_{12}Co_{88}$/NaY catalyst the C_2 selectivity is low, but the contribution of the higher hydrocarbons is significantly higher. After post-hydrogenation at 400°C using a 1.3% H_2/He mixture further hydrocarbons can be removed from the catalyst surface as shown in Table 3.

In Table 4, a comparison is shown between the classical two-step methane conversion and the one-step process carried out on $Pd_{67}Co_{33}/SiO_2$ sample, when only one pulse of methane (22.3 μmol) is added into the gas stream. In the one-step process, 1.3 vol.% H_2/He was used as carrier gas and in the two-step process, methane was chemisorbed first in pure helium at 250°C and the hydrogenation was carried out in 1.3 vol.% H_2/He mixture as used in the one-step process at the same temperature. In Row 1, the products formed in one-step process are shown and amount to 7.2 $\mu mol/g_{cat}$, while in the two-step process presented in Rows 2 and 3, the amount of products is about 2.5-fold lower. This result undoubtedly demonstrates the advantage of the one-step over the two-step one.

Methane conversion carried out over the Pd–Co/SiO_2 and Pt–Co/NaY samples are compared and the results presented in Table 5. On Pd–Co/SiO_2 larger amount of C_{2+} hydrocarbons is formed than on zeolite-supported Pt–Co sample. Selectivities are also different in the C_2 production. The key issue in this process is the presence of small, but constant hydrogen coverage on the metal surface. Earlier studies have indicated that the CH_x should contain two hydrogen atoms for optimum performance in methane conversion [3].

Table 3
Effect of post-hydrogenation after one-step process at 250°C over 100 mg $Pt_{12}Co_{88}$/NaY catalysts using one methane pulse in a 1.3 vol.% H_2/He mixture

Sample	Products C_{2+} (μmol)	Rate ($\mu mol\, s^{-1}\, g^{-1}$)	C_2 selectivity (%)	C_{3+} selectivity (%)	Condition
$Pt_{12}Co_{88}$	0.082	2.74	24.8	75.2	H_2/He at 250°C
$Pt_{12}Co_{88}$	0.062	–	11.9	88.1	H_2 at 400°C for 1 h

Table 4
Comparison of one- and two-step reactions in methane conversion over 100 mg $Pd_{67}Co_{33}/SiO_2$ catalyst using a 1.3 vol.% H_2/He mixture at 250°C

Methods	Products (μmol/100 mg_{cat})	C_2 selectivity (%)	C_{3+} selectivity (%)	Conditions
One-step process	0.72	5.6	94.4	One CH_4 pulse in 1.3% H_2/He
Two-step process				
First step CH_4 (ads)	0.18	23.4	86.6	One CH_4 pulse at 250°C in He
Second step in H_2/He	0.13	31.0	69.0	At 250°C for 10 min
First plus second steps	0.31	–	–	–
Third step in H_2/He	4.48[a]	21.7	88.3	At 400°C for 1 h

[a] Hydrogenation of the sample after the accomplishment of first and second steps.

Maintaining small, but definite hydrogen coverage on the surface, the CH_4 dissociation can be controlled in a way which ensures optimum performance.

In order to be able to interpret the results, following facts must be considered. First, the one-step process is primarily assigned to the metallic cobalt particles whose reduction is facilitated by the presence of platinum and palladium. Secondly, there is a significant cobalt enrichment on the catalyst surface [1] thus we have a good reason to assume the metallic cobalt as working site during methane chemisorption. Since the platinum ions are exchanged first followed by decomposition, the bimetallic particles with cobalt are formed in the supercage. Thus, cobalt ions are reduced to a large extent. Due to the intimate contact between Pt and Co, C_2 and C_{3+} have the highest selectivity because hydrogen activation takes place easily over Pt sites surrounding the cobalt atoms. Although the nominal composition of the two samples are different, the particle size of the bimetallic particles is similar (3 and 6 nm for Pt–Co and Pd–Co, respectively). That is, despite the difference in composition between Pt–Co and Pd–Co samples the surface morphology is not too far from each other.

The question arises whether or not the present process can be considered a real one-step methane conversion. If we analyze what happens at the surface, we arrive at the conclusion that as the nearly square shape methane pulse moves along the catalyst bed, after the pulse hydrogen is still present on the surface resulting from the carrier gas, which contains already hydrogen. Consequently, the surface CH_x species can be swept off the surface in form of larger hydrocarbon molecules. It is indeed the case, but methane dissociation is assisted by hydrogen content on the surface, thus the x value in the surface CH_x species is controlled by the dissociation on hydrogen containing metal surface. According to the proposed mechanism it is suggested that small amount of H_2 in He during methane chemisorption maintains certain hydrogen coverage on the metal surface, consequently the total removal of hydrogen from the surface CH_x species is prevented. When the x value is $2 \geq x > 0$, the surface chain growth already starts during methane chemisorption. When hydrogen coverage is too high, $x \geq 3$, consequently dissociation of CH_4 is hampered. When hydrogen coverage is too low, significantly larger fraction of the chemisorbed methane is transferred into surface carbon whose conversion and subsequent hydrogenation is hardly impossible. This is the reason why additional hydrogenation at 400°C for 1 h results in a further removal of the long-chain hydrocarbons.

Table 5
Comparison of one-step methane conversion performed at 250°C

Sample	Products C_{2+} (μmol)	C_2 selectivity (%)	C_{3+} selectivity (%)	Conversion (%)
$Pt_{12}Co_{88}$/NaY	0.08	24.4	75.6	0.3
$Pd_{67}Co_{33}/SiO_2$	0.72	5.6	94.4	3.2

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