

УДК 546

## Dechlorinative Oligomerization of Multiply Chlorinated Methanes Catalyzed by Activated Carbon Supported Pt-Co

Vladimir I. Kovalchuk<sup>a,\*</sup>

William D. Rhodes<sup>a</sup> and Mark A. McDonald<sup>b</sup>

<sup>a</sup> Department of Chemical and Petroleum Engineering,  
University of Pittsburgh, Pittsburgh, PA 15261, United States

<sup>b</sup> National Energy Technology Laboratory (NETL),  
United States Department of Energy,  
Pittsburgh, PA 15236, United States <sup>1</sup>

Received 2.03.2012, received in revised form 9.03.2012, accepted 16.03.2012

*The hydrodechlorination of dichloromethane, trichloromethane, and their mixtures catalyzed by a Pt-Co/C catalyst has been investigated in an effort to elucidate the chemistry associated with the generation of hydrocarbon oligomerization products. In the reaction of dichloromethane with hydrogen, the catalyst did not exhibit deactivation and maintained the steady-state activity within 18 h on stream at 523 K; whereas, when trichloromethane was added or converted in the absence of dichloromethane, significant deactivation occurred within the first 5 h on stream. Hydrocarbon oligomerization products were observed with all three reaction mixtures; the selectivity followed the order dichloromethane + dihydrogen < trichloromethane + dihydrogen < dichloromethane + trichloromethane + dihydrogen. The generation of ethane and propane was virtually independent of the reaction mixture composition. However, selectivity toward ethylene and propylene was significantly greater with the trichloromethane + dihydrogen and dichloromethane + trichloromethane + dihydrogen mixtures compared to the dichloromethane + dihydrogen feed. It was concluded that the saturated hydrocarbon products are formed by means of the alkyl mechanism of hydrocarbon chain growth; whereas, the alkenyl mechanism is responsible for the formation of the unsaturated hydrocarbons.*

*Keywords: hydrodechlorination, chloromethanes, dehalogenative oligomerization, Fischer-Tropsch synthesis, reaction mechanism, platinum, cobalt.*

### Introduction

The interest in halocarbon chemistry is motivated by the fact that the halogenated molecules remain important intermediates and products of the chemical process industries [1] and they have detrimental

\* Corresponding author E-mail address: vkovalch@gmail.com

<sup>1</sup> © Siberian Federal University. All rights reserved

impact on the environment [2,3]. Hence, low cost methods to detoxify unwanted halocarbons and their wastes can be considered a societal need. The value of such methods would be significantly increased if they generated valuable products. From this standpoint, dehalogenative oligomerization of  $C_1$  halocarbons to form unsaturated and saturated  $C_{2+}$  hydrocarbons or halocarbons is more valuable than the simple and well-established hydrodechlorination process in which halogen atoms in a  $C_1$  halocarbon are replaced by hydrogen to form methane [4-7].

Among halomethanes, the dehalogenation of  $CF_2Cl_2$ ,  $CCl_4$ , and, to the much lesser extent,  $CHCl_3$  has drawn attention. Dichlorodifluoromethane, a common refrigerant in the recent past, is still present in various applications; whereas,  $CHCl_3$  and  $CCl_4$  are widely used solvents and now are the most prevalent ground water contaminants [7].

It has been shown that dechlorinative oligomerization of  $CCl_4$  and  $CHCl_3$  to form  $C_1$ - $C_7$  hydrocarbons with selectivity greater than 90% is catalyzed by supported Pd [8-14] in the temperature range of 423-643 K and with chloromethane to  $H_2$  ratios of 5-15. Under similar conditions, Pt catalyzes the oligomerization of  $CCl_4$  to partially or completely chlorinated  $C_2$  hydrocarbons with selectivity ranging from 90 to a few percent [15-18] depending on the catalyst precursor, type of the catalyst support, and reaction conditions. There are no  $C_{2+}$  products in the Pt catalyzed hydrodechlorination of  $CHCl_3$  [8].

A comparative investigation of  $CF_2Cl_2$  hydrodechlorination and hydrodehalogenative oligomerization catalyzed by activated carbon-supported Group VIII noble metals revealed the high oligomerization selectivity of Pd/C (~ 75%), which produced mainly saturated and unsaturated  $C_2$ - $C_3$  hydrocarbons at 523 K and  $CF_2Cl_2$  to  $H_2$  mole ratio of 1 [19]. The oligomerization selectivity of Pt/C under the same reaction conditions was less than 5% [19].

The selectivity of supported Pt toward oligomerization products in the  $CF_2Cl_2 + H_2$  reaction changes dramatically in bimetallic catalysts. For example, addition of Co to Pt/C results in the steady-state selectivity toward  $C_{2+}$  hydrocarbons of 50%, with  $C_2$ - $C_3$  olefins and paraffins as the main oligomerization products (523 K,  $CF_2Cl_2$  to  $H_2$  mole ratio of 1) [20]. For the Pt-Cu/C catalysts, the oligomerization selectivity under the same reaction conditions is a function of Pt/Cu atomic ratio and time on stream [21]. This selectivity is low initially but increases with time to exceed 70% toward  $C_{2+}$  hydrocarbons at steady state for the catalysts with Cu/Pt atomic ratio greater than 6.

Based on the research noted, it should be concluded that dehalogenative oligomerization of multiply halogenated methanes is not uncommon in the catalysis of halocarbon dehalogenation and under certain conditions could be considered an alternative route to hydrodechlorination. Surprisingly, investigations of dehalogenative oligomerization of multiply halogenated methanes are not abundant. Specifically, the mechanism of the hydrocarbon chain growth during  $C_1$  halocarbon dehalogenative oligomerization has not been studied. As the oligomerization product distribution follows the Anderson-Schulz-Flory statistics, it was speculated that the hydrocarbons are formed via a polymerization of surface  $C_1$  species [8,9,11] similar to the carbide mechanism of the Fischer-Tropsch synthesis [22]. However, no suggestion on the nature of the  $C_1$  species ( $CH$ ,  $CH_2$ , or  $CH_3$ ) was speculated [8,9,11]. This is quite understandable since the dehalogenative oligomerization investigation of  $CF_2Cl_2$  or  $CCl_4$  [9-14,19,21] does not allow one to address the question of which  $CH_x$  moieties couple to initiate C-C chain growth because both C-Cl and C-F bonds readily dissociate on the transition metal surface to form bare carbon atoms [9,19]. Subsequent interaction of the carbon atoms with adsorbed H atoms will

result in a set of  $\text{CH}_x$  species of different stoichiometry; any possible combination of which may initiate the C-C oligomerization.

