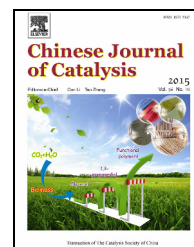


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Article

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

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ABSTRACT

Traditional Shilov reactions (performed in aqueous solution with a PtCl₂ 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 isotope generations have similar activation energies, suggesting that the highest mono-substitution selectivity cannot be greater than 50%.

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1. Introduction

Natural gas (NG), which is primarily composed of methane (typically 85%–90%), is one of the most abundant hydrocar-

bon-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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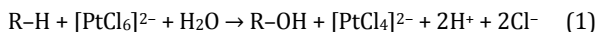
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hinders its transportation and use. Methane conversion to high-value liquid chemicals and fuel products has long been regarded as the “Holy Grail” by chemists, because this is key to use NG as an important chemical feedstock. Recently, the increase 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 CH₄, to other hydrocarbon chemicals such as CH₃OH and CH₃Cl via three key steps.

- (1) A C–H activation step – formation of a methylplatinum(II) intermediate from the reaction of CH₄ with Pt(II) (i.e., [PtCl₆]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., [PtCl₄]²⁻) back to Pt(II).

The net reaction is



One of the most important features of the original Shilov system is that it can activate the stable C–H bond in CH₄ 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:



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)PtCl₂ [bpym = η²-(2,2'-bispyrimidyl)] [10–12]. This system shows excellent efficiency and selectivity in the conversion of CH₄ to CH₃SO₃H, which can be further hydrolyzed to CH₃OH. In contrast to the original Shilov system, which is performed in aqueous solution, Catalytica's catalyst is deactivated by water and the CH₃OH 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 CH₄ 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 CH₄ 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 CH₄ 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

K₂PtCl₄ and H₂PtCl₆ were purchased from Sigma-Aldrich. The ILs 1-methylimidazolium bisulfate ([1mim][HSO₄]) and 1-methylimidazolium chloride ([1mim][Cl]) were purchased from Fluka, and pyrazinium bisulfate ([pyrz][HSO₄]) was synthesized by protonation of pyrazine with sulfuric acid. For the H/D exchange experiments, only K₂PtCl₄ was used as the catalyst, and D-substituted chemicals, i.e., water (D₂O), CH₃COOH (CD₃COOD), sulfuric acid (D₂SO₄), and hydrogen chloride (DCl), were purchased from Sigma-Aldrich and used as additives. For example, 30% CD₃COOD solution was obtained by mixing CD₃COOD with pure D₂O. 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)

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