Chinese Journal of Catalysis 36 (2015) 1777–1784 催化学报 2015年 第36卷 第10期 | www.chxb.cn

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Article

High-temperature Shilov-type methane conversion reaction: Mechanistic and kinetic studies

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ARTICLE INFO

Article history:
Received 20 March 2015
Accepted 17 August 2015
Published 20 October 2015

Keywords:
Shilov reaction
Catalyst deactivation
Reaction mechanism and kinetics
Reactivity and selectivity
Deuterium-isotope exchange

ABSTRACT

Traditional Shilov reactions (performed in aqueous solution with a $PtCl_2$ catalyst) for methane conversion suffer from catalyst deactivation at high temperatures (> 100 °C), therefore only very low conversion rates have been achieved. In this paper, we show that Shilov-type C–H activations are achievable at much higher temperatures (~200 °C) by addition of concentrated aqueous solutions of Cl^- to inhibit Pt catalyst precipitation. Various chloride-based ionic liquids also stabilized the Pt catalyst at mild reaction temperatures (~140 °C). Under high-pressure conditions (> 25.5 MPa), achieved using a specially designed sealed gold-tube reactor, very high methane conversion rates (> 90%) were obtained; this is attributed to the improved methane solubility in aqueous solution. Deuterium isotope (H/D) exchange between methane and water was used to examine the reaction reactivity and selectivity. Multiply D-substituted products were observed, indicating that multiple C–H activations occurred. A comprehensive network reaction that included all the chain reactions was set up to clarify the reactivities and product selectivities of the methane activation reactions. The reaction network consisted of a series of parallel first-order reactions, which can be described by the Arrhenius equation. The kinetic parameters such as the frequency factor, activation energies, and stoichiometric coefficients were obtained by fitting the experimental data. Because all four C–H bonds in a methane molecule are equivalent, multiple substitutions during methane conversion cannot be avoided. Our studies indicate that mono-substituted and di-substituted methane isotopologue generations have similar activation energies, suggesting that the highest mono-substitution selectivity cannot be greater than 50%.

1. Introduction

Natural gas (NG), which is primarily composed of methane (typically 85%–90%), is one of the most abundant hydrocarbon-based feedstocks. NG is considerably more efficient and cleaner than other fossil fuels, because of its higher H/C ratio and British thermal unit value. However, the economic value of NG is greatly underplayed, partly because its gaseous nature

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This work was partially supported by US Department of Energy (DE-EE0003461) and financially supported by the National Basic Research Program of China (973 Program, 2012CB215303).
DOI: 10.1016/S1872-2067(15)60966-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 10, October 2015

hinders its transportation and use. Methane conversion to high-value liquid chemicals and fuel products has long been regarded as the "Holy Grail" by chemists, because this is key to use NG as an important chemical feedstock. Recently, the increase in global NG reserves and the successful extraction of unconventional shale gas have greatly stimulated the development of gas-to-liquid (GTL) technologies.

The Shilov system, first reported in 1972, has had significant impacts on the development of organometallic GTL C1 chemistry [1–3]. The Shilov process converts alkanes, including CH_4, to other hydrocarbon chemicals such as CH_3OH and CH_3Cl via three key steps.

(1) A C–H activation step – formation of a methylplatinum(II) intermediate from the reaction of CH_4 with Pt(II) (i.e., $[PtCl_6]^{2-}$).

(2) A functionalization step – oxidation of the methylplatinum(II) species to form a methylplatinum(IV) complex.

(3) A catalyst regeneration step – nucleophilic addition at the methyl carbon to yield an organic product, with reduction of the Pt(IV) complex (i.e., $[PtCl_4]^{2-}$) back to Pt(II).

The net reaction is

$$R\text{–}H + [PtCl_6]^{2-} + H_2O \rightarrow R\text{–}OH + [PtCl_4]^{2-} + 2H^+ + 2Cl^- \quad (1)$$

One of the most important features of the original Shilov system is that it can activate the stable C–H bond in CH_4 at temperatures as low as 80 °C. However, further increasing the reaction temperature (> 120 °C) often results in irreversible disproportionation and combination of Pt(II) complexes to form Pt(IV) and Pt(0), which destabilizes the Pt(II) catalyst as a result of metallic Pt(0) precipitation from the aqueous solution:

$$2\,[PtCl_4]^{2-} \rightarrow Pt(0) + [PtCl_6]^{2-} + 2Cl^- \quad (2)$$

Consequently, only low reaction temperatures can be used, resulting in low conversion rates.

Significant efforts have been devoted to improving the stabilities and reactivities of Pt(II)-based catalytic systems using different organic ligand molecules, but commercially practical solutions have not been found [4–9]. For instance, one of the best-known systems was developed by Periana at Catalytica in the 1990s; the catalyst in the system is (bpym)$PtCl_2$ [bpym = η^2-(2,2'-bispyrimidyl)] [10–12]. This system shows excellent efficiency and selectivity in the conversion of CH_4 to CH_3SO_3H, which can be further hydrolyzed to CH_3OH. In contrast to the original Shilov system, which is performed in aqueous solution, Catalytica's catalyst is deactivated by water and the CH_3OH produced; therefore, the conversion reaction can only be performed in highly concentrated (> 96%) sulfuric acid, which limits its commercial feasibility [13].

