Supporting Information

Epitaxially-Directed Iridium Nanostructures on Titanium Dioxide for the Selective Hydrodechlorination of Dichloromethane

Ali J. Saadun, Guido Zichittella, Vladimir Paunović, Bittor A. Markaide-Aiastui, Sharon Mitchell, and Javier Pérez-Ramírez*

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland

* Corresponding author. E-mail: jpr@chem.ethz.ch

Cotolysta	$S_{\rm BET}{}^a$ / m ² g ⁻¹	$V_{\rm pore}{}^b$ / cm ³ g ⁻¹	<i>X</i> (CH ₂ Cl ₂) / %
Catalysis	fresh (used) ^c	fresh (used) ^c	1 h (10 h) ^d
Ir/SiO ₂ -LSA	1 (1)	0.02 (0.02)	22 (2)
Ir/SiO ₂	260 (254)	0.80 (0.77)	21 (7)
Ir/TiO ₂ -r	3 (3)	0.01 (0.01)	21 (8)

Table S1. Characterization data and CH₂Cl₂ hydrodechlorination activity of selected iridium-based catalysts.

^{*a*} BET model. ^{*b*} Volume of N₂ adsorbed at $p/p_0 = 0.98$. ^{*c*} After 10 h in CH₂Cl₂ hydrodechlorination. ^{*d*} Time under CH₂Cl₂ hydrodechlorination. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_T/W_{cat} = 100-150$ cm³ min⁻¹ g_{cat}⁻¹, T = 473 K, and P = 1 bar.

Catalysts	Ir(0) / % ^a	Ir(II) / %a	Ir(III) / %a	Ir(IV) / %a
Ir/TiO ₂ -r-1023	70.7 (62.3)	- (37.7)	- (-)	29.3 (-)
Ir/TiO ₂ -r-NC	61.0 (53.2)	- (-)	- (9.9)	39.0 (36.9)
Ir/SiO ₂	79.8 (73.2)	- (-)	- (-)	20.2 (26.8)

Table S2. Individual contributions of metallic and oxidized iridium derived by fitting of the Ir 4f XPS core level spectra of the catalysts in fresh form and after 10 h in CH₂Cl₂ hydrodechlorination.

^{*a*} Values of the used catalyst in brackets.

Catalysta	Microscopy ^a (TOF / h ⁻¹)	CO chemisorption		
Catalysis		Volumetric ^{b} (TOF / h ⁻¹)	Dynamic ^b (TOF / h^{-1})	
Ir/SiO ₂	67 (54)	$72 \pm 7 (50 \pm 5)$	58 ± 8 (62 ± 10)	
Ir/TiO ₂ -r-NC	28 (135)	-	23 ± 3 (163 ± 25)	
Ir/TiO ₂ -r	-	37 ± 4 (128 ± 15)	$28 \pm 4 (168 \pm 30)$	
Ir/TiO ₂ -r-823	-	-	$21 \pm 3 (235 \pm 40)$	
Ir/TiO ₂ -r-1023	-	$12 \pm 1 \; (428 \pm 40)$	$19 \pm 3 \ (270 \pm 50)$	

Table S3. Iridium dispersion and *TOF* values of selected iridium-based catalysts.

^{*a*} HAADF-STEM. ^{*b*} The standard deviation of volumetric and dynamic chemisorption are ca. 10% and 15%, respectively. Dispersion is expressed in %. The conditions specified in the caption of **Figure 9** of the manuscript apply here.



Figure S1. Assessment of the absence of **a**) extraparticle and **b**) intraparticle mass-transfer limitations in CH₂Cl₂ hydrodechlorination over Ir/TiO₂-r-1023 at **a**) variable flow rates and constant space velocity and **b**) variable catalyst particle size and constant flow rates. Each catalytic data point was gathered using materials in fresh form in order to exclude the possible influence of catalyst deactivation. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_{T}/W_{cat} = 150 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473 K, P = 1 bar, and tos = 0.25 h.



Figure S2. a) TGA profiles of the IrCl₄-based precursors and of the IrO₂-based analogues obtained after calcination of the former materials at a temperature T_{calc} , indicated by the vertical dashed lines. The horizontal dashed lines denote the theoretical weight loss for the transformation of the IrCl₄-based precursors to their oxide-analogue. **b)** H₂-TPR profiles of the IrO₂-based precursors and the Ir-based catalysts obtained by the reduction of the former materials in H₂ at a temperature T_{red} , which is indicated by the vertical dashed lines.



Figure S3. XRD analysis of the Ir-based catalysts in fresh form and after CH₂Cl₂ hydrodechlorination. Reference diffraction patterns are shown as vertical lines below the measured diffractograms and are identified with their ICDD-PDF numbers. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_T/W_{cat} = 150 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473 K, P = 1 bar, and tos = 1 or 10 h.



Figure S4. HAADF-STEM micrographs and derived particle size distribution, d_{Ir} , (inset) of **a**) Ir/ZrO₂, **b**) Ir/Al₂O₃, **c**) Ir/MgO, **d**) Ir/CeO₂, and **e**) Ir/TiO₂-a in fresh form.