The objective of the present research is to shed light on the nature of the  $\text{C}_1$  species that are responsible for initiation and propagation of the hydrocarbon chain in the reaction of dehalogenative oligomerization of multiply halogenated methanes. It has been established that C-Cl bonds of chloromethanes readily dissociate on the surface of Group VIII metals before any carbon-hydrogen bond is broken [6,23,24]. Hence, it is reasonable to suggest that the dissociative adsorption of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  on the metal surfaces will result in the formation of  $\text{CH}_2$  and  $\text{CH}$  species, respectively. Thus, the reaction of  $\text{CH}_2\text{Cl}_2 + \text{H}_2$ ,  $\text{CHCl}_3 + \text{H}_2$ , and  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  mixtures catalyzed by Pt-Co/C was investigated in an effort to differentiate between the so-called “alkyl” [25,26] and the “alkenyl” [27] mechanisms of hydrocarbon formation from multiply-halogenated methanes under conditions of halocarbon hydrodehalogenation. The catalyst choice was due to its high oligomerization selectivity in the  $\text{CF}_2\text{Cl}_2 + \text{H}_2$  reaction [20].

## Experimental

### *Preparation of bimetallic Pt-Co/C*

Activated carbon (Calgon Carbon BPLF3, 6-16 mesh) was crushed and sieved. A 24-60 mesh fraction ( $1400 \text{ m}^2 \text{ g}^{-1}$ , 2.4 nm average pore diameter) was used as the support. The catalyst was prepared by pore volume co-impregnation of the support with solutions of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Alfa, 99.9%) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich, 98%) in 1 N aqueous HCl (EM Science). The concentrations of metal precursors in the impregnating solution were adjusted to obtain a metal loading of 0.3% Pt and 0.9% Co (1:10, atomic ratio). After impregnation, the material was allowed to equilibrate overnight before drying at ambient temperature and pressure for 24 h and then at 373 K for 2 h in vacuum ( $\sim 25$  Torr).

### *Kinetics experiments*

Dechlorination of  $\text{CH}_2\text{Cl}_2$  (Aldrich, purity > 98%),  $\text{CHCl}_3$  (Aldrich, purity > 99%), and their mixture was performed at ambient pressure in a stainless-steel flow reaction system connected to a down-flow quartz microreactor (15 mm i.d.) in which the catalyst was supported on a quartz frit. The reactor zone containing the catalyst was heated by an electric furnace. The temperature of the catalyst was measured and controlled with an accuracy of  $\pm 1$  K with a temperature controller (Athena Series 6075). Gaseous reactants were metered using mass flow controllers (Tylan General, FC-280) and mixed prior to entering the reactor. Liquid  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  maintained at 274 K and 297 K, respectively, were metered into the reaction system via saturators; He was the carrier gas. Saturation was confirmed by varying the He flow rate through the saturators and quantifying the gas phase  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  by a gas chromatograph (GC) (HP 5890 series II).

Prior to the reaction, the catalyst was reduced in a mixture of  $\text{H}_2$  ( $20 \text{ ml min}^{-1}$ ) and He ( $30 \text{ ml min}^{-1}$ ) (Butler, each >99.99%) as it was heated from ambient temperature to 673 K at the rate of  $25 \text{ K min}^{-1}$  and then held at 673 K for 2 h. Next, the catalyst was cooled in He ( $30 \text{ ml min}^{-1}$ ) to the reaction temperature. For the dechlorination reaction, 0.30 g of catalyst was used and the total flow of the reactant mixture through the reactor was  $55 \text{ ml min}^{-1}$ . The flow consisted of  $\text{CH}_2\text{Cl}_2$  (43,640 ppm),  $\text{H}_2$  (43,640 ppm), and He (balance) for the  $\text{CH}_2\text{Cl}_2 + \text{H}_2$  reaction;  $\text{CHCl}_3$  (43,640 ppm),  $\text{H}_2$  (43,640 ppm), and He (balance) for the  $\text{CHCl}_3 + \text{H}_2$  reaction; and  $\text{CH}_2\text{Cl}_2$  (21,820 ppm),  $\text{CHCl}_3$  (21,820 ppm),  $\text{H}_2$  (43640 ppm), and

He (balance) for the  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  reaction. The reaction temperature was maintained at 523 K. The reactor effluent was analyzed on-line by a GC to identify the reaction products. The GC was equipped with a 9 m 80/100 Porapak Q packed column (Supelco) and a flame ionization detector (FID) capable of detecting concentrations  $> 1$  ppm for all chlorocarbons and hydrocarbons involved in this study. Hydrogen chloride, a reaction byproduct, was not quantified.

The kinetics behavior of the three sets of reactants was compared at similar conversion levels (2-3%). The conversion ( $X$ ) was calculated as follows:

$$X = \frac{C_{\text{CHxCl}_y} - \sum n_i C_i}{C_{\text{CHxCl}_y}} \times 100\%,$$

where  $C_{\text{CHxCl}_y}$  is the mole fraction of halomethane(s) in the feed,  $n_i$  and  $C_i$  are the number of carbon atoms in a product molecule and the mole fraction of the product  $i$  in effluent gas, respectively. As the true conversion of each reactant for the mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  could not be determined herein, the combined conversion was obtained in this case, calculated as the mole fraction of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  converted to reaction products. The selectivities ( $S_i$ ) toward detectable carbon-containing products were calculated as follows:

$$S_i = \frac{n_i C_i}{\sum n_i C_i} \times 100\%.$$

## Results

The Pt-Co/C catalyzed all three  $\text{CH}_2\text{Cl}_2 + \text{H}_2$ ,  $\text{CHCl}_3 + \text{H}_2$ , and  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  reactions to form reactant-specific sets of partially and completely dechlorinated products. The pure support showed negligible activity initially and was completely inactive thereafter. The highest initial activity on a per mass of catalyst basis was observed for the  $\text{CHCl}_3 + \text{H}_2$  reaction mixture; whereas, with the  $\text{CH}_2\text{Cl}_2 + \text{H}_2$  mixture, the catalyst exhibited the lowest initial activity (Fig. 1). This activity order is similar to that reported elsewhere for supported Pd [9].

The characteristic feature of the  $\text{CH}_2\text{Cl}_2 + \text{H}_2$  feed was the absence of catalyst deactivation; after an initial 50% increase, the activity level attained steady-state ( $0.14$  to  $0.18 \mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$ ) within 3 h on stream. In contrast, with the  $\text{CHCl}_3 + \text{H}_2$  and  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  feeds, significant deactivation occurred (a factor of 12 and 20 during the first 5 h, respectively) until steady state at essentially the same level was achieved after  $\sim 10$  h on stream for both cases (Fig. 1). The  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  mixture also caused deactivation of Pd/TiO<sub>2</sub> as reported elsewhere [28]. The Pt-Co/C catalyst activities for all three reaction mixtures were very close ( $0.10$  to  $0.17 \mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$ ) after 2 h on stream (Fig. 1). This activity level range corresponds to the conversion range of 2-3%.