Ionic liquids (ILs) are superior solvents for a wide variety of organic and inorganic compounds, and have many advantages over conventional volatile organic solvents. ILs are therefore ideal coordination ligands for organometallic catalysts and are good solvents for many catalytic systems [14,15]. Our recent studies have identified several N-heterocyclic ILs that are both thermally and chemically stable under extreme C–H bond activation reaction conditions, which involve powerful Pt-based catalysts at ~200 °C [16]. We anticipated that addition of selected ILs to the Shilov system would reverse the Pt(0) precipitation reaction by maintaining a significant amount of the Pt catalyst in solution, therefore a higher reaction temperature could be used, and the CH_4 conversion rate and catalytic efficiency would be improved.

In this study, we focused on developing mechanistic and kinetic understandings of high-temperature Shilov systems, to improve the stability and reactivity. Pt(II)-catalyzed CH_4 conversion reactions were performed using a specially designed sealed gold-tube mini-reactor, to enable high-pressure (25.5 MPa) conditions to be used, to improve the CH_4 gas solubility in aqueous solution. The solubility of methane in aqueous solution under ambient conditions is low (0.0012 g/kg of water at 60 °C), and is enhanced 1000-fold under high pressure (0.1202 g/kg of water at 20.0 MPa, and 0.1531 g/kg of water at 30.0 MPa, at 60 °C) [17]. H/D exchange experiments were performed to determine the reactivities and selectivities of the reactions. Possible mechanisms for stabilizing the Pt catalyst in aqueous solution are discussed. The stability at high temperatures is attributed to the effect of concentrated Cl^-. A comprehensive reaction network using a series of first-order parallel sequential substitution reactions, described by the Arrhenius equation, was set up to determine the detailed reaction kinetics of the high-temperature Shilov process.

2. Experimental

2.1. *Materials*

K_2PtCl_4 and H_2PtCl_6 were purchased from Sigma-Aldrich. The ILs 1-methylimidazolium bisulfate ([1mim][HSO_4]) and 1-methylimidazolium chloride ([1mim][Cl]) were purchased from Fluka, and pyrazinium bisulfate ([pyrz][HSO_4]) was synthesized by protonation of pyrazine with sulfuric acid. For the H/D exchange experiments, only K_2PtCl_4 was used as the catalyst, and D-substituted chemicals, i.e., water (D_2O), CH_3COOH (CD_3COOD), sulfuric acid (D_2SO_4), and hydrogen chloride (DCl), were purchased from Sigma-Aldrich and used as additives. For example, 30% CD_3COOD solution was obtained by mixing CD_3COOD with pure D_2O. In the reactions, the only hydrogen source was therefore activated methane.

2.2. *Sealed gold-tube mini-reactor*

A mini gold-tube (length 10 cm, inner diameter 1.09 cm) was used as the mini-reactor. We chose gold as the material for the mini-reactor because of its chemical inertness, and its flexibility, which allows volume expansion and contraction by external control of the confining pressure. It ensured 100% mass balance, and uniform temperature control was provided by a large box furnace. Efficient contact between the gas-phase methane and liquid-phase reaction media containing the catalysts and liquid stabilizers was achieved by applying external hydraulic pressure.

2.3. *Methods*

The Pt catalyst was dissolved in various reaction media at desired concentrations. The prepared reaction liquid (0.3 mL) was loaded into the gold-tube reactor, which was presealed at one end. CH_4 gas (0.34 MPa, with 3% Ar as an internal standard) was also loaded into the reactor, and the other end was sealed by arc welding. The sealed gold-tube was placed in a stainless-steel autoclave and an external hydraulic pressure of up to 25.5 MPa was applied. The autoclave with the gold-tube was placed in a box furnace to maintain the required reaction temperature through hot-air circulation. After reaction, the sealed gold tube was inserted into a vacuum line and all gas compounds were analyzed using gas chromatography (GC). The remaining liquid and solid residues (if any) were collected and analyzed. The total weights of the sealed gold-tube before and after the reaction were recorded and compared. Typical weight differences were within 0.1 mg, indicating no leakages during the reaction.

2.4. *Analyses*

A Hewlett-Packard 6890 GC with a J&W GS-GASPRO column, thermal conductivity detector, and mass selective detector was used to determine the gas composition and for D-isotopic analyses. The amount of methane gas was deduced from the internal standard Ar integration, and the methane isomers were identified from their characteristic ion masses, i.e., 20 for CD_4, 19 for CHD_3, 18 for CH_2D_2, and 17 for CH_3D. All standard methane isomer samples (16-CH_4, 17-CHD_3, 18-CH_2D_2, 19-CH_3D, and 20-CD_4) were previously analyzed using the same GC-MS instrument to determine their fragmentation patterns, and stored for use as internal references. The methane isomer compositions were derived from the sample fragmentation patterns using the deconvolution method.

3. Results and discussion

3.1. *Mechanistic studies – high-temperature Shilov system*

Pt(0) precipitation in the Shilov system and the effects of different stabilizers at 140 and 185 °C were investigated, with a focus on examining the effects of Cl^- concentration on Pt stabilization. Table 1 summarizes the experimental results obtained under various conditions. The total H/D exchange ratio reflects the degree of CH_4 conversion, and the relative H/D exchange ratio for CH_3D and $CH_{4-x}D_x$ is used as an indication of product selectivity. The turnover number (TON) was determined from the ratio of the molar quantity of activated CH_4 to that of catalyst. Inductively coupled plasma-atomic emission spectroscopy (ICPAES; Leeman Labs Prodigy) was used to confirm that the precipitated deposit was metallic Pt(0). A piece of the opened gold tube with precipitates was immersed in 2% HNO_3 solution in an ultrasonic washer overnight, cleaned with deionized water, and dried under vacuum. The total weight of the solid sample was recorded. The sample was then dissolved in chloroacetic acid and subjected to ICP-AES to determine the concentrations of the elements in the sample solution. The results showed that the only metallic elements in the solid residue from the precipitates were Pt (0.15 wt%, 906.1 μg/g) and Au (99.85 wt%).