Figure S5. XRD analysis of Ir/SiO₂-LSA in fresh form and after CH₂Cl₂ hydrodechlorination. Reference diffraction patterns are shown as vertical lines below or as a symbol above the measured diffractograms and are identified with their ICDD-PDF numbers. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473 K, P = 1 bar, and tos = 10 h.



Figure S6. HAADF-STEM micrographs of Ir/SiO₂-LSA in **a**) fresh form and **b**) after 10 h in CH₂Cl₂ hydrodechlorination. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473 K, and P = 1 bar.



Figure S7. a) TGA profiles of the IrCl₄-based precursors and of the IrO₂-based analogues obtained after calcination of the former materials. The horizontal dashed line indicates the theoretical weight loss for the transformation of the IrCl₄-based precursors to their oxide analogues. **b)** H₂-TPR profiles of the IrO₂ and the IrCl₄-based precursors, and the Ir-based catalysts obtained after the reduction of the former materials in H₂ at a temperature T_{red} , indicated by the vertical dashed lines.



Figure S8. XRD analysis of the metal-based catalysts in fresh form and after CH₂Cl₂ hydrodechlorination. Reference diffraction patterns are shown as vertical lines below or as symbols above the measured diffractograms and are identified with their ICDD-PDF numbers. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_T/W_{cat} = 100-150 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473 K, P = 1 bar, and tos = 10 h.



Figure S9. HAADF-STEM micrograph of the IrCl₄/TiO₂-r sample and corresponding elemental map.





IrO₂/TiO₂-r-823



IrO₂/TiO₂-r-1023

Figure S10. HRTEM micrographs of IrO₂-based precursors on TiO₂-r prepared by calcination at 623 (top), 823 (middle) and 1023 K (bottom), revealing the evolution of the nanostructures with increasing temperature. The inset in the top right micrograph shows a zoom confirming the crystalline structure of IrO₂.



Figure S11. HAADF-STEM micrographs and derived particle size distribution, d_{Ir} , (inset) of Ir/TiO₂-r-NC in **a**) fresh form and **b**) after 10 h in CH₂Cl₂ hydrodechlorination. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, $F_T/W_{cat} = 150 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473 K, and P = 1 bar.



Figure S12. HAADF-STEM micrographs of **a**) Ir/TiO₂-r-NC, **b**) Ir/TiO₂-r-823, and **c**) Ir/TiO₂-r-1023 in fresh form.



Figure S13. Ir 4f XPS core level spectra of selected Ir-based catalysts in fresh form and after 10 h in CH₂Cl₂ hydrodechlorination. The solid lines and the open circles represent the overall fit and the raw data, respectively, while the colored area beneath them indicate the different Ir 4f contributions.



Figure S14. HAADF-STEM micrographs of a) Ru/SiO₂ and b) Ru/TiO₂-r in fresh form.



Figure S15. a) CH_2Cl_2 conversion as a function of temperature and b) product selectivity as a function of CH_2Cl_2 conversion adjusted by changing the temperature in CH_2Cl_2 hydrodechlorination over the Ir-based catalysts. Bulk iridium was well mixed with SiC to

achieve the nominal Ir-content in the mixture equivalent to that of the supported systems (2 wt. %). Each catalytic data point was gathered using materials in fresh form in order to exclude the possible influence of catalyst deactivation. Reaction conditions: $CH_2Cl_2:H_2:Ar:He = 5:10:2:83$, $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{cat}^{-1}$, T = 473-573 K, P = 1 bar, and tos = 0.25 h.



Figure S16. a) CH_2Cl_2 conversion as a function of the space velocity and b) product selectivity as a function of CH_2Cl_2 conversion adjusted by changing the space velocity in CH_2Cl_2 hydrodechlorination over the Ir-based catalysts. Each catalytic data point was gathered using

materials in fresh form in order to exclude the possible influence of catalyst deactivation. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83, F_T/W_{cat} = 25-200 cm³ min⁻¹ g_{cat}⁻¹, T = 473 K, P = 1 bar, and *tos* = 0.25 h.



Figure S17. Stability tests over selected iridium-based catalysts in CH₂Cl₂ hydrodechlorination. Filled symbols correspond to a CH₂Cl₂:H₂ ratio of 1:2 and open symbols to a ratio of 1:12. Reaction conditions: CH₂Cl₂:H₂:Ar:He = 5:10:2:83 or 5:60:2:33, $F_{\rm T}/W_{\rm cat} = 140-180$ cm³ min⁻¹ g_{cat}⁻¹, T = 473 K, P = 1 bar, and *tos* = 10 h.

