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Kinetic study of the hydrodechlorination of chloromethanes with activated carbon-supported metallic catalysts

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Keywords: Hydrodechlorination, Reaction Kinetics, Chloromethanes, Metallic Catalysts, LHHW, Activated Carbon.

Abstract

The kinetics of the hydrodechlorination (HDC) of dichloromethane (DCM) and chloroform (TCM) with Pd, Pt, Rh and Ru on activated carbon catalysts has been studied at temperatures between 100 and 250 °C. Different kinetic models have been checked namely pseudo-first order and Langmuir-Hinshelwood-Hougen-Watson (LHHW) with adsorption, chemical reaction and desorption control. The HDC of DCM and TCM with the Pd and Pt catalysts was well described by the LHHW model with reactant adsorption as the controlling step. However, with Rh and Ru catalysts chemical reaction and desorption of the reaction products appear to be the rate-controlling steps in the HDC of DCM and TCM, respectively. In this last case, different sets of complex reactions seem to occur on the surface of the catalyst depending on the temperature and confident values of activation energy could not be obtained, because of the formation of oligomeric coke-like deposits and the subsequent severe deactivation of these catalysts. The corresponding kinetic parameters for the proposed models were calculated.

1. Introduction

Dichloromethane (DCM) and chloroform (TCM), are versatile compounds which are extensively used as solvents and intermediates in the chemical and pharmaceutical industry, dry-cleaning, degreasing, among other applications. However, they are hazardous pollutants due to their high toxicity and carcinogenic character. Moreover, they contribute to global warming, the depletion of the ozone layer and the formation of photochemical smog ¹⁻³. Because of their unique physical and chemical properties (as their stability and no inflammability), not suitable and more environmental friendly substitutes have been found for many of their applications. Consequently, large amounts of these compounds are still released in industrial waste effluents and their treatment becomes necessary to comply with the stringent emission regulations. Catalytic hydrodechlorination (HDC) has emerged as a potential technology for the treatment of organochlorinated pollutants since it operates at moderate conditions leading to much less harmful reaction products which can be recovered or destroyed by incineration ^{4,5}. In the recent literature, a number of publications concerning to the HDC of chloromethanes (CM) with supported metallic catalysts can be found. Nevertheless, most of the publications are devoted to test the activity of different catalysts ⁶⁻⁸, analyze the reactivity of different chlorinated organic compounds ^{9,10} or learn on the influence of the reaction conditions ^{11,12}. To the best of our knowledge, so far there is scarce information on the kinetics of the process, which is needed for design purposes. López et al. ¹³ carried out a kinetic study on the gas-phase hydrodechlorination of DCM with a Pd/Al₂O₃ catalyst. Under the operating conditions used (space-times between 0.4 and 2 min·g·mmol⁻¹ and a temperature of 250 °C), they proposed a pseudo-first order kinetic model, reporting a value of 24 mmol·min⁻¹·g⁻¹·MPa⁻¹ for the rate constant. From differential kinetic data, González et al. ¹⁴ reported rate constant values within the range of 7-14 L·g⁻¹·min⁻¹ at 200 °C with Pd over γ -Al₂O₃ and TiO₂ on DCM hydrodechlorination at different metal loads. In a recent study, de Pedro et al. ¹⁵ examined the

kinetics of DCM hydrodechlorination with a commercial Pd on activated carbon catalyst within the 200-350 °C temperature range. The Langmuir-Hinshelwood model with DCM adsorption as the rate controlling step described fairly well the experimental results with an apparent activation energy value of 23.9 kJ·mol⁻¹ for DCM disappearance. In an experimental and theoretical study of the kinetics of chloromethanes (MCM, DCM and TCM) HDC with a Pd/carbon catalyst, Chen et al. ¹⁶ found a correlation between the reaction rate and the C-Cl bonding energy, suggesting that the dissociative adsorption of the chloromethanes was the rate-determining step. Moreover, they reported that the activation energy was linearly related to the energy of dissociation of the first C-Cl bond broken.

In previous studies of our group, the gas-phase HDC of DCM and TCM with own-made catalysts based on Pd, Pt, Rh or Ru supported on activated carbon (C) was investigated ¹⁷⁻²⁰, with frankly promising results in terms of activity and selectivity to non-chlorinated products. In those studies the influence of the physico-chemical characteristics of the catalysts on their activity in the HDC of different chloromethanes was analyzed, as well as the effect of the operating conditions, the reaction mechanisms, and the stability of the catalysts upon time on stream.

The aim of this contribution is to learn on the kinetics of the HDC of two chloromethanes, DCM and TCM, with the above mentioned catalysts (Pd/C, Pt/C, Rh/C and Ru/C) previously investigated. Several kinetic models are checked to fit the experimental results obtained in a fixed bed reactor at different space time of 0.04-1.73 kg·h·mol⁻¹ and temperature (100-250 °C).

2. Experimental

2.1 Catalyst preparation

Four catalysts were prepared, using Pd, Pt, Rh and Ru as active phases and a commercial activated carbon as support. Their characteristics have been reported elsewhere ²⁰. Summarizing, their preparation was carried out by incipient wetness impregnation, using aqueous solutions of PdCl₂, H₂PtCl₆, RhCl₃ and RuCl₃ (supplied by Sigma-Aldrich) of appropriate concentration to obtain 1 wt% metal nominal load. The catalysts were dried overnight at room temperature and heated to 100 °C. This temperature was reached at 20 °C·h⁻¹ heating rate and maintained for 2 h. The activation of all the catalysts was carried out by reduction under continuous H₂ flow (50 Ncm³·min⁻¹, supplied by Praxair with a minimum purity of 99.999%), at 250 °C for 2 h (heating rate 10 °C·min⁻¹).

2.2 Hydrodechlorination experiments

The HDC experiments were conducted in a continuous flow reaction system described elsewhere ¹², consisting in an electrically heated quartz fixed bed micro-reactor, coupled to a gas-chromatograph with a FID detector to analyze the reaction products. The operating conditions were: Atmospheric pressure, a total feeding (CM/N₂ + H₂) flow rate of 100 Ncm³·min⁻¹, with a H₂/CM molar ratio of 100. The inlet concentration of CM was adjusted to 1000 ppmv. Different values of space-time and reaction temperatures were tested within the ranges of 0.04 - 1.73 kg·h·mol⁻¹ and 100 – 250 °C, respectively.

2.3 Kinetic analysis

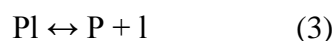
Different kinetic models were checked to fit the experimental values of CM conversion vs space-time: pseudo-first order and Langmuir-Hinshelwood-Hougen-Watson (LHHW) with adsorption, reaction or desorption as rate-controlling steps.

The pseudo-first order rate equation has been previously used by other authors^{13,15} to describe the disappearance of CM in HDC. With that rate equation in the mass balance for a fixed bed reactor, the following expression is obtained upon integration

$$\tau = \frac{1}{K' \cdot [CM]