3.1.1. *Effects of chelation with carboxylic anions*

Shilov suggested that addition of CH_3COOH might signifi-

Table 1

H/D exchange experiments for Pt-catalyzed high-temperature Shilov methane conversion reactions.

Entry	Catalyst		Reaction media	Ionic liquid	Temp. (°C)	Time (h)	D/H exchange ratio			TON
	Compound	Conc. (mmol/L)					$CH_{4-x}D_x$	CH_3D	D/H	C–H
1	K_2PtCl_4	50	D_2O	—	140	4	7.2	3.3	10.5	0.5
2	K_2PtCl_4	20	D_2O + CD_3COOD (30%)	—	140	4	13.0	5.1	18.1	2.1
3	K_2PtCl_4	20	D_2O + CD_3COOD (30%)	—	140	12	13.1	5.0	18.1	2.1
4	K_2PtCl_4	50	D_2O + F_3COOD (30%)	—	140	5	18.0	9.9	27.9	2.6
5	H_2PtCl_6	20	D_2O + CD_3COOD (30%)	—	140	12	19.4	7.3	26.7	3.2
6	K_2PtCl_4 + H_2PtCl_6	20 + 100	D_2O + CD_3COOD (30%)	—	140	12	31.4	8.3	39.7	0.8
7	K_2PtCl_4	20	D_2O + CD_3COOD (30%) + DCl (8.4 mol/L)	—	140	4	2.8	2.0	4.8	0.5
8	K_2PtCl_4	20	D_2O + CD_3COOD (30%) + D_2SO_4 (1 mol/L)	—	140	4	2.9	1.0	3.9	0.5
9	K_2PtCl_4	20	D_2O + CD_3COOD (30%) + DCl (8.4 mol/L)	—	185	24	66.5	22.5	89.0	37.7
10	K_2PtCl_4	20	D_2O + CD_3COOD (30%) + D_2SO_4 (4.2 mol/L)	—	185	4	35.5	18.0	53.5	5.9
11	K_2PtCl_4	20	D_2O (30%) + DCl (8.4 mol/L)	—	185	24	54.1	11.8	65.9	30.6
12	K_2PtCl_4	20	CD_3COOD (30%) + DCl (8.4 mol/L)	—	185	4	22.6	11.2	33.8	3.8
13	K_2PtCl_4	50	D_2O	[pyrz][HSO_4][a]	140	4	1.9	1.8	3.7	0.1
14	K_2PtCl_4	50	D_2O	[pyrz][HSO_4][b]	140	4	2.0	1.7	3.7	0.1
15	K_2PtCl_4	20	D_2O + CD_3COOD (30%)	[1mim][Cl][a]	140	4	2.2	1.7	3.9	0.4
16	K_2PtCl_4	20	D_2O + CD_3COOD (30%)	[1mim][Cl][b]	140	4	3.1	2.2	5.3	0.5
17	H_2PtCl_6	20	D_2O + CD_3COOD (30%)	[1mim][Cl][b]	140	12	6.2	3.5	9.7	1.0
18	K_2PtCl_4	20	D_2O + CD_3COOD (30%)	[1mim][HSO_4][a]	140	4	2.2	1.8	4.0	0.4
19	K_2PtCl_4	20	D_2O + CD_3COOD (30%)	[1mim][Cl][b]	185	4	9.5	5.0	14.5	1.6
20	H_2PtCl_6	20	D_2O + CD_3COOD (30%)	[1mim][Cl][b]	185	4	15.9	8.8	24.7	2.7

[a] The ionic liquid and Pt-catalyst were heated at 150 °C for 30 min, then added into the CD_3COOD solution after cooling down.

[b] The ionic liquid, Pt-catalyst, and CD_3COOD solution were mixed together at room temperature.

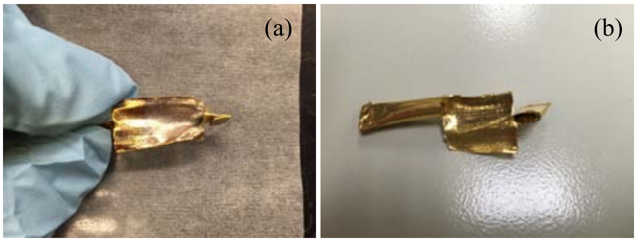

Fig. 1. Inner surface of gold tube after reactions with coated film (a) and clean surface (b).

cantly increase methane conversion (~30 times) in low-temperature, low-conversion reactions. He attributed this to chelate formation between carboxylic anions and the Pt catalyst, which would prevent Pt precipitation. Without the addition of a chelating agent, the H/D exchange ratio was quite small in pure D_2O, even when we applied a high external pressure (3700 psi) to increase methane solubility in the aqueous phase (Table 1, entry 1). Addition of 30% CD_3COOD significantly promoted H/D exchange (Table 1, entry 2), even for small amounts of catalyst; this is in general agreement with Shilov's observations. However, at 150 °C, extensive Pt(0) precipitation still occurred. This was supported by the finding that performing the reaction under the same conditions for a longer time (12 h, Table 1, entry 3) did not significantly improve the TON, suggesting that the catalyst was deactivated within 4 h, and the coating Pt(0) layer did not catalyze C–H activation. However, CF_3COOD enhanced the reactivity to a lesser extent, even at a higher catalyst concentration and longer reaction time (Table 1, entry 4, 150 °C, 5 h). This is probably because the stronger electrophilicity of F atoms makes the chelating ability of the F_3COO group lower than that of the D_3COO group. Changing the catalytic system from K_2PtCl_4 to H_2PtCl_6 or their mixture (Table 1, entries 5 and 6) did not improve the Pt stability. These results suggest that the addition of CH_3COOH is not enough to prevent Pt(0) precipitation at high temperatures. The substantial increases in the conversion could arise from the enhanced CH_4 solubility.