Kinetic models of CH₂Cl₂ hydrodechlorination

The hydrodechlorination of CH₂Cl₂ can be described by means of a Langmuir-Hinshelwood mechanism.¹⁻³ The corresponding rate equations are derived below, using the following symbols:

p(i)	partial pressure of compound <i>i</i>
r _i	reaction rate of compound <i>i</i>
r_n	reaction rate of step <i>n</i>
k_n	rate constant for step <i>n</i>
$ heta_i^*$	surface coverage of compound <i>i</i>
$\overline{ heta}^{*}$	fraction of vacant sites
K_i	equilibrium constant for adsorption of compound <i>i</i> , $K_i = \frac{k_{ads}}{k_{des}}$

The reaction order is investigated by applying the following equation:

$$\mathbf{n}(\mathbf{H}_{2}) = p(\mathbf{H}_{2}) \frac{\partial \ln r}{\partial p(\mathbf{H}_{2})}$$

A concise overview of the kinetic models is provided in **Tables S4-S6**. Therein, r.d.s. stands for 'rate determining step'. The derivation of these models is described in more detail in the section 'Derivation of the kinetic models'.

Table S4. Kinetic model of CH₂Cl₂ hydrodechlorination for the production of CH₄.

CH ₄ production				
(A1) ^{<i>a</i>}	$H_2 + 2^* \rightarrow 2H^*$	k_1	$r \approx r_1 = r_{+1}$ (r.d.s.)	
(A2)	$CH_2Cl_2 + * \dot{E} CH_2Cl_2 + +$	$k_2; k_{-2}$	$r_2 = r_{+2} - r_{-2}$	
(A3)	$CH_2Cl_2* + *\dot{E}$ $CH_2Cl* + Cl*$	$k_3; k_{-3}$	$r_3 = r_{+3} - r_{-3}$	
(A4)	$CH_2Cl^* E CH_2^* + Cl^*$	$k_4; k_{-4}$	$r_4 = r_{+4} - r_{-4}$	
(A5)	$CH_2^* + H^* \dot{E} CH_3^* + *$	$k_5; k_{-5}$	$r_5 = r_{+5} - r_{-5}$	
(A6)	$CH_3* + H* \dot{E} CH_4* + *$	$k_{6};k_{-6}$	$r_6 = r_{+6} - r_{-6}$	
(A7)	CH4* E CH4 + *	$k_7; k_{-7}$	$r_7 = r_{+7} - r_{-7}$	
(A8)	$Cl^* + H^* \dot{E} HCl^* + *$	$k_8; k_{-8}$	$r_8 = r_{+8} - r_{-8}$	
(A9)	HCl* É HCl+*	$k_9; k_{-9}$	$r_9 = r_{+9} - r_{-9}$	
Assumptions		Rate expression and reaction order of H ₂	Limiting cases	
-(A1) is the rate determining step -formation of H* is irreversible -pseudo-equilibrium for all other steps		$r_{\rm CH_4} = \frac{k_1 p(\rm H_2)}{\left(1 + K_2 p(\rm CH_2 Cl_2)\right)^2}$	$n(H_2) = 1$	
$(r_{+n} = r_{-n})$ -p(CH4) and p(HCl) are negligibly small		$n(H_2) = p(H_2)\frac{\partial \ln r}{\partial p(H_2)} = 1$	(2)	

^{*a*} The elementary steps (A) correspond to the pathway indicated in Figure 13.

CH ₃ Cl production				
$(B1)^a$	$H_2 + 2* E 2H_2*$	<i>k</i> ₁ ; <i>k</i> ₋₁	$r_1 = r_{+1} - r_{-1}$	
(B2)	$CH_2Cl_2 + 2*E$ $CH_2Cl* + Cl*$	$k_2; k_{-2}$	$r_2 = r_{+2} - r_{-2}$	
(B3)	$\mathrm{CH_2Cl}^* \to \mathrm{CH_2}^* + \mathrm{Cl}^*$	<i>k</i> ₃	$r \approx r_3 = r_{+3}$ (r.d.s.)	
(B4)	$CH_2* + H* \dot{E} CH_3* + *$	$k_4; k_{-4}$	$r_4 = r_{+4} - r_{-4}$	
(B5)	CH_3 * + Cl * \dot{E} CH_3Cl * + *	$k_5; k_{-5}$	$r_5 = r_{+5} - r_{-5}$	
(B6)	$CH_3Cl^* E CH_3Cl + *$	$k_6; k_{-6}$	$r_6 = r_{+6} - r_{-6}$	
(B7)	Cl*+H*E HCl* + *	$k_7; k_{-7}$	$r_7 = r_{+7} - r_{-7}$	
(B8)	HCl*E HCl+*	$k_8; k_{-8}$	$r_8 = r_{+8} - r_{-8}$	
Assumptions		Rate expression and reaction order of H ₂	Limiting cases	
 -(B3) is the rate determining step -formation of CH₂* is irreversible -CH₂* and CH₃* in steady-state -pseudo-equilibrium for all other steps - Cl* is the most abundant reaction intermediate 		$r = \frac{k_{3}K_{2}K_{8}\sqrt{K_{1}p(H_{2})}p(CH_{2}CI_{2})}{p(HCl)\left(1 + \frac{p(HCl)}{K_{8}\sqrt{K_{1}p(H_{2})}}\right)}$ $n(H_{2}) = \frac{p(H_{2})K_{8}\sqrt{K_{1}p(H_{2})} + 2p(HCl)}{2p(H_{2})\left(K_{8}\sqrt{K_{1}p(H_{2})} + p(HCl)\right)}$	$\lim_{H_2 \to 0} = 0$ $\lim_{H_2 \to \infty} = \frac{1}{2}$	

Table S5. Kinetic model of CH₂Cl₂ hydrodechlorination for the production of CH₃Cl.

