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

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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

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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 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 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 CH_2Cl_2 and CHCl_3 on the metal surfaces will result in the formation of CH_2 and 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 (~ 25 Torr).

Kinetics experiments

Dechlorination of CH_2Cl_2 (Aldrich, purity > 98%), 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 ± 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 CH_2Cl_2 and 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 CH_2Cl_2 and CHCl_3 by a gas chromatograph (GC) (HP 5890 series II).

Prior to the reaction, the catalyst was reduced in a mixture of H_2 (20 ml min^{-1}) and He (30 ml min^{-1}) (Butler, each >99.99%) as it was heated from ambient temperature to 673 K at the rate of 25 K min^{-1} and then held at 673 K for 2 h. Next, the catalyst was cooled in He (30 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 ml min^{-1} . The flow consisted of CH_2Cl_2 (43,640 ppm), H_2 (43,640 ppm), and He (balance) for the $\text{CH}_2\text{Cl}_2 + \text{H}_2$ reaction; CHCl_3 (43,640 ppm), H_2 (43,640 ppm), and He (balance) for the $\text{CHCl}_3 + \text{H}_2$ reaction; and CH_2Cl_2 (21,820 ppm), CHCl_3 (21,820 ppm), 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_{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 CH_2Cl_2 and CHCl_3 could not be determined herein, the combined conversion was obtained in this case, calculated as the mole fraction of CH_2Cl_2 and 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 ~ 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/TiO₂ 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, CH_4 and CH_3Cl were the major and minor C_1 products, respectively (Fig. 2). Methylene chloride and 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, CH_2Cl_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* CH_2Cl_2 product

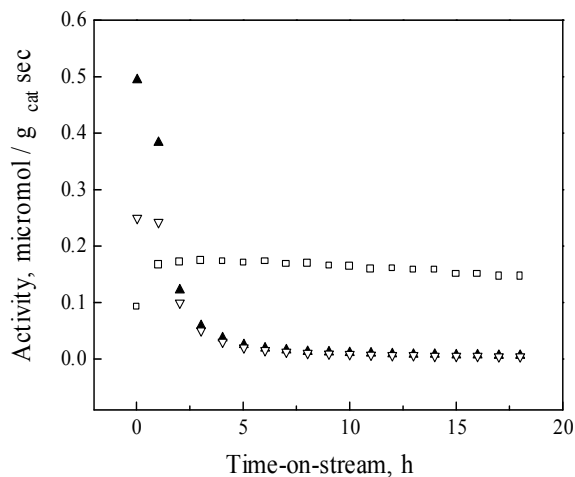


Fig. 1. Activity on per gram of catalyst basis vs. time-on-stream for Pt-Co/C; (□) – CH₂Cl₂ + H₂, (▲) – CHCl₃ + H₂, (▽) – CH₂Cl₂ + CHCl₃ + H₂

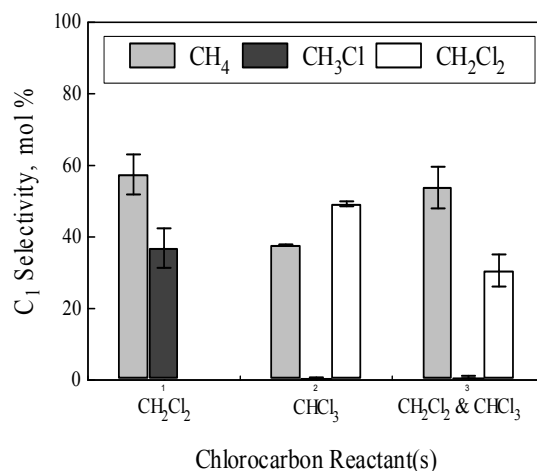


Fig. 2. C₁ product distribution after 2 h on steam for the CH₂Cl₂ + H₂, CHCl₃ + H₂, and CH₂Cl₂ + CHCl₃ + H₂ reactions catalyzed by Pt-Co/C

selectivity by assuming that none of the CH₂Cl₂ reactant was converted. Accordingly, for the case where both CH₂Cl₂ and CHCl₃ were reactants, the major and minor C₁ products were CH₄ and CH₂Cl₂, respectively.