3.1.2. *Effects of acid stabilizers*

The addition of excess DCl and D_2SO_4 at 140 °C can also effectively prevent Pt(0) precipitation (Table 1, entries 7 and 8). Even at a higher temperature (185 °C) and a longer reaction time (24 h), the addition of DCl stabilizes the Pt catalyst in aqueous media, but D_2SO_4 does not (Table 1, entries 9 and 10). The stabilizing effect of DCl is independent of the addition of carboxylic acid (Table 1, entries 11 and 12), but the Cl^- concentration has a significant effect. These results suggest that Cl^- strongly affects Pt stabilization, as a result of the equilibrium reaction:

$$Pt(0) + [PtCl_6]^{2-} + 2\ Cl^- \rightarrow [PtCl_4]^{2-} \qquad (3)$$

This is the reverse of the Pt(0) precipitation reaction (reaction (2)). More importantly, the proton concentration and solution acidity have less effect on Pt(0) stabilization, because sulfuric acid did not prevent Pt(0) precipitation at 185 °C. This suggests the possibility of replacing high concentrations of H^+ with more eco-friendly cations, while maintaining a high Cl^- concentration, using ILs such as [1mim][Cl].

3.1.3. *Effects of ILs*

The addition of various ILs (Table 1, entries 13–18) resulted in virtually no Pt precipitation at 140 °C, indicating that selected ILs stabilized the Pt catalyst. However, the overall H/D exchange rates also decreased. Possible explanations are that the added ILs do not improve the CH_4 solubility and/or formation of Pt–IL complexes decreases the catalytic activity (as in the case of Catalytica's system, which required a temperature of ~220 °C). The selected ILs did not stabilize the Pt catalyst at 185 °C (Table 1, entries 19 and 20).

3.1.4. *Effect of Cl^- concentration*

The maximum Cl^- effect was determined from a series of H/D exchange experiments at various DCl concentrations (Table 2, entries 21–27, and Fig. 2). All reactions were conducted at 200 °C and an external hydraulic pressure of 25.5 MPa for 4 h in 30% CD_3COOD with 20 mmol/L K_2PtCl_4 as the catalyst. The results clearly show that the amount of silver coating decreased with the increasing Cl^- concentration, and the conversion also decreased. These results suggest that a highly concentrated Cl^- solution effectively prevented Pt(0) precipitation at high temperatures, but the activity of the Pt catalyst was also reduced.

Table 2
High-temperature Shilov reactions with addition of various concentrations of Cl^-.

Entry	Stabilizer	DCl concentration (mol/L)	D/H exchange ratio			Coating
			$CH_{4-x}D_x$	CH_3D	D/H	
21	DCl + D_2O	0.7	61.0	29.0	90.0	Silver
22	DCl + D_2O	2.8	60.7	33.7	94.4	Silver
23	DCl + D_2O	4.2	61.1	31.1	92.2	Silver
24	DCl + D_2O	4.9	65.5	34.5	100.0	Slightly
25	DCl + D_2O	5.6	58.8	29.8	88.6	No
26	DCl + D_2O	6.3	43.3	20.5	63.8	No
27	DCl + D_2O	8.4	22.7	10.0	32.7	No

Reaction system consisted of K_2PtCl_4 (20 mmol/L) + CD_3COOD (30%) + CH_4, and reaction temperature was 185 °C.

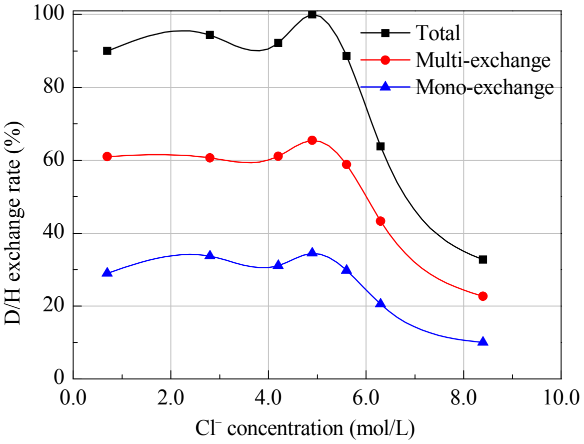

Fig. 2. H/D exchange rates for high-temperature Shilov reaction at 185 °C with various Cl^- concentrations. Pt(0) precipitation occurred at lower Cl^- concentrations (< 5.0 mol/L). Reaction slowed down if Cl^- concentration was too high.

3.2. *Kinetic studies of sequential H/D exchanges*

The addition of highly concentrated Cl^- and use of a high-pressure reactor enabled high CH_4 conversions to be achieved. Under these conditions, multiply substituted methane isotopologues such as CH_3D, CH_2D_2, CHD_3, and CD_4 were observed, indicating that multiple C–H bond activations occurred. The high-temperature Shilov system therefore involves a complex network of multiple and sequential reactions.