Product selectivities for the three different reaction mixtures were compared at the 2-h point since this is where all mixtures attained similar conversion levels. The reaction products were classified in two categories:  $C_1$  and  $C_{2+}$  (oligomerization). With the  $\text{CH}_2\text{Cl}_2 + \text{H}_2$  feed,  $\text{CH}_4$  and  $\text{CH}_3\text{Cl}$  were the major and minor  $C_1$  products, respectively (Fig. 2). Methylene chloride and  $\text{CH}_4$  were the major and minor  $C_1$  products with the  $\text{CHCl}_3 + \text{H}_2$  mixture (Fig. 2). In the case of  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  feed,  $\text{CH}_2\text{Cl}_2$  was both a reactant and a product. Hence, a compromise was necessary to extract meaningful product selectivity information. The approach taken was to determine the *minimum*  $\text{CH}_2\text{Cl}_2$  product

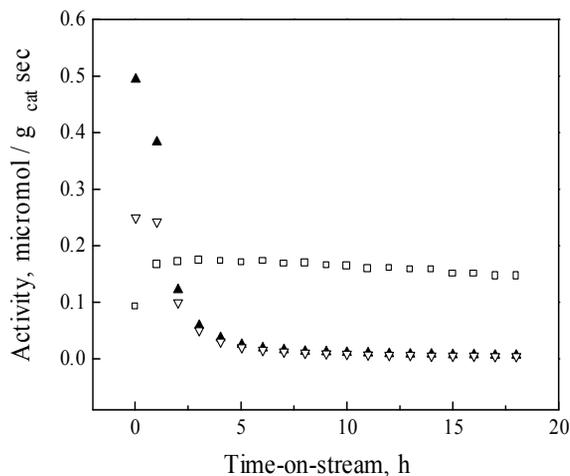


Fig. 1. Activity on per gram of catalyst basis vs. time-on-stream for Pt-Co/C; (□) – CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, (▲) – CHCl<sub>3</sub> + H<sub>2</sub>, (▽) – CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub>

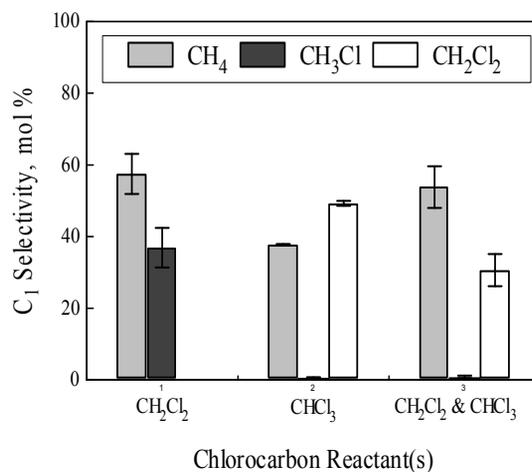


Fig. 2. C<sub>1</sub> product distribution after 2 h on steam for the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, CHCl<sub>3</sub> + H<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reactions catalyzed by Pt-Co/C

selectivity by assuming that none of the CH<sub>2</sub>Cl<sub>2</sub> reactant was converted. Accordingly, for the case where both CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were reactants, the major and minor C<sub>1</sub> products were CH<sub>4</sub> and CH<sub>2</sub>Cl<sub>2</sub>, respectively.

The oligomerization products of the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, CHCl<sub>3</sub> + H<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reactions catalyzed by Pt-Co/C consisted of saturated and unsaturated C<sub>2</sub>-C<sub>4</sub> hydrocarbons (Fig. 3). The CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub> feed resulted in the total C<sub>2+</sub> selectivity of approximately 5.5%; whereas, the oligomerization selectivities for the CHCl<sub>3</sub> + H<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reaction mixtures were 9.5 and 11.5%, respectively. With the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub> mixture, the C<sub>2+</sub> product distribution indicates that the hydrocarbons may have formed according to the classic Anderson-Schulz-Flory statistics for

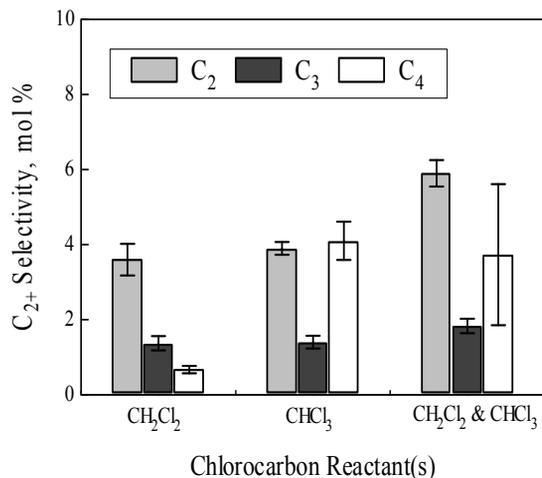


Fig. 3. C<sub>2-4</sub> product distribution after 2 h on stream for the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, CHCl<sub>3</sub> + H<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reactions catalyzed by Pt-Co/C

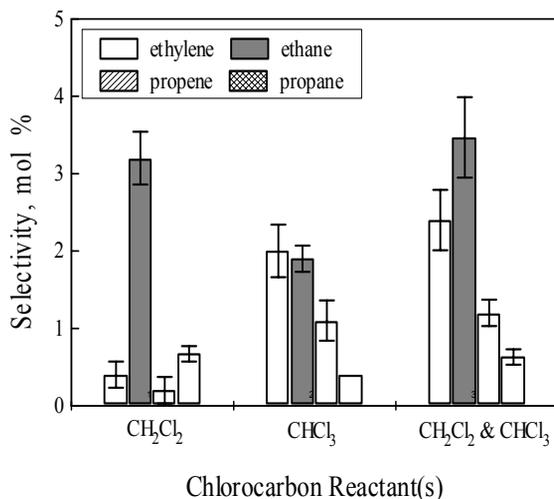


Fig. 4. C<sub>2,3</sub> product distribution after 2 h on stream for the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, CHCl<sub>3</sub> + H<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reactions catalyzed by Pt-Co/C

polymerization of surface C<sub>1</sub> species [29]. However, with the other two reaction mixtures, abnormally high selectivity toward C<sub>4</sub> hydrocarbons as compared to that toward C<sub>2</sub> and C<sub>3</sub> was observed (Fig. 3).

A characteristic feature of the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub> feed was the prevalence of saturated hydrocarbons among C<sub>2</sub> and C<sub>3</sub> oligomerization products (Fig. 4). The C<sub>2</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/C<sub>3</sub>H<sub>6</sub> mole ratios were 7.7 and 3.5, respectively. (The GC column employed in the present investigation did not allow determination of the olefin fraction for C<sub>4</sub> hydrocarbons.) With the CHCl<sub>3</sub> + H<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reaction mixtures, selectivity toward propylene exceeded that toward propane by a factor of 2-3; whereas, selectivities toward ethane and ethylene were comparable (Fig. 4).