^{*a*} The elementary steps (B) correspond to the pathway indicated in **Figure 13**.

	CH ₃ Cl production, alternative reaction pathway			
$(C1)^a$	$H_2 + 2* \dot{E} 2H_2*$	$k_1; k_{-1}$	$r_1 = r_{+1} - r_{-1}$	
(C2)	$CH_2Cl_2 + 2*\dot{E}$ $CH_2Cl* + Cl*$	$k_2; k_{-2}$	$r_2 = r_{+2} - r_{-2}$	
(C3)	$CH_2Cl^* + H^* \dot{E} CH_3Cl^* + *$	<i>k</i> ₃	$r_3 = r_{+3} - r_{-3}$	
(C4)	CH ₃ Cl* E CH ₃ Cl+*	$k_4; k_{-4}$	$r_4 = r_{+4} - r_{-4}$	
(C5)	$Cl*+H*\dot{E}$ $HCl*+*$	$k_5; k_{-5}$	$r_5 = r_{+5} - r_{-5}$	
(C6)	HCl*E HCl+*	$k_{6};k_{-6}$	$r_6 = r_{+6} - r_{-6}$	
Assump	otions	Rate expression and reaction order of H ₂	Limiting	
-(C2) is -formati - CH ₂ Cl -pseudo	the rate determining step ion of CH ₂ Cl* is irreversible * in steady state -equilibrium for all other steps	$r = \frac{k_2 p (CH_2 Cl_2)}{\left(1 + \frac{p (HCl)}{K_5 K_6 \sqrt{K_1 p (H_2)}}\right)^2}$	$\lim_{H_2 \to 0} = 0$	
- Cl* 18 intermed	diate	$n(H_2) = \frac{-p(H_2)K_1p(HCl)}{K_5K_6\sqrt{K_1p(H_2)} + K_1p(H_2)p(HCl)}$	$\lim_{H_2 \to \infty} = -1$	
-(C3) is -formati -pseudo - Cl* is intermed	the rate determining step ion of CH ₃ Cl* is irreversible -equilibrium for all other steps the most abundant reaction diate	$r = \frac{k_3 K_1 K_2 K_5 K_6 p(H_2) p(CH_2 Cl_2)}{p(HCl) \left(1 + \frac{p(HCl)}{K_5 K_6 \sqrt{K_1 p(H_2)}}\right)^2}$	$\lim_{H_2 \to 0} = 0$	
		$n(H_2) =$	$\lim_{H_2 \to \infty} = 1$	
		$K_1 K_5 K_6 p(H_2)^3 \sqrt{K_1 p(H_2)} + 2K_1 p(HCl) p(H_2)$		
		$K_1 p(\mathrm{H}_2)^2 \left(K_5 K_6 \sqrt{K_1 p(\mathrm{H}_2)} + p(\mathrm{HCl}) \right)$		
-(C5) is -formati -pseudo - Cl* is intermed	the rate determining step ion of HCl* is irreversible -equilibrium for all other steps the most abundant reaction diate	$r = \frac{k_5 K_1 K_2 K_3 K_4 p(H_2) p(CH_2 Cl_2)}{p(CH_3 Cl) \left(1 + \frac{K_2 K_3 K_4 \sqrt{K_1 p(H_2)} p(CH_2 Cl_2)}{p(CH_3 Cl)}\right)^2}$ $n(H_2) = \frac{p(CH_3 Cl)}{K_2 K_2 K_2 K_1 p(CH_2 Cl_2) \sqrt{K_1 p(H_2)} + p(CH_2 Cl_2)}$	$\lim_{\substack{H_2 \to 0 \\ H_2 \to \infty}} = 0$	
		$\frac{1}{2} \frac{1}{2} \frac{1}$		

Table S6. Kinetic model of CH₂Cl₂ hydrodechlorination for the production of CH₃Cl following an alternative reaction pathway.

^{*a*} The elementary steps (C) correspond to the pathway indicated in Figure 13.