3.2.1. *Experimental data*

A series of isothermal experiments were conducted at 200 °C (25.5 MPa external pressure). The reaction system consisted of K_2PtCl_4 (5 mmol/L) as the catalyst, and 30% CD_3COOD and DCl (9 mol/L in D_2O solution) as the reaction medium. A number of gold-tube mini-reactors loaded with the same reactants were extracted from the box furnace at reaction times of 4, 8, 20, 24, 32, and 100 h. When the gold tube was opened after the reactions, no silver coating was observed, indicating that severe catalyst deactivation had not occurred, because of the addition of excess Cl^-. Individual D-substituted methane compounds were identified using GC-MS; the data are summarized in Table 3.

3.2.2. *Reaction network*

The kinetics of the high-temperature Shilov system, which involves multiple substitution reactions, was investigated using a reaction network involving a number of parallel reactions:

$$CH_4 \rightarrow a_{11}CH_3D + a_{12}CH_2D_2 + a_{13}CHD_3 + a_{14}CD_4 \quad (4)$$

$$CH_3D \rightarrow a_{21}CH_2D_2 + a_{22}CHD_3 + a_{23}CD_4 \quad (5)$$

$$CH_2D_2 \rightarrow a_{31}CHD_3 + a_{32}CD_4 \quad (6)$$

$$CHD_3 \rightarrow CD_4 \quad (7)$$

If the reactions are assumed to be first order, the rate constant k of each reaction can be determined from the Arrhenius equation:

$$k = A_f\exp(-E_a/RT) \quad (8)$$

where A_f is the frequency factor, E_a is the activation energy, T is the absolute temperature, and R is the gas constant. Because nearly 100% mass balance can be achieved with our experimental setup, we consider the redistributions of five different methane isotopologues to be kinetically controlled by reactions (4) to (7). The stoichiometric coefficients a_{ij} can be determined from the optimized reaction kinetics, based on the experimental data listed in Table 3.

Table 3
Results of isothermal high-temperature Shilov reactions.

Entry	Time (h)	H/D exchange ratio (‰)				
		CH_3D	CH_2D_2	CHD_3	CD_4	$CH_{4\text{-}y}D_y/CH_4$
28	4	34.70	14.30	0.00	0.00	49.00
29	8	81.05	68.85	29.10	0.00	179.00
30	20	197.70	164.50	144.10	86.90	227.10
31	24	149.30	193.40	302.30	264.80	909.80
32	32	180.10	183.80	263.10	248.10	875.10
33	100	0.00	0.00	130.70	869.30	1000.00

Reaction system consisted of K_2PtCl_4 (5 mmol/L) + CD_3COOD (30%) + DCl (9 mol/L in D_2O) + CH_4, and reaction temperature was 200 °C.

We developed a precursor kinetic scheme to optimize the kinetic parameters and stoichiometric coefficients. For example, the reaction kinetics for production of each of the D-substituted isotopologues (CH_3D, CH_2D_2, CHD_3, and CD_4) from CH_4, represented by equation (4), will be different. Four precursors, p-CH_3D, p-CH_2D_2, p-CHD_3, and p-CD_4 are introduced:

$$CH_4 \rightarrow a_{11}p\text{-}CH_3D + a_{12}p\text{-}CH_2D_2 + a_{13}p\text{-}CHD_3 + a_{14}p\text{-}CD_4 \quad (4a)$$

$$p\text{-}CH_3D \rightarrow CH_3D \quad (4b)$$

$$p\text{-}CH_2D_2 \rightarrow CH_2D_2 \quad (4c)$$

$$p\text{-}CHD_3 \rightarrow CHD_3 \quad (4d)$$

$$p\text{-}CD_4 \rightarrow CHD_4 \quad (4e)$$

Reaction (4a) is considered to be fast (low activation), and CH_4 is quickly transformed to the four precursors, which follow different reaction kinetics, (4b), (4c), (4d), and (4e), to generate four isotopologues. Similarly, for reactions (5) and (6), three-precursor and two-precursor schemes, respectively, were used. There are therefore 13 reactions in the overall reaction network, i.e., five for isotopic substitutions of CH_4 (one for precursor generation, four for reactions of individual components), four for isotopic substitutions of CH_3D (one for precursor generation, three for reactions of individual components), three for isotopic substitutions of CH_2D_2 (one for precursor generation, two for reactions of individual components), and one for isotopic substitution of CHD_3 to form CD_4. It is worth noting that we assume that the kinetic processes have not achieved final equilibrium, therefore all reactions are kinetically controlled, i.e., there are no recombination reactions involved.

3.2.3. *Optimization*

Optimization and parameter fitting were performed iteratively. The concentrations of all methane isotopologues were computed for a given parameter set (frequency factor, activation energies, and stoichiometric coefficients). An error function summing the square of errors between the calculated and measured concentrations was minimized using the simplex optimization method. In theory, the frequency factor A_f depends on the reaction conditions such as temperature and pressure, and reflects the degree of molecular collisions. All the reactions considered have similar mechanisms, therefore we assume a constant frequency factory, $A_f = 10^9$, for all reactions. There are a total of nine stoichiometric coefficients and 10 activation energies that need to be optimized (we assume that the three precursor generation reactions are fast, and their activation energies are small, i.e., 20 kcal/mol). The commercially available Kinetics05 and OptimRx1.35.0 software packages were used for the optimization procedure.

3.2.4. *Kinetics of high-temperature Shilov reactions*

The optimized kinetic parameters are listed in Table 4, and the theoretical predictions made based on optimized kinetic fitting with the experimental data are shown in Fig. 3.