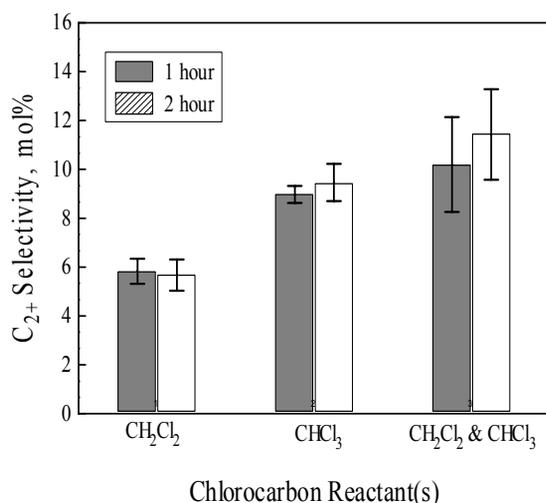


Fig. 5. Oligomerization product selectivity at the early stage of time on stream for the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, CHCl<sub>3</sub> + H<sub>2</sub>, and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> reactions catalyzed by Pt-Co/C

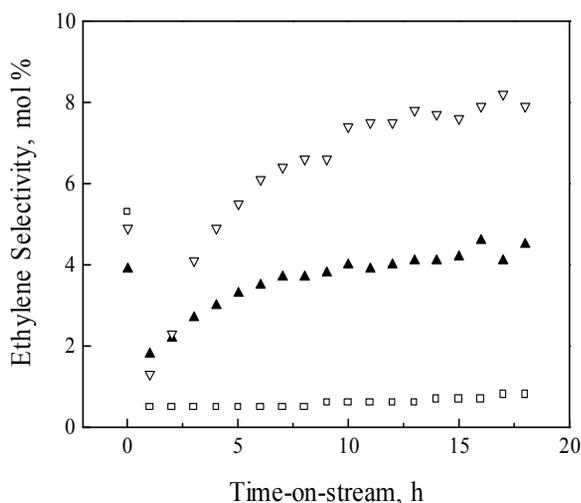


Fig. 6. Ethylene selectivity vs. time-on-stream for Pt-Co/C; (□) – CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>, (▲) – CHCl<sub>3</sub> + H<sub>2</sub>, (▼) – CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub>

Oligomerization selectivity improved with time on stream for the CHCl<sub>3</sub> + H<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> + H<sub>2</sub> feeds but remained essentially invariant for the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub> mixture (Fig. 5). The most profound effect of time on stream was observed for the ethylene selectivity (Fig. 6). For the CH<sub>2</sub>Cl<sub>2</sub> + CHCl<sub>3</sub> feed, the ethylene selectivity increased from 1% after 1 h on stream to 8% after 14 h; with the CHCl<sub>3</sub> + H<sub>2</sub> feed, the increase was from 2 to 5 % for the same time on stream. Similar to the overall oligomerization selectivity, ethylene selectivity did not depend on time on stream for the CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub> mixture. Finally, the selectivity toward ethane did not depend on time on stream for all three reaction mixtures.

## Discussion

A molecular-level understanding of the reaction pathways that lead to the formation of  $C_{2+}$  hydrocarbons from multiply-halogenated methanes is crucial for the development of economical routes to the elimination of chlorinated hydrocarbons by dechlorinative oligomerization. In addition, this understanding will contribute to the knowledge base of  $C_1$  chemistry. However, the mechanism of the hydrocarbon chain growth during  $C_1$  halocarbon dehalogenative oligomerization has not been studied. Although it had been speculated that the mechanism is similar to that of the  $CO+H_2$  (Fischer-Tropsch) reaction, without further details [8,9,11].

For the  $CO+H_2$  reaction two main mechanisms have been discussed in literature: the so-called alkyl [25,26] and the alkenyl mechanism [30-34]. According to the alkyl mechanism (Fig. 7), the chain is initiated by reaction of an H adatom and a methylene to form a methyl species that reacts with another methylene to form an ethyl species. Subsequently, methylene species add step-wise for chain growth. Lastly, chain growth is either terminated by  $\beta$ -elimination of hydride to form  $\alpha$ -alkenes (primary reaction products), or hydrogenolysis of the metal-alkyl bond results in the formation of alkanes. According to the alkenyl mechanism (Fig. 8), ethylene forms via the coupling of the CH and  $CH_2$  species to form a surface vinyl radical followed by hydrogenolysis of the metal-vinyl bond. The  $C_{2+}$  olefins form via  $CH_2$  group insertion into the metal-vinyl or metal-alkylvinyl bond. And chain termination occurs with hydrogenolysis of the metal alkenyl bond. Both alkyl and alkenyl mechanisms of chain growth are supported by the results of theoretical calculations [35-39].

The present investigation provides evidence that different mechanisms are responsible for the formation of  $C_{2+}$  products from the  $CH_2Cl_2 + H_2$  and from the  $CHCl_3 + H_2$  and  $CH_2Cl_2 + CHCl_3 + H_2$  reaction mixtures. The kinetics results are consistent with the suggestion that with the former mixture, hydrocarbons form predominantly by means of the alkyl mechanism; whereas, the alkenyl mechanism of oligomerization product formation prevails with the latter two reaction mixtures.

Indeed, with the  $CH_2Cl_2 + H_2$  reaction mixture, methylene ( $CH_2$ ) should be a dominant  $C_1$  surface species during the dechlorination reaction as C-Cl bonds of hydrocarbons readily dissociate on Group VIII metals [6,23,24]. Even though both Pt and Co are able to dissociate hydrocarbon C-H bonds at temperatures of several hundred Kelvins to form surface  $CH_x$  species [40-42], their further decomposition is significantly suppressed in the presence of hydrogen [23,24]. This is not surprising because the dissociation of C-H bonds is a reversible reaction [43]; it is not likely to occur on a catalyst surface covered with hydrogen, as the dissociation of  $H_2$  is not an activated process on both Pt and Co [44,45]. Nevertheless, the classic alkyl mechanism of the  $C_{2+}$  hydrocarbon formation (Fig. 7) would hardly take place with the  $CH_2Cl_2 + H_2$  feed. The hydrocarbon chain initiation by the coupling of  $CH_2$  and  $CH_3$  (Fig. 7) does not seem likely because this elementary step has a high activation barrier on metal surfaces [37]. Formation of propylene by  $\beta$ -elimination of hydride from adsorbed alkyl species (Fig. 7) does not look likely either. This elementary step is reversible and should be suppressed on metal surfaces saturated with hydrogen. Thus, the only feasible option is that  $C_2$ - $C_4$  hydrocarbons in the  $CH_2Cl_2 + H_2$  reaction catalyzed by Pt-Co/C form by surface oligomerization of  $CH_2$  species followed by the hydrogenolysis of adsorbed  $(CH_2)_n$  with surface hydrogen to form alkanes. This is consistent with the prevalence of ethane and propane among  $C_2$  and  $C_3$  hydrocarbon products (Fig. 4).