Derivation of the kinetic models

CH4 formation

The proposed reaction scheme is shown in **Table S4**. Therein, * identifies surface species. The total rate of reaction can be written as:

$$r \approx r_{\rm CH_4} + r_{\rm CH_3Cl}$$
 Eq. 1

 CH_4 is the main product over nanoparticle-based catalysts. <u>H₂ dissociation</u> (A1) is considered the rate-limiting step. Therefore, the rate of reaction can be simplified to:

$$r \approx r_{\text{CH}_4} \approx k_1 p(\text{H}_2) \theta^{*2}$$
 Eq. 2

Assuming the other steps are in quasi-equilibrium, we have:

$$CH_2Cl_2 + *E CH_2Cl_2 + k_2 p(CH_2Cl_2)\theta^* = k_{-2}\theta^*_{CH_2Cl_2}$$
 Eq. 3

$$CH_2Cl_2* + *E CH_2Cl* + Cl* k_3\theta_{CH_2Cl_2}^*\theta^* = k_{-3}\theta_{CH_2Cl}^*\theta_{Cl}^* Eq. 4$$

CH₂Cl* + * É CH₂* + Cl*
$$k_4 \theta_{CH_2Cl}^* \theta^* = k_{-4} \theta_{CH_2}^* \theta_{Cl}^*$$
 Eq. 5

$$CH_2^* + H^* \to CH_3^* + * \qquad k_5 \theta_{CH_2}^* \theta_H^* = k_{-5} \theta_{CH_3}^* \theta^*$$
 Eq. 6

$$CH_{3}^{*} + H^{*} \dot{E} CH_{4}^{*} + * \qquad k_{6} \theta_{CH_{3}}^{*} \theta_{H}^{*} = k_{-6} \theta_{CH_{4}}^{*} \theta^{*} \qquad Eq. 7$$

$$CH_{4}^{*} \dot{E} CH_{4} + * \qquad k_{6} \theta_{CH_{3}}^{*} \theta_{H}^{*} = k_{-6} \theta_{CH_{4}}^{*} \theta^{*} \qquad Eq. 7$$

HCl* É HCl+*
$$k_9 \theta_{\text{HCl}}^* = k_{-9} p(\text{HCl}) \theta^*$$
 Eq. 10

Leading to:

$$\theta_{\rm H}^* = \frac{\sqrt{K_2 p({\rm HCl})}}{\sqrt{K_8 K_9} \sqrt{\left(\sqrt{K_3 K_4 K_5 p({\rm CH}_2 {\rm Cl}_2)}\right)}} \theta^*$$
Eq. 11

$$\theta_{\mathrm{CH}_{2}\mathrm{Cl}_{2}}^{*} = K_{2} p \left(\mathrm{CH}_{2}\mathrm{Cl}_{2}\right) \theta^{*}$$
 Eq. 12

$$\theta_{\rm CH_2Cl}^* = \frac{K_8 K_9 p(\rm CH_4) \left(\sqrt{K_3 K_4 K_5 p(\rm CH_2 Cl_2)} \right)}{K_2 K_4 K_5 p(\rm HCl)} \theta^*$$
Eq. 13

$$\theta_{CH_2}^* = \frac{K_8 K_9 p(CH_4) \left(\sqrt{K_3 K_4 K_5 p(CH_2 Cl_2)} \right)}{K_2 K_5 K_6 K_7 p(HCl)} \theta^*$$
Eq. 14

$$\theta_{\mathrm{CH}_{3}}^{*} = \frac{\sqrt{K_{8}K_{7}}p(\mathrm{CH}_{4})\sqrt{\left(\sqrt{K_{3}K_{4}K_{5}p(\mathrm{CH}_{2}\mathrm{Cl}_{2})}\right)}}{K_{6}K_{7}\sqrt{K_{2}p(\mathrm{HCl})}}\theta^{*} \qquad \text{Eq. 15}$$

$$\theta_{\mathrm{CH}_4}^* = \frac{p(\mathrm{CH}_4)}{K_7} \theta^*$$
 Eq. 16

$$\theta_{\text{Cl}}^* = \frac{\sqrt{K_8 K_9} p(\text{HCl}) \sqrt{\left(\sqrt{K_3 K_4 K_5 p(\text{CH}_2 \text{Cl}_2)}\right)}}{K_8 K_9 \sqrt{K_2 p(\text{HCl})}} \theta^*$$
Eq. 17

$$\theta_{\rm HCl}^* = \frac{p(\rm HCl)}{K_9} \theta^*$$
 Eq. 18

The conservation of the total number of active sites leads to the site balance expression:

$$\theta^* + \theta^*_{\rm H} + \theta^*_{\rm CH_2Cl_2} + \theta^*_{\rm CH_2Cl} + \theta^*_{\rm CH_2} + \theta^*_{\rm CH_3} + \theta^*_{\rm CH_4} + \theta^*_{\rm Cl} + \theta^*_{\rm HCl} = 1$$
 Eq. 19

At low conversions, $p(CH_4)$ and p(HCl) are negligibly small, leading to the following simplification:

$$\theta^* = \frac{1}{1 + K_2 p(\mathrm{CH}_2 \mathrm{Cl}_2)}$$
Eq. 20

Consequently, the reaction rate catalysts is:

$$r_{CH_4} = \frac{k_1 p(H_2)}{\left(1 + K_2 p(CH_2 Cl_2)\right)^2}$$
Eq. 21

The order of the reaction with respect to H₂ can be expressed as:

$$n(H_2) = p(H_2) \frac{\partial \ln r}{\partial p(H_2)} = 1$$
 Eq. 22

CH₃Cl formation

The proposed reaction scheme is shown in **Table S5**. The total rate of reaction can be written as:

$$r \approx r_{\rm CH_4} + r_{\rm CH_3Cl}$$
 Eq. 23

 CH_3Cl is the main product over film-based catalysts. The <u>formation of CH*</u> (B3) is considered the rate-limiting step. Therefore, the rate of reaction can be simplified to:

$$r \approx r_{\text{CH}_3\text{Cl}} \approx k_3 \theta_{\text{CH}_2\text{Cl}}^* \theta^*$$
 Eq. 24