First, the activation energy of $CH_4 \rightarrow CH_2D_2$ (29.9 kcal/mol) is nearly equal to that of $CH_4 \rightarrow CH_3D$ (29.9 kcal/mol), but much less than those of $CH_4 \rightarrow CHD_3$ (39.7 kcal/mol) and $CH_4 \rightarrow CD_4$ (40.0 kcal/mol), indicating that the primary generation reac-

Table 4
Reactions in methane H/D exchange experiments for kinetic fitting, and preliminary fitting results.

Reaction	E_a (kcal/mol)	
$CH_4 \rightarrow a_{11}CH_3D\text{-p1} + a_{12}CH_2D_2\text{-p1} + a_{13}CHD_3\text{-p1} + a_{14}CD_4\text{-p1}$	$E_{04} = 20$	(4)
$a_{11} = 0.561$, $a_{12} = 0.437$, $a_{13} = 0.00207$, $a_{14} = 0.0000142$		
$CH_3D\text{-p1} \rightarrow CH_3D$	$E_{4a} = 29.9$	(4a)
$CH_2D_2\text{-p1} \rightarrow CH_2D_2$	$E_{4b} = 29.9$	(4b)
$CHD_3\text{-p1} \rightarrow CHD_3$	$E_{4c} = 39.7$	(4c)
$CD_4\text{-p1} \rightarrow CD_4$	$E_{4d} = 40.0$	(4d)
$CH_3D \rightarrow a_{21}CH_2D_2\text{-p2} + a_{22}CHD_3\text{-p2} + a_{23}CD_4\text{-p2}$	$E_{05} = 20$	(5)
$a_{21} = 0.396$, $a_{22} = 0.591$, $a_{23} = 0.013$		
$CH_2D_2\text{-p2} \rightarrow CH_2D_2$	$E_{5a} = 29.8$	(5a)
$CHD_3\text{-p2} \rightarrow CHD_3$	$E_{5b} = 29.5$	(5b)
$CD_4\text{-p2} \rightarrow CD_4$	$E_{5c} = 31.1$	(5c)
$CH_2D_2 \rightarrow a_{31}CHD_3\text{-p3} + a_{32}CD_4\text{-p3}$	$E_{06} = 20$	(6)
$a_{31} = 0.682$, $a_{32} = 0.318$		
$CHD_3\text{-p3} \rightarrow CHD_3$	$E_{6a} = 29.9$	(6a)
$CD_4\text{-p3} \rightarrow CD_4$	$E_{6b} = 28.9$	(6b)
$CHD_3 \rightarrow CD_4$	$E_{07} = 30.4$	(7)

tions from CH_4 to CH_3D and CH_2D_2 occur simultaneously. Secondly, the activation energies of $CH_3D \rightarrow CH_2D_2$ (29.8 kcal/mol), $CH_3D \rightarrow CHD_3$ (29.5 kcal/mol), and $CH_3D \rightarrow CD_4$ (31.1 kcal/mol), $CH_2D_4 \rightarrow CHD_3$ (29.9 kcal/mol) and $CH_2D_2 \rightarrow CD_4$ (28.9 kcal/mol), and $CHD_3 \rightarrow CD_4$ (30.4 kcal/mol) are all very close to or less than those of the first generations of CH_2D_2 and CHD_3. This suggests that because all four C–H bonds are equivalent, the activation conditions for the second, third, and fourth C–H bonds are the same as those for the first C–H bond. Thirdly, the stoichiometric coefficients of $CH_4 \rightarrow CHD_3$ and CD_4 are much smaller (< 0.1%) than those of CH_3D and CH_2D_2. CH_3D and CH_2D_2 will therefore both be initially generated from CH_4. After more than 20 h, further isotopic replacements occur such that CHD_3 and CD_4 are generated from CH_3D and CH_2D_2. After 100 h, all multi-substituted compounds also become reactive, and the overall process is no longer kinetically controlled. The thermodynamic equilibrium effect becomes predominant; our results indicate that CH_3D and CD_4 are more energetically stable than CH_2D_2 and CHD_3.

4. Conclusions

The original Pt-catalyzed Shilov system for CH_4 activation can be stabilized at high temperature (~200 °C) by the inclusion of excess Cl^- in the aqueous solution. The CH_4 conversion rate can be further improved by enhancing the gas solubility using a high-pressure reactor. The mechanism of Pt stabilization with concentrated Cl^- is attributed to an equilibrium shift for the reaction $Pt(0) + PtCl_6^{2-} + 2\,Cl^- \leftrightarrow 2\,PtCl_4^{2-}$; this inhibits Pt(0) precipitation. Selected chloride-based ILs also stabilize the Pt catalyst at a lower reaction temperature (~140 °C). The carboxylic group from CH_3COOH or CF_3COOH can chelate with the Pt catalyst, but the stabilization effects are smaller than that of Cl^-.