An increase in total oligomerization selectivity and dramatically different olefin to paraffin ratios among  $C_2$  and  $C_3$  hydrocarbon products with the  $CHCl_3 + H_2$  and  $CH_2Cl_2 + CHCl_3 + H_2$  reaction

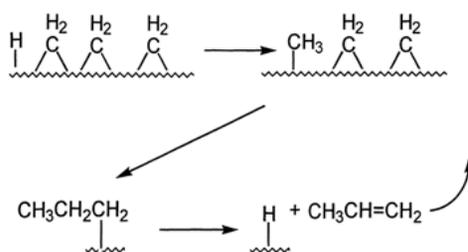


Fig. 7. Schematic of the alkyl mechanism for the polymerization of surface methylene to surface alkyls. (Reproduced with permission from Ref. [27])

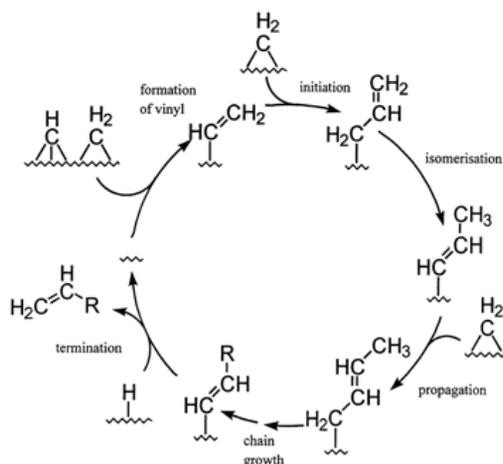


Fig. 8. Schematic of a catalytic cycle for the formation of alkenes, incorporating the alkenyl mechanism for the polymerization of surface methylene involving surface alkenyls. (Reproduced with permission from Ref. [27])

mixtures as compared to the  $\text{CH}_2\text{Cl}_2 + \text{H}_2$  feed (Fig. 3, 4) suggest the involvement of the CH species in surface oligomerization. The CH (methylidyne) species play a crucial role in the alkenyl mechanism of chain initiation (Fig. 8). If the formation of  $\text{C}_2$  surface species occurred solely by the alkyl mechanism, methylidyne would basically be a surface spectator until hydrogenated to a methylene and no enhancement in oligomerization selectivity would be observed with the  $\text{CHCl}_3$ -containing feeds. In addition, when CH species participate in hydrocarbon chain initiation, the chain termination occurs by addition of hydrogen to the surface species resulting in olefins formation (Fig. 8), not paraffins as it is expected for the alkyl mechanism. Hence, the greater olefin-to-paraffin ratios for  $\text{CHCl}_3$ -containing reaction mixtures, as compared to  $\text{CH}_2\text{Cl}_2 + \text{H}_2$  (Fig. 4), is consistent with the alkenyl mechanism of the oligomerization product formation.

Abnormally high selectivity toward  $\text{C}_4$  hydrocarbons in the  $\text{CHCl}_3 + \text{H}_2$  and  $\text{CH}_2\text{Cl}_2 + \text{CHCl}_3 + \text{H}_2$  reactions compared to that toward  $\text{C}_3$  products is another support for the alkenyl mechanism of oligomerization with the  $\text{CHCl}_3$ -containing reaction mixtures. It has been shown, that dimerization of vinyl,  $\text{CH}=\text{CH}_2$ , species is a facile reaction on metal surfaces [31,46,47]. Addition of vinylic probes to ruthenium- and rhodium-catalyzed Fischer-Tropsch reaction resulted in much higher incorporation of

the probes into  $C_4$  hydrocarbons than into  $C_3$  ones [31,47] suggesting that vinyl dimerization occurs at a greater rate than the  $CH_2$  insertion into metal-vinyl bond (Fig. 8).

Based on a lower reactivity of  $CH_2Cl_2$  in hydrodechlorination reactions in comparison with  $CHCl_3$  [9] and the absence of  $CH_3Cl$  among the  $C_1$  reaction products with the  $CH_2Cl_2 + CHCl_3 + H_2$  feed (Fig. 2), one may conclude that  $CH_2Cl_2$  does not convert to reaction products being mixed with  $CHCl_3$ . However, if  $CH_2Cl_2$  did not convert, the olefin-to-paraffin ratios for the  $C_2$ - $C_3$  hydrocarbon products would be similar for the  $CHCl_3 + H_2$  and  $CH_2Cl_2 + CHCl_3 + H_2$  reaction mixture. However, the ratios are sufficiently lower for the latter feed (Fig. 4). This result is consistent with the formation of a fraction of the  $C_{2+}$  products by the alkyl mechanism resulting in paraffins, which is characteristic of the  $CH_2Cl_2$  dechlorinative oligomerization as discussed above.

There are distinct differences in time-on-stream performance of the Pt-Co/C catalyst with different reaction mixtures. The  $CHCl_3 + H_2$  and  $CH_2Cl_2 + CHCl_3 + H_2$  feeds cause severe catalyst deactivation and a significant increase in oligomerization product selectivity with time on stream; whereas, with the  $CH_2Cl_2 + H_2$  mixture, both the catalyst activity and  $C_{2+}$  product selectivity remained essentially invariant during the course of the dechlorination reaction (Fig. 1, 5, and 6).

In general, there are two possible phenomena that may result in catalyst deactivation with time on stream: accumulation of chlorine adatoms on the metal surface and the formation of carbonaceous deposits [48]. The lack of marked catalyst deactivation with the  $CH_2Cl_2 + H_2$  feed provides strong evidence that surface chlorine does not affect catalyst activity. Moreover, the virtual independence of the activity on time on stream (Fig. 1) supports the suggestion (*vide supra*) that the dehydrogenation of surface methylene to the coke-precursor methylidyne species is not facile on the Pt-Co/C catalyst under the reaction conditions, even though CH is the most stable thermodynamically species on Co and Ru [36,49]. It is worth noting that, in the absence of catalyst deactivation, an increase in catalyst activity due to chlorine-induced metal redispersion [50-52] becomes observable for the  $CH_2Cl_2 + H_2$  feed at early times on stream (Fig. 1).

In contrast to the  $CH_2Cl_2$  case, when  $CHCl_3$  is included in the reaction feed stream, significant deactivation occurs immediately (Fig. 1). The deactivation could be related to methylidyne surface species formation. However, the straightforward dissociation of CH moieties to form carbonaceous deposits is not likely. First of all, the dissociation is an endothermic process on metal surfaces [36,53-55]. Secondly, as with any reversible surface reaction, it is disfavored by co-adsorbed hydrogen atoms. Most likely, the deactivation is caused by blocking the catalyst surface by high molecular-weight unsaturated hydrocarbons formed by surface polymerization of the CH species.