CH₂* and CH₃* are assumed to be in steady-state:

$$0 = k_3 \theta_{CH_2CI}^* - k_4 \theta_{CH_2}^* \theta_H^*$$
 Eq. 25

$$0 = k_4 \theta_{CH_2}^* \theta_H^* - k_5 \theta_{CH_3}^* \theta_{CI}^*$$
 Eq. 26

Assuming the other steps are in quasi-equilibrium, we have:

$$H_2 + 2* \dot{E} 2H_2* \qquad k_1 p(H_2) \theta^{*2} = k_{-1} \theta_{H_2}^{*2} \qquad Eq. 27$$

$$CH_{2}Cl_{2} + 2* \dot{E} CH_{2}Cl^{*} + Cl^{*} \qquad k_{2}p(CH_{2}Cl_{2})\theta^{*2} = k_{-2}\theta^{*}_{CH_{2}Cl}\theta^{*}_{Cl} \qquad Eq. 28$$

CH₂Cl* É CH₂* + Cl*
$$k_3 \theta_{CH_2Cl}^* = k_{-3} \theta_{CH_2}^* \theta_{Cl}^*$$
 Eq. 29

$$CH_{3}^{*} + Cl^{*} \rightarrow CH_{3}Cl^{*} + * \qquad k_{5}\theta_{CH_{3}}^{*}\theta_{Cl}^{*} = k_{-5}\theta_{CH_{3}Cl}^{*}\theta^{*} \qquad \text{Eq. 30}$$

$$CH_{2}Cl^{*}\dot{F} \quad CH_{2}Cl + * \qquad k_{6}\theta^{*} - k_{-5}\theta_{CH_{3}Cl}^{*}\theta^{*} \qquad \text{Eq. 31}$$

HCl*E HCl+*
$$k_8 \theta_{\text{HCl}}^* = k_{-8} p(\text{HCl}) \theta^*$$
 Eq. 33

Leading to:

$$\theta_{\rm H}^* = \sqrt{K_1 p({\rm H}_2)} \theta^*$$
 Eq. 34

$$\theta_{\mathrm{CH}_{2}\mathrm{Cl}}^{*} = \frac{K_{2}K_{8}\sqrt{K_{1}p(\mathrm{H}_{2})p(\mathrm{CH}_{2}\mathrm{Cl}_{2})}}{p(\mathrm{HCl})}\theta^{*}$$
Eq. 35

$$\theta_{\rm CH_3Cl}^* = \frac{p(\rm CH_3Cl)}{K_6} \theta^*$$
 Eq. 36

$$\theta_{\rm Cl}^* = \frac{p(\rm HCl)}{K_8 \sqrt{K_1 p(\rm H_2)}} \theta^*$$
 Eq. 37

$$\theta_{\rm HCl}^* = \frac{p(\rm HCl)}{K_8} \theta^*$$
 Eq. 38

The conservation of the total number of active sites leads to the site balance expression:

$$\theta^* + \theta^*_{\rm H} + \theta^*_{\rm CH_2Cl} + \theta^*_{\rm CH_3Cl} + \theta^*_{\rm Cl} + \theta^*_{\rm HCl} = 1$$
 Eq. 39

Cl* is considered the most abundant reaction intermediate, leading to the simplification:

$$\theta^* = \frac{1}{1 + \frac{p(\text{HCl})}{K_8 \sqrt{K_1 p(\text{H}_2)}}}$$
Eq. 40

Consequently, the reaction rate is:

$$r = \frac{k_3 K_2 K_8 \sqrt{K_1 p(\mathrm{H}_2)} p(\mathrm{CH}_2 \mathrm{Cl}_2)}{p(\mathrm{HCl}) \left(1 + \frac{p(\mathrm{HCl})}{K_8 \sqrt{K_1 p(\mathrm{H}_2)}}\right)}$$
Eq. 41

The order of the reaction with respect to H_2 can be expressed as:

$$n(H_2) = p(H_2)\frac{\partial \ln r}{\partial p(H_2)} = p(H_2)\frac{K_8\sqrt{K_1p(H_2)} + 2p(HCl)}{2p(H_2)(K_8\sqrt{K_1p(H_2)} + p(HCl))}$$
Eq. 42