CH_4 is a highly symmetric (tetrahedral symmetry, T_d) molecule in which all four C–H bonds are equivalent. A catalytic system with reaction conditions under which a C–H bond can be activated will probably also activate the other three C–H bonds,

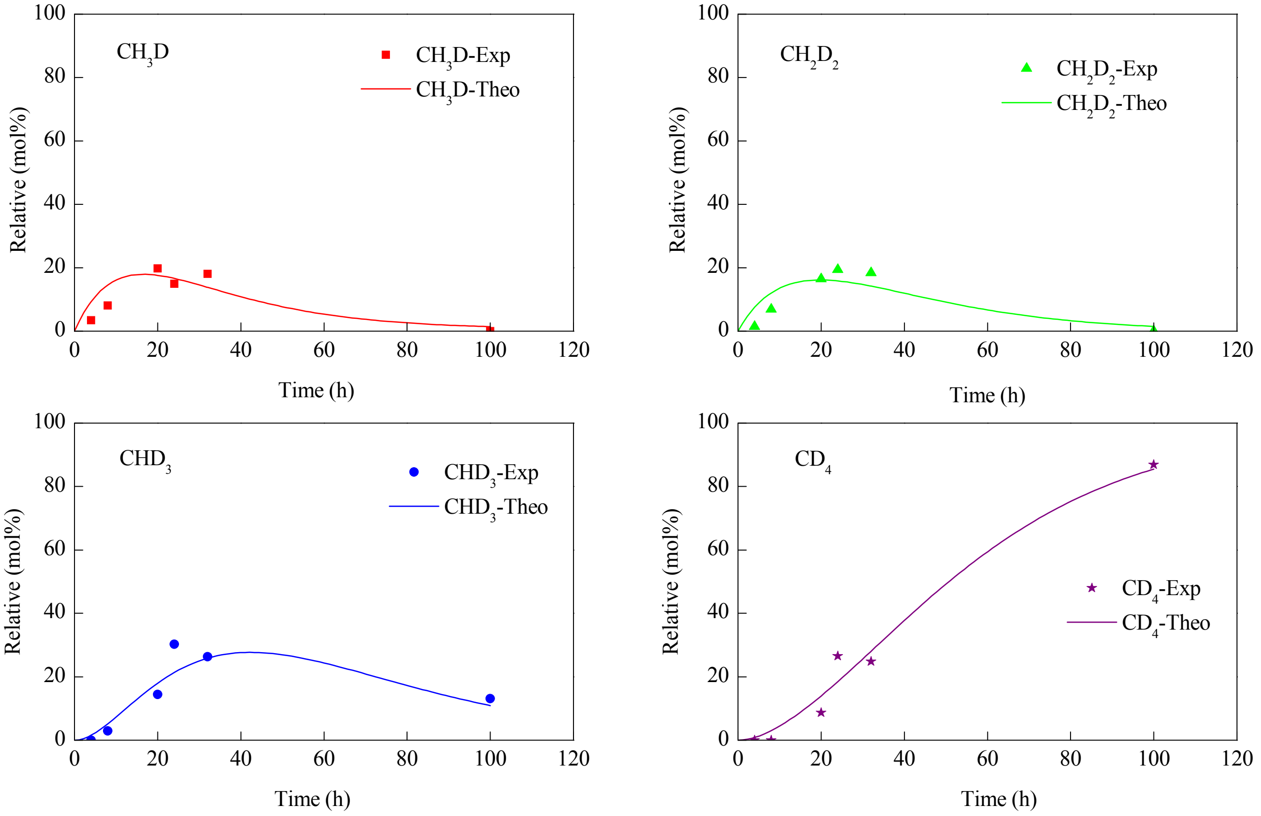

Fig. 3. Kinetic fitting results based on reaction network, and experimental data.

and such sequential reactions often lead to poor product selectivity. We used a high-pressure reactor and excess Cl^- to maintain the catalytic activity at higher reaction temperatures and achieved nearly 100% CH_4 conversion in a Shilov-type reaction. We were therefore able to study the detailed mechanism and kinetics of the reaction, including C–H over-activation reactions. A reaction network consisting of a series of parallel chemical reactions was established, and the kinetic parameters (activation energies and stoichiometric coefficients) were optimized by fitting the experimental data.

The following conclusions were drawn.

1. The H atoms in CH_4 are substituted with D atoms to give CH_3D or CH_2D_2 via a first-order substitution reaction. The theoretical fitting results gave similar activation energies (~29.9 kcal/mol), reflecting the experimental observation of early generation of both CH_3D and CH_2D_2.

2. Direct tri- or tetra-substitutions of CH_4 to form CHD_3 and CD_4 require much higher energies (39.7 kcal/mol and 40.0 kcal/mol) than mono- and di-substitutions. Direct conversions from CH_4 to CHD_3 and CD_4, i.e., simultaneous activations of three or four C–H bonds, are therefore more difficult.

3. The activation energies for the conversions of CH_3D and CH_2D_2 fall within the same range as their generation from CH_4 (~29.9 kcal/mol). This suggests that mono- or di-substituted methane isotopologues are subject to further substitutions, because if a reaction system can activate one C–H bond of CH_4, it is probable that other C–H bonds will also be activated.

4. In our system, where a sufficient supply of D atoms is available, the final products are CHD_3 and CD_4 in a molar ratio of 80:20, suggesting that multiply D-substituted CH_4 molecules are thermally more stable than mono-substituted ones.

5. For CH_4 conversion to CH_3Cl and other CH_4 chlorination reactions, excess CH_4 is typically present, therefore the final product distribution will be determined by the availability of Cl atoms. If $CHCl_3$ or CCl_4 is the target end product, a significantly large amount of Cl^- is needed.

6. It is difficult to achieve high selectivity for singly substituted methane (i.e., CH_3Cl), not only because of possible higher substitution reactions, but also because the formation of CH_2Cl_2 is possible. Even if higher substitution reactions can be prevented, the best achievable CH_3Cl selectivity is probably 50%.