There is evidence in literature suggesting that halogen atoms affect the chemistry of hydrocarbon radicals on metallic surfaces [43,56-58]. However, the literature results are controversial in terms of how the adsorbed halogen atoms influence the  $CH_x$  coupling chemistry. Results of reaction kinetics investigations suggest that surface halogen atoms promote coupling [5]; whereas, ultrahigh vacuum studies infer that adsorbed halogen atoms suppress coupling chemistry by blocking sites adjacent to the adsorbed  $CH_x$  species [58,59].

The conclusion that surface halogen atoms favor the oligomerization of surface  $C_1$  species comes from the fact that the oligomerization selectivity in halomethane dehalogenation reactions increases with time on stream in parallel with an increase in the surface concentration of halogen atoms [5]. It is quite possible that at early times on stream – when the concentration of halogen adatoms is low –

the major fraction of CH species polymerize to form high molecular-weight hydrocarbons, which do not desorb, and the oligomerization selectivity stays low. In fact, it is an apparent selectivity because these heavy hydrocarbons are not taken into account at the selectivity calculation. As the catalyst equilibrates with the reaction medium, the concentration of halogen adatoms increases until it reaches steady state. This increase results in blocking a fraction of sites around CH surface species turning the polymerization of the CH species into di-, tri-, and tetramerization. As a consequence, the oligomerization selectivity increases as observed in the present investigation (Fig. 5, 6). In ultrahigh vacuum experiments, when CH<sub>x</sub> species on the single crystal surfaces are obtained by the dissociation of chloro- or bromomethanes, the concentration of halogen adatoms is high initially and does not change with time in the absence of H adatoms. The halogen concentration is too high to allow coupling reactions to occur.

### Conclusion

The distribution of oligomerization products in the reactions of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl and their equimolar mixtures with hydrogen catalyzed by Pt-Co/C sheds light on the mechanism of hydrocarbon chain growth in the dehalogenative oligomerization of multiply halogenated methanes. The reaction of CH<sub>2</sub>Cl<sub>2</sub> with hydrogen resulted in predominantly saturated C<sub>2+</sub> hydrocarbons as the oligomerization products. When CHCl<sub>3</sub> alone or in the mixture with CH<sub>2</sub>Cl<sub>2</sub> was converted, olefins dominated among the hydrocarbon products. This is consistent with the suggestion that CH surface species play a crucial role in the formation of unsaturated C<sub>2+</sub> hydrocarbons by means of the alkenyl mechanism, while the alkyl mechanism is responsible for the formation of paraffins by surface oligomerization of CH<sub>2</sub> species. A concomitant effect of the CH species presence on the catalyst surface is catalyst deactivation, probably due to the facile polymerization of the CH moieties to form high molecular weight hydrocarbons. Continuous increase in oligomerization selectivity vs. time on stream with CHCl<sub>3</sub>-containing feeds was interpreted in terms of the accumulation of the Cl adatoms, which suppress the polymerization of CH moieties favoring their oligomerization.

### Acknowledgment

This research was made possible by the NETL Regional University Alliance (NETL-RUA), an applied research collaboration that combines NETL's fossil energy expertise with the broad capabilities of nationally recognized, regional universities, in this case the University of Pittsburgh.

### References

1. Kroschwitz, J. I.; Howe-Grant, M., *Kirk-Othmer encyclopedia of chemical technology*. 4th ed.; Wiley: New York, 1994; Vol. 11.
2. Molina, M. J.; Rowland, F. S., Stratospheric sink for chlorofluoromethanes. Chlorine atom-catalyzed destruction of ozone. *Nature* **1974**, 249, (5460), 810-812.
3. Kalnes, T. N.; James, R. B., Hydrogenation and recycle of organic waste streams. *Environmental Progress* **1988**, 7, (3), 185-191.
4. Bo, Y.; Gang, Y., Reductive Destruction of Environmental Pollutants by Hydrogenation Process. *Progress in Chemistry* **2009**, 21, (1), 217-226.

5. Kovalchuk, V. I.; d'Itri, J. L., Catalytic chemistry of chloro- and chlorofluorocarbon dehalogenation: from macroscopic observations to molecular level understanding. *Applied Catalysis A: General* **2004**, 271, (1-2), 13-25.
6. Fung, S. C.; Sinfelt, J. H., Hydrogenolysis of methyl chloride on metals. *Journal of Catalysis* **1987**, 103, (1), 220-223.
7. Urbano, F. J.; Marinas, J. M., Hydrogenolysis of organohalogen compounds over palladium supported catalysts. *Journal of Molecular Catalysis A: Chemical* **2001**, 173, (1-2), 329-345.
8. Mori, T.; Kikuchi, T.; Kubo, J.; Morikawa, Y., Hydrodechlorination of Trichloromethane to Higher Hydrocarbons over Pd/SiO<sub>2</sub> Catalyst. *Chemistry Letters* **2001**, 30, (9), 936-937.
9. Mori, T.; Hirose, K.; Kikuchi, T.; Kubo, J.; Morikawa, Y., Formation of Higher Hydrocarbons from Chloromethanes via Hydrodechlorination over Pd/SiO<sub>2</sub> Catalyst. *Journal of the Japan Petroleum Institute* **2002**, 45, (4), 256-259.
10. Golubina, E. V.; Lokteva, E. S.; Lunin, V. V.; Turakulova, A. O.; Simagina, V. I.; Stoyanova, I. V., Modification of the supported palladium catalysts surface during hydrodechlorination of carbon tetrachloride. *Applied Catalysis A: General* **2003**, 241, (1-2), 123-132.
11. Dal Santo, V.; Dossi, C.; Recchia, S.; Colavita, P. E.; Vlaic, G.; Psaro, R., Carbon tetrachloride hydrodechlorination with organometallics-based platinum and palladium catalysts on MgO. *Journal of Molecular Catalysis A: Chemical* **2002**, 182-183, 157-166.
12. Dal Santo, V.; Dossi, C.; Psaro, R.; Recchia, S.; Sordelli, L., Carbon tetrachloride hydrodechlorination with organometallics based platinum and palladium catalysts on MgO: EXAFS characterization and catalytic studies. *Studies in Surface Science and Catalysis* **2001**, 140, 185-194.
13. Lokteva, E. S.; Simagina, V. I.; Golubina, E. V.; Stoyanova, I. V.; Lunin, V. V., Formation of C<sub>1</sub>-C<sub>5</sub> Hydrocarbons from CCl<sub>4</sub> in the Presence of Carbon-Supported Palladium Catalysts. *Kinetics and Catalysis* **2000**, 41, (6), 776-781.
14. Lokteva, E. S.; Lunin, V. V.; Golubina, E. V.; Simagina, V. I.; Egorova, M.; Stoyanova, I. V., C-C bond formation during hydrodechlorination of CCl<sub>4</sub> on Pd-containing catalysts. *Studies in Surface Science and Catalysis* **2000**, 130C, 1997-2002.
15. Kim, S. Y.; Choi, H. C.; Yang, O. B.; Lee, K. H.; Lee, J. S.; Kim, Y. G., Hydrodechlorination of tetrachloromethane over supported Pt catalysts. *Journal of the Chemical Society, Chemical Communications* **1995**, (21), 2169-2170.
16. Choi, H. C.; Choi, S. H.; Yang, O. B.; Lee, J. S.; Lee, K. H.; Kim, Y. G., Hydrodechlorination of Carbon Tetrachloride over Pt/MgO. *Journal of Catalysis* **1996**, 161, (2), 790-797.
17. Choi, H. C.; Choi, S. H.; Lee, J. S.; Lee, K. H.; Kim, Y. G., Effects of Pt Precursors on Hydrodechlorination of Carbon Tetrachloride over Pt/Al<sub>2</sub>O<sub>3</sub>. *Journal of Catalysis* **1997**, 166, (2), 284-293.
18. Bae, J. W.; Park, E. D.; Lee, J. S.; Lee, K. H.; Kim, Y. G.; Yeon, S. H.; Hun, S. B., Hydrodechlorination of CCl<sub>4</sub> over Pt/γ-Al<sub>2</sub>O<sub>3</sub>: Effects of reaction pressure and diluent gases on distribution of products and catalyst stability. *Applied Catalysis A: General* **2001**, 217, (1-2), 79-89.
19. Kulkarni, P. P.; Deshmukh, S. S.; Kovalchuk, V. I.; D'Itri, J. L., Hydrodechlorination of dichlorodifluoromethane on carbon-supported group VIII noble metal catalysts. *Catalysis Letters* **1999**, 61, (3-4), 161-166.