Limiting cases:

$$\lim_{H_2 \to 0} = 0$$
 and $\lim_{H_2 \to \infty} = \frac{1}{2}$ Eq. 43

CH₃Cl formation via an alternative pathway

An alternative reaction pathway leading to CH_3Cl over film-based systems is shown in **Table S6**. The <u>formation of CH_3Cl^* </u> (C3) is considered the rate-limiting step. Therefore, the rate of reaction is:

$$r \approx r_{\text{CH}_3\text{Cl}} \approx k_3 \theta_{\text{CH}_2\text{Cl}}^* \theta^*$$
 Eq. 44

Assuming the other steps are in quasi-equilibrium, we have:

$$H_2 + 2* \dot{E} 2H_2*$$
 $k_1 p(H_2) \theta^{*2} = k_{-1} \theta_{H_2}^{*2}$ Eq. 45

$$CH_2Cl_2 + 2* E CH_2Cl^* + Cl^* \qquad k_2 p (CH_2Cl_2) \theta^{*2} = k_{-2} \theta^{*}_{CH_2Cl} \theta^{*}_{Cl} \qquad Eq. 46$$

$$CH_2Cl^* + H^* \rightarrow CH_3Cl^* + * \qquad k_2 \theta^{*}_{CH_2Cl} \theta^{*}_{H} = k_{-2} \theta^{*}_{CH_2Cl} \theta^{*}_{Cl} \qquad Eq. 47$$

$$\operatorname{CH}_{3}\operatorname{Cl}_{2}\operatorname{Cl}_{H} \stackrel{*}{\operatorname{H}} \stackrel{*}{\to} \operatorname{CH}_{3}\operatorname{Cl}_{H} \stackrel{*}{\to} \operatorname{CH}_{4}\operatorname{CH}_{4$$

Cl*+H*E HCl* + *
$$k_5 \theta_{Cl}^* \theta_{H}^* = k_{-5} \theta_{HCl}^* \theta_{HCl}^*$$
 Eq. 49

HCl*É HCl+*
$$k_6 \theta_{\text{HCl}}^* = k_{-6} p(\text{HCl}) \theta^*$$
 Eq. 50

Leading to:

$$\theta_{\rm H}^* = \sqrt{K_1 p({\rm H}_2)} \theta^*$$
 Eq. 51

$$\theta_{\mathrm{CH}_{2}\mathrm{Cl}}^{*} = \frac{K_{2}K_{5}K_{6}\sqrt{K_{1}p(\mathrm{H}_{2})p(\mathrm{CH}_{2}\mathrm{Cl}_{2})}}{p(\mathrm{HCl})}\theta^{*}$$
Eq. 52

$$\theta_{\rm CH_3Cl}^* = \frac{p(\rm CH_3Cl)}{K_4} \theta^*$$
 Eq. 53

$$\theta_{\rm Cl}^* = \frac{p(\rm HCl)}{K_5 K_6 \sqrt{K_1 p(\rm H_2)}} \theta^*$$
Eq. 54

$$\theta_{\rm HCl}^* = \frac{p(\rm HCl)}{K_6} \theta^*$$
 Eq. 55

Cl* is considered the most abundant reaction intermediate, leading to the simplification:

$$\theta^{*} = \frac{1}{1 + \frac{K_{2}K_{5}K_{6}\sqrt{K_{1}p(H_{2})}p(CH_{2}Cl_{2})}{p(CH_{3}Cl)}}$$
Eq. 56

Consequently, the reaction rate is:

$$r = \frac{k_3 K_1 K_2 K_5 K_6 p(H_2) p(CH_2 Cl_2)}{p(HCl) \left(1 + \frac{p(HCl)}{K_5 K_6 \sqrt{K_1 p(H_2)}}\right)^2}$$
Eq. 57

The order of the reaction with respect to H₂ can be expressed as:

$$n(H_{2}) = p(H_{2})\frac{\partial \ln r}{\partial p(H_{2})} = \frac{p(H_{2})K_{1}K_{5}K_{6}p(H_{2})^{2}\sqrt{K_{1}p(H_{2})} + 2K_{1}p(HCl)p(H_{2})}{K_{1}p(H_{2})^{2}(K_{5}K_{6}\sqrt{K_{1}p(H_{2})} + p(HCl))}$$
Eq. 58

Limiting cases:

$$\lim_{H_2 \to 0} = 0 \text{ and } \lim_{H_2 \to \infty} = 1$$
 Eq. 59

In the case $\underline{CH_2Cl_2}$ dissociation is considered as the rate determining step (C2), the rate equation changes to:

$$r \approx k_2 p \left(CH_2 Cl_2 \right) \theta^{*2}$$
 Eq. 60

Assuming steady state for CH₂Cl* and the other steps in quasi-equilibrium leads to:

$$\theta_{\rm H}^* = \sqrt{K_1 p({\rm H}_2)} \theta^*$$
 Eq. 61

$$\theta_{\mathrm{CH}_{2}\mathrm{CI}}^{*} = \frac{k_{2}p(\mathrm{CH}_{2}\mathrm{Cl}_{2})}{k_{3}\sqrt{K_{1}p(\mathrm{H}_{2})}}\theta^{*}$$
Eq. 62

$$\theta_{\rm CH_3Cl}^* = \frac{p(\rm CH_3Cl)}{K_4} \theta^*$$
 Eq. 63

$$\theta_{\text{Cl}}^* = \frac{p(\text{HCl})}{K_5 K_6 \sqrt{K_1 p(\text{H}_2)}} \theta^*$$
Eq. 64

$$\theta_{\rm HCl}^* = \frac{p(\rm HCl)}{K_6} \theta^*$$
 Eq. 65

Considering Cl* as the most abundant reaction intermediate leads to the simplification:

$$\theta^* = \frac{1}{1 + \frac{p(\text{HCl})}{K_5 K_6 \sqrt{K_1 p(\text{H}_2)}}}$$
Eq. 66