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Graphical Abstract

Chin. J. Catal., 2015, 36: 1777–1784 doi: 10.1016/S1872-2067(15)60966-4

High-temperature shilov-type methane conversion reaction: Mechanistic and kinetic studies

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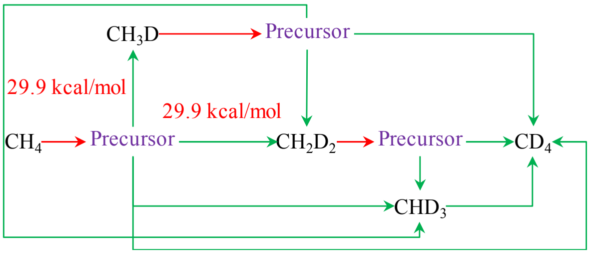

Kinetic studies indicate that multiple substitutions in methane conversion are inevitable. Mono- and di-substituted methane isotopologue generation reactions have similar activation energies. The highest mono-substitution selectivity cannot exceed 50%.

高温Shilov甲烷转化反应的机理和反应动力学研究

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摘要: 传统的Shilov反应是以$PtCl_2$作为催化剂在水溶液中实现甲烷转化的, 该反应的条件温和, 在低至80 °C时即可将甲烷中非常稳定的C–H键活化. 然而, 如果将反应温度提高达100 °C以上, 催化剂Pt(II)则非常容易发生歧化反应转化为Pt(0)或者Pt(IV), 其中Pt(0)将会以沉淀的形式存在于反应溶液中. 所以该反应只能在较低的温度进行, Shilov体系也只能得到较低的甲烷转化率, 因此如何避免高温时催化剂因沉淀失活成为了提高反应转化率的研究重点. 本文重点考察了高温条件下Shilov体系的反应机理和反应动力学, 从而寻求提高催化体系活性和稳定性的途径. 我们在特殊设计的金管反应器中进行了一系列的H/D置换实验, 通过GC根据产物不同的分子量来分析检测. 实验中, 利用特殊设计的金管反应器可将反应压力增加到25.5 MPa, 此时甲烷的溶解度与常温条件下(~60 °C)相比可被提高1000倍以上, 因此甲烷的转化率大大提高.

在高温(~200 °C)条件下的Shilov体系的水溶液中添加了CD_3COOD, F_3COOD, D_2SO_4, DCl和一系列阳离子为$[1mim]^+$的离子液体来考察它们对催化剂沉淀的抑制作用, 结果发现, 在140 °C时添加30%CD_3COOD可在少量催化剂存在的条件下就能够明显促进H/D交换, 与Shilov的结论吻合. 这可能是由于CD_3COO基团的螯合作用造成的, 但将反应温度升到150 °C时则不可避免的生成了Pt(0)沉淀. 而F_3COOD却在较多催化剂的条件下仍未表现出明显作用, 可能是因为F较强的亲电子性使得F_3COO基团的螯合作用变弱所致. 在140 °C时, D_2SO_4和DCl均能有效抑制Pt(0)沉淀的生成, 尤其是DCl, 在185 °C反应24 h后仍能够稳定水溶液中的Pt基催化剂, 但是在该条件下D_2SO_4却并没有作用. 我们还发现, Cl^-的浓度与沉淀的抑制直接相关, 浓度越高对Pt基催化剂的稳定作用越强, 但质子浓度的增加则对沉淀现象没有太大影响, 我们推断原因是大量的Cl^-能够在$[PtCl_6]^{2-}$的共同作用下将Pt(0)重新转化为了$[PtCl_6]^{2-}$. 在140 °C进行反应时, 各类离子液体的添加能够使Pt(0)沉淀得到抑制, 但是对H/D交换率却没有影响, 可能是因为离子液体与Pt基催化剂螯合形成了Pt-离子液复合物而削弱了催化活性. 在此基础上, 我们特别考察了Cl^-浓度对催化剂沉淀的影响, 发现在200 °C时将Cl^-浓度提高到一定程度, 就能够完全抑制Pt(0)的生成, 但Pt基催化剂的活性也会被同时削弱.

由于高压金管反应器的应用和高浓度Cl^-的添加, 使得甲烷的转化率达到90%以上, 因此, 我们设计了H/D同位素交换实验来考察反应的活性和选择性, 从而针对高温Shilov体系的反应动力学进行研究. 反应在200 °C时进行, 催化剂为K_2PtCl_4, 反应介质为30% CD_3COOD和DCl的水溶液, 实验产物中检测到了CH_3D, CH_2D_2, CHD_3和CD_4四种甲烷的多重氘代同位素体, 说明了交换反应中有多个C–H键被活化. 在此基础上, 为了对甲烷活化过程进行全面描述, 我们建立了涵盖所有连锁反应在内的综合反应网络, 其中包含了H/D交换过程中涉及到的一系列平行的一级反应, 基于实验数据通过阿伦尼乌斯方程计算得到了全部反应的频率因子、活化能和化学计量系数等反应动力学参数. 结果证明, 由于甲烷中所有的C–H键均相同, 因此多重氘代产物的生成在甲烷转化过程中是不可避免的. 其中, 甲烷的单一氘代反应活化能为29.9 kcal/mol, 双重氘代反应活化能为29.8 kcal/mol, 两者十分相近, 因此甲烷活化后的单一氘代产物的选择性最高不会超过50%.

关键词: Shilov反应; 催化剂失活; 反应机理和动力学; 活性和选择性; 氘-同位素置换

收稿日期: 2015-03-20. 接受日期: 2015-08-17. 出版日期: 2015-10-20.
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基金来源: 美国能源部项目(DE-EE0003461); 国家重点基础研究发展计划(973计划, 2012CB215303).
本文的英文电子版由Elsevier出版社在ScienceDirect上出版(http://www.sciencedirect.com/science/journal/18722067).