The oligomerization products of the CH₂Cl₂ + H₂, CHCl₃ + H₂, and CH₂Cl₂ + CHCl₃ + H₂ reactions catalyzed by Pt-Co/C consisted of saturated and unsaturated C₂-C₄ hydrocarbons (Fig. 3). The CH₂Cl₂ + H₂ feed resulted in the total C₂₊ selectivity of approximately 5.5%; whereas, the oligomerization selectivities for the CHCl₃ + H₂, and CH₂Cl₂ + CHCl₃ + H₂ reaction mixtures were 9.5 and 11.5%, respectively. With the CH₂Cl₂ + H₂ mixture, the C₂₊ product distribution indicates that the hydrocarbons may have formed according to the classic Anderson-Schulz-Flory statistics for

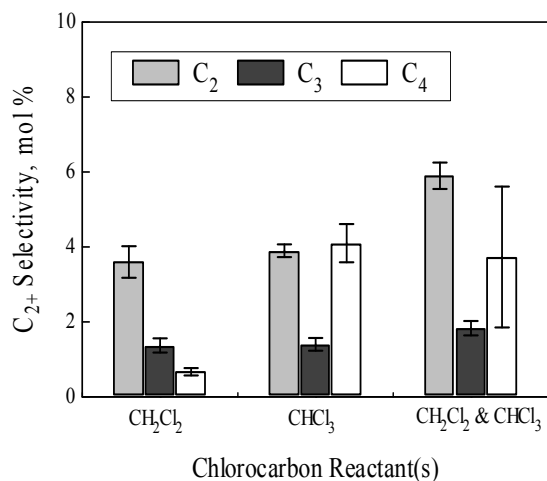


Fig. 3. C₂₋₄ product distribution after 2 h on stream for the CH₂Cl₂ + H₂, CHCl₃ + H₂, and CH₂Cl₂ + CHCl₃ + H₂ reactions catalyzed by Pt-Co/C

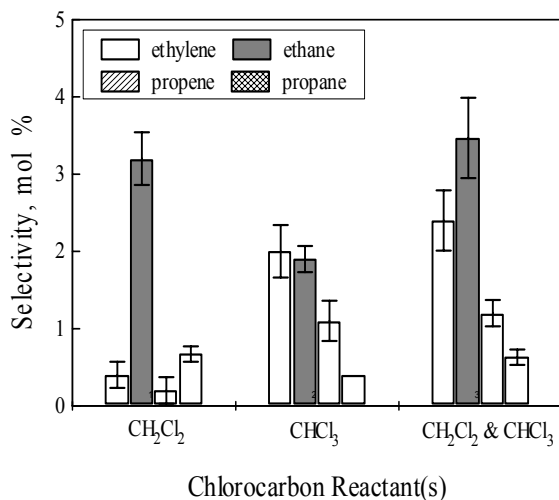


Fig. 4. C₂₋₃ product distribution after 2 h on stream for the CH₂Cl₂ + H₂, CHCl₃ + H₂, and CH₂Cl₂ + CHCl₃ + H₂ reactions catalyzed by Pt-Co/C

polymerization of surface C₁ species [29]. However, with the other two reaction mixtures, abnormally high selectivity toward C₄ hydrocarbons as compared to that toward C₂ and C₃ was observed (Fig. 3).

A characteristic feature of the CH₂Cl₂ + H₂ feed was the prevalence of saturated hydrocarbons among C₂ and C₃ oligomerization products (Fig. 4). The C₂H₆/C₂H₄ and C₃H₈/C₃H₆ 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 C₄ hydrocarbons.) With the CHCl₃ + H₂ and CH₂Cl₂ + CHCl₃ + H₂ 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).

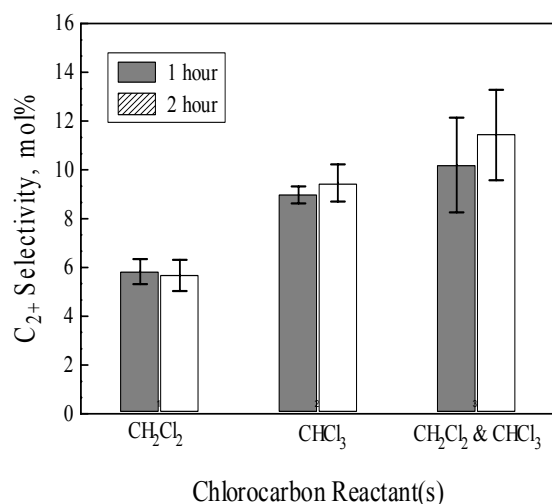


Fig. 5. Oligomerization product selectivity at the early stage of time on stream for the CH₂Cl₂ + H₂, CHCl₃ + H₂, and CH₂Cl₂ + CHCl₃ + H₂ reactions catalyzed by Pt-Co/C

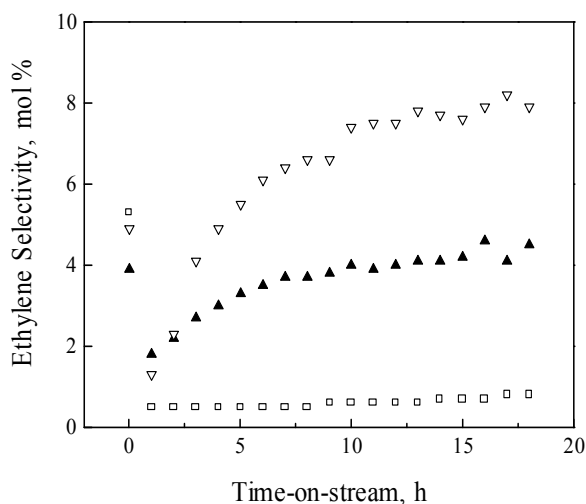


Fig. 6. Ethylene selectivity vs. time-on-stream for Pt-Co/C; (□) – CH₂Cl₂ + H₂, (▲) – CHCl₃ + H₂, (▼) – CH₂Cl₂ + CHCl₃ + H₂