Consequently, the reaction rate is:

$$r = \frac{k_2 p (\mathrm{CH}_2 \mathrm{Cl}_2)}{\left(1 + \frac{p (\mathrm{HCl})}{K_5 K_6 \sqrt{K_1 p (\mathrm{H}_2)}}\right)^2}$$
Eq. 67

The order of the reaction with respect to H_2 can be expressed as:

$$n(H_2) = p(H_2)\frac{\partial \ln r}{\partial p(H_2)} = -p(H_2)\frac{K_1p(HCl)}{K_5K_6\sqrt{K_1p(H_2)} + K_1p(H_2)p(HCl)}$$
Eq. 68

Limiting cases:

$$\lim_{H_2 \to 0} = 0 \quad \text{and} \quad \lim_{H_2 \to \infty} = -1$$
 Eq. 69

In case <u>Cl* removal</u> is rate determining (C5), the rate equation changes to:

$$r \approx r_{\rm CH_3Cl} \approx k_5 \theta_{\rm Cl}^* \theta_{\rm H}^*$$
 Eq. 70

Assuming all other steps are in quasi-equilibrium leads to:

$$\theta_{\rm H}^* = \sqrt{K_1 p({\rm H}_2)} \theta^*$$
 Eq. 71

$$\theta_{\mathrm{CH}_{2}\mathrm{CI}}^{*} = \frac{p(\mathrm{CH}_{3}\mathrm{Cl})}{K_{3}K_{4}\sqrt{K_{1}p(\mathrm{H}_{2})}}\theta^{*}$$
Eq. 72

$$\theta_{\rm CH_3Cl}^* = \frac{p(\rm CH_3Cl)}{K_4} \theta^*$$
 Eq. 73

$$\theta_{\text{Cl}}^* = \frac{K_2 K_3 K_4 \sqrt{K_1 p(\text{H}_2)} p(\text{CH}_2 \text{Cl}_2)}{p(\text{CH}_3 \text{Cl})} \theta^*$$
Eq. 74

$$\theta_{\rm HCl}^* = \frac{p(\rm HCl)}{K_6} \theta^*$$
 Eq. 75

Assuming Cl* as the most abundant reaction intermediate leads to:

$$\theta^* = \frac{1}{1 + \frac{\sqrt{K_1 p(H_2)} K_3 K_4 K_2 p(CH_2 Cl_2)}{p(CH_3 Cl)}}$$
Eq. 76

Consequently, the reaction rate is:

$$r = \frac{k_5 K_1 K_2 K_3 K_4 p(H_2) p(CH_2 Cl_2)}{p(CH_3 Cl) \left(1 + \frac{K_2 K_3 K_4 \sqrt{K_1 p(H_2)} p(CH_2 Cl_2)}{p(CH_3 Cl)}\right)^2}$$
Eq. 77

The order of the reaction with respect to H₂ can be expressed as:

$$n(H_2) = p(H_2)\frac{\partial \ln r}{\partial p(H_2)} = p(H_2)\frac{p(CH_3Cl)}{p(H_2)(K_2K_3K_4p(CH_2Cl_2)\sqrt{K_1p(H_2)} + p(CH_3Cl))}$$
Eq. 78

Limiting cases:

$$\lim_{H_2 \to 0} = 0 \quad \text{and} \quad \lim_{H_2 \to \infty} = 0$$
 Eq. 79

References

- Ordóñez, S.; Díez, F. V.; Sastre, H. Catalytic Hydrodechlorination of Chlorinated Olefins over a Pd/Al₂O₃ Catalyst: Kinetics and Inhibition Phenomena. *Ind. Eng. Chem. Res.* 2002, 41, 505-511.
- (2) de Pedro, Z. M.; Casas, J. A.; Gómez-Sainero, L. M.; Rodriguez, J. J. Hydrodechlorination of Dichloromethane with a Pd/AC Catalyst: Reaction Pathway and Kinetics. *Appl. Catal. B Environ.* 2010, 98, 79-85.
- (3) Álvarez-Montero, M. A.; Martin-Martinez, M.; Gómez-Sainero, L. M.; Arevalo-Bastante A.; Bedia J.; Rodriguez, J. J. Kinetic Study of the Hydrodechlorination of Chloromethanes with Activated-Carbon-Supported Metallic Catalysts. *Ind. Eng. Chem. Res.* 2015, 54, 2023-2029.