20. Kulkarni, P. P.; Kovalchuk, V. I.; d'Itri, J. L., Oligomerization pathways of dichlorodifluoromethane hydrodechlorination catalyzed by activated carbon supported Pt-Cu, Pt-Ag, Pt-Fe, and Pt-Co. *Applied Catalysis B: Environmental* **2002**, 36, (4), 299-309.
21. Chakraborty, D.; Kulkarni, P. P.; Kovalchuk, V. I.; d'Itri, J. L., Dehalogenative oligomerization of dichlorodifluoromethane catalyzed by activated carbon-supported Pt-Cu catalysts: effect of Cu to Pt atomic ratio *Catalysis Today* **2004**, 88, (3-4), 169-181.
22. Storch, H. H.; Golumbic, N.; Anderson, R. B., *The Fischer-Tropsch and Related Syntheses*. John Wiley & Sons: New York, 1951; p 603.
23. Campbell, J. S.; Kemball, C., Catalytic fission of the carbon-halogen bond. I. Reactions of ethyl chloride and ethyl bromide with hydrogen on evaporated metal films. *Transactions of the Faraday Society* **1961**, 57, 809-820.
24. Anderson, J. R.; McConkey, B. H., Reactions of methyl chloride and of methylene chloride at metal surfaces : II. Reactions over evaporated films of titanium and other metals. *Journal of Catalysis* **1968**, 11, (1), 54-70.
25. Brady, R. C., III; Pettit, R., Reactions of diazomethane on transition-metal surfaces and their relationship to the mechanism of the Fischer-Tropsch reaction. *Journal of the American Chemical Society* **1980**, 102, (19), 6181-6182.
26. Brady, R. C., III; Pettit, R., Mechanism of the Fischer-Tropsch reaction. The chain propagation step. *Journal of the American Chemical Society* **1981**, 103, (5), 1287-1289.
27. Maitlis, P. M.; Quyoum, R.; Long, H. C.; Turner, M. L., Towards a chemical understanding of the Fischer-Tropsch reaction: alkene formation. *Applied Catalysis A: General* **1999**, 186, (1-2), 363-374.
28. González, C. A.; Bartoszek, M.; Martin, A.; De Correa, C. M., Hydrodechlorination of light organochlorinated compounds and their mixtures over Pd/TiO<sub>2</sub>-washcoated minimonoliths. *Industrial and Engineering Chemistry Research* **2009**, 48, (6), 2826-2835.
29. Anderson, R. B., Schulz-Flory equation. *Journal of Catalysis* **1978**, 55, (1), 114-115.
30. Joyner, R. W., Mechanism of hydrocarbon synthesis from carbon monoxide and hydrogen. *Journal of Catalysis* **1977**, 50, (1), 176-180.
31. Turner, M. L.; Long, H. C.; Shenton, A.; Byers, P. K.; Maitlis, P. M., The Alkenyl Mechanism for Fischer-Tropsch Surface Methylene Polymerisation; the Reactions of Vinylic Probes with CO/H<sub>2</sub> over Rhodium Catalyst. *Chemistry – A European Journal* **1995**, 1, (8), 549 – 556.
32. Ma, F.; Sunley, G. J.; Saez, I. M.; Maitlis, P. M., Evidence for vinylic intermediates in the Fischer-Tropsch reaction to give alkenes and alkanes. *Journal of the Chemical Society, Chemical Communications* **1990**, (18), 1279 – 1280.
33. Turner, M. L.; Byers, P. K.; Long, H. C.; Maitlis, P. M., Vinyl initiation of Fischer-Tropsch polymerization over rhodium. *Journal of the American Chemical Society* **1993**, 115, (10), 4417-4418.
34. Gaube, J.; Klein, H.-F., Studies on the reaction mechanism of the Fischer-Tropsch synthesis on iron and cobalt. *Journal of Molecular Catalysis A: Chemical* **2008**, 283, (1-2), 60-68.
35. Cheng, J.; Gong, X.-Q.; Hu, P.; Lok, C. M.; Ellis, P.; French, S., A quantitative determination of reaction mechanisms from density functional theory calculations: Fischer-Tropsch synthesis on flat and stepped cobalt surfaces. *Journal of Catalysis* **2008**, 254, (2), 285-295.
36. Ciobîcă, I. M.; Kramer, G. J.; Ge, Q.; Neurock, M.; van Santen, R. A., Mechanisms for Chain Growth in Fischer-Tropsch Synthesis over Ru(0001). *Journal of Catalysis* **2002**, 212, (2), 136-144.