Oligomerization selectivity improved with time on stream for the CHCl₃ + H₂ and CH₂Cl₂ + CHCl₃ + H₂ feeds but remained essentially invariant for the CH₂Cl₂ + H₂ mixture (Fig. 5). The most profound effect of time on stream was observed for the ethylene selectivity (Fig. 6). For the CH₂Cl₂ + CHCl₃ feed, the ethylene selectivity increased from 1% after 1 h on stream to 8% after 14 h; with the CHCl₃ + H₂ 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 CH₂Cl₂ + H₂ 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 β -elimination of hydride to form α -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 β -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

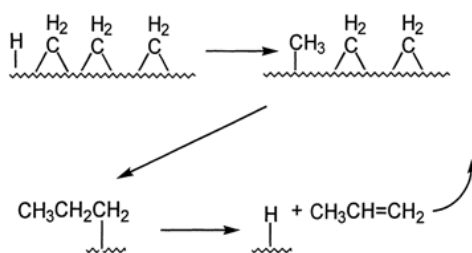


Fig. 7. Schematic of the alkyl mechanism for the polymerization of surface methylene to surface alkyls. (Reproduced with permission from Ref. [27])

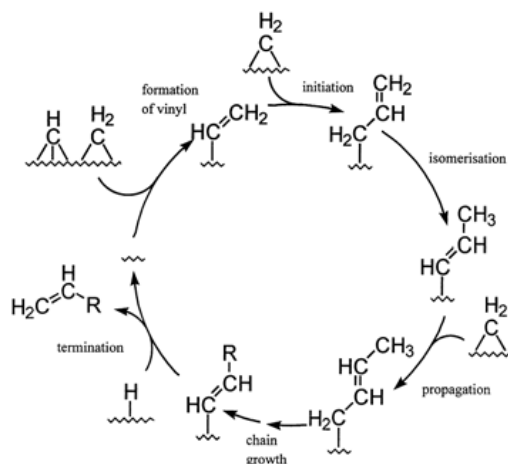


Fig. 8. Schematic of a catalytic cycle for the formation of alkenes, incorporating the alkenyl mechanism for the polymerization of surface methylene involving surface alkenyls. (Reproduced with permission from Ref. [27])

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 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 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 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 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 C_3 products is another support for the alkenyl mechanism of oligomerization with the 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 C₄ hydrocarbons than into C₃ ones [31,47] suggesting that vinyl dimerization occurs at a greater rate than the CH₂ insertion into metal-vinyl bond (Fig. 8).

Based on a lower reactivity of CH₂Cl₂ in hydrodechlorination reactions in comparison with CHCl₃ [9] and the absence of CH₃Cl among the C₁ reaction products with the CH₂Cl₂ + CHCl₃ + H₂ feed (Fig. 2), one may conclude that CH₂Cl₂ does not convert to reaction products being mixed with CHCl₃. However, if CH₂Cl₂ did not convert, the olefin-to-paraffin ratios for the C₂-C₃ hydrocarbon products would be similar for the CHCl₃ + H₂ and CH₂Cl₂ + CHCl₃ + H₂ 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 C₂₊ products by the alkyl mechanism resulting in paraffins, which is characteristic of the CH₂Cl₂ 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 CHCl₃ + H₂ and CH₂Cl₂ + CHCl₃ + H₂ feeds cause severe catalyst deactivation and a significant increase in oligomerization product selectivity with time on stream; whereas, with the CH₂Cl₂ + H₂ mixture, both the catalyst activity and C₂₊ 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 CH₂Cl₂ + H₂ 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 CH₂Cl₂ + H₂ feed at early times on stream (Fig. 1).

In contrast to the CH₂Cl₂ case, when CHCl₃ 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 C₁ 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_x 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 CH₂Cl₂, CH₃Cl 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 CH₂Cl₂ with hydrogen resulted in predominantly saturated C₂₊ hydrocarbons as the oligomerization products. When CHCl₃ alone or in the mixture with CH₂Cl₂ 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 C₂₊ hydrocarbons by means of the alkenyl mechanism, while the alkyl mechanism is responsible for the formation of paraffins by surface oligomerization of CH₂ 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 CHCl₃-containing feeds was interpreted in terms of the accumulation of the Cl adatoms, which suppress the polymerization of CH moieties favoring their oligomerization.

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Олигомеризация полихлорированных метанов в C_{2+} углеводороды в присутствии Pt-Co/C катализаторов

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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.