37. Liu, Z.-P.; Hu, P., A New Insight into Fischer–Tropsch Synthesis. *Journal of the American Chemical Society* **2002**, 124, (39), 11568–11569.
38. Ciobică, I. M.; Frechard, F.; van Santen, R. A.; Kleyn, A. W.; Hafner, J., A theoretical study of CH<sub>x</sub> chemisorption on the Ru(0001) surface. *Chemical Physics Letters* **1999**, 311, (3-4), 185-192.
39. Zheng, C.; Apeloig, Y.; Hoffmann, R., Bonding and coupling of C<sub>1</sub> fragments on metal surfaces. *Journal of the American Chemical Society* **1988**, 110, (3), 749–774.
40. Marsh, A. L.; Becraft, K. A.; Somorjai, G. A., Methane Dissociative Adsorption on the Pt(111) Surface over the 300–500 K Temperature and 1–10 Torr Pressure Ranges. *Journal of Physical Chemistry B* **2005**, 109, (28), 13619–13622.
41. Guzzi, L.; Sarma, K. V.; Borkó, L., Non-oxidative methane coupling over Co-Pt/NaY bimetallic catalysts. *Catalysis Letters* **1996**, 39, (1-2), 43-47.
42. Koerts, T.; van Santen, R. A., The reaction path for recombination of surface CH<sub>x</sub> species. *Journal of Molecular Catalysis* **1991**, 70, (1), 119-127.
43. Zaera, F., Reversibility of C<sub>1</sub> hydrogenation-dehydrogenation reactions on platinum surfaces under vacuum. *Langmuir* **1991**, 7, (10), 1998–1999.
44. Anderson, J. R., *Structure of Metallic Catalysts*. Academic Press: London, 1975; p 478.
45. Christmanna, K., Interaction of hydrogen with solid surfaces. *Surface Science Reports* **1988**, 9, (1-3), 1-163.
46. Rodriguez, E.; Leconte, M.; Basset, J.-M.; Tanaka, K., Molecular approach to the mechanisms of C–C bond formation and cleavage on metal surfaces: Hydrogenolysis, homologation, and dimerization of ethylene over Ru/SiO<sub>2</sub> catalysts. *Journal of Catalysis* **1989**, 119, (1), 230-237.
47. Long, H. C.; Turner, M. L.; Fornasiero, P.; Каљар, J.; Graziani, M.; Maitlis, P. M., Vinylic initiation of the Fischer-Tropsch reaction over ruthenium on silica catalysts. *Journal of Catalysis* **1997**, 167, (1), 172-179.
48. Wiersma, A.; van de Sandt, E. J. A. X.; den Hollander, M. A.; van Bekkum, H.; Makkee, M.; Moulijn, J. A., Comparison of the Performance of Activated Carbon-Supported Noble Metal Catalysts in the Hydrogenolysis of CCl<sub>2</sub>F<sub>2</sub>. *Journal of Catalysis* **1998**, 177, (1), 29-39.
49. Koerts, T.; van Santen, R. A., Mechanism of carbon–carbon bond formation by transition metals. *Journal of Molecular Catalysis* **1992**, 74, (1-3), 185-191.
50. Birke, P.; Engels, S.; Becker, K.; Neubauer, H. D., Principles of Reactivation of Reforming Catalysts. *Chemische Technik (Leipzig)* **1979**, 31, (9), 473-479.
51. Foger, K.; Jaeger, H., The effect of chlorine treatment on the dispersion of platinum metal particles supported on silica and  $\gamma$ -alumina. *Journal of Catalysis* **1985**, 92, (1), 64-78.
52. D’Aniello, M. J., Jr.; Monroe, D. R.; Carr, C. J.; Krueger, M. H., The redispersion of sintered Pt, Rh, and Pt/Rh catalysts. *Journal of Catalysis* **1988**, 109, (2), 407-422.
53. Ciobica, I. M.; van Santen, R. A., A DFT Study of CH<sub>x</sub> Chemisorption and Transition States for C–H Activation on the Ru(1120) Surface. *Journal of Physical Chemistry B* **2002**, 106, (24), 6200–6205.
54. Ciobică, I. M.; Frechard, F.; van Santen, R. A.; Kleyn, A. W.; Hafner, J., A DFT Study of Transition States for C–H Activation on the Ru(0001) Surface. *Journal of Physical Chemistry B* **2000**, 104, (14), 3364–3369.
55. Paul, J.-F.; Sautet, P., Chemisorption and Transformation of CH<sub>x</sub> Fragments (x = 0–3) on a Pd(111) Surface: A Periodic Density Functional Study. *Journal of Physical Chemistry B* **1998**, 102, (9), 1578–1585.

56. Bent, B. E., Mimicking Aspects of Heterogeneous Catalysis: Generating, Isolating, and Reacting Proposed Surface Intermediates on Single Crystals in Vacuum. *Chemical Reviews* **1996**, 96, (4), 1361–1390.

57. Radhakrishnan, G.; Stenzel, W.; Hemmen, R.; H. Conrad; Bradshaw, A. M., The photon-induced reactions of chemisorbed  $\text{CH}_3\text{Br}$  on  $\text{Pt}\{111\}$ . **1991**, 95, (6), 3930-3938.

58. Fairbrother, D. H.; Peng, X. D.; Viswanathan, R.; Staira, P. C.; Trenary, M.; Fan, J., Carbon-carbon coupling of methyl groups on  $\text{Pt}(111)$ . *Surface Science* **1993**, 285, (1-2), L455-L460.

59. Solymosi, F., Thermal stability and reactions of  $\text{CH}_2$ ,  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  species on the metal surfaces. *Catalysis Today* **1996**, 28, (3), 193-203.

## **Олигомеризация полихлорированных метанов в $\text{C}_{2+}$ углеводороды в присутствии Pt-Co/C катализаторов**

**В.И. Ковальчук<sup>а</sup>,**

**В.Д. Роудс<sup>а</sup>, М.А. Макдональд<sup>б</sup>**

<sup>а</sup> *Департамент химической и нефтехимической технологии,  
Питсбургский университет, Питсбург,  
Пенсильвания 15261, США*

<sup>б</sup> *Национальная лаборатория энергетических технологий,  
Государственный департамент энергии, Питсбург,  
Пенсильвания 15236, США*

---

*Изучено дегидрохлорирование дихлорметана, трихлорметана и их смесей в присутствии Pt-Co/C катализатора с целью выяснения механизма образования высших углеводородов. Установлено, что в реакции дихлорметана с водородом при 523 К катализатор не подвергается дезактивации и сохраняет постоянную активность в течение, по крайней мере, 18 ч, в то время как присутствие трихлорметана в реакционной смеси вызывает значительную дезактивацию катализатора в течение первых 5 ч работы. Углеводородные продукты наблюдались во всех реакционных смесях с селективностью дихлорметан + водород < трихлорметан + водород < дихлорметан + трихлорметан + водород. При этом селективность по этану и пропану не зависела от состава реакционной смеси. В то же время селективность по этилену и пропилену была существенно выше в случае дехлорирования трихлорметана и дехлорирования смеси дихлорметана и трихлорметана, чем в случае дехлорирования дихлорметана. На основании полученных результатов сделано заключение, что насыщенные углеводороды образуются в соответствии с так называемым алкильным механизмом роста цепи, в то время как непредельные углеводороды образуются по алкенильному механизму.*

*Ключевые слова: дегидрохлорирование, хлорметаны, восстановительная олигомеризация, синтез Фишера-Тропша, реакционный механизм, платина, кобальт.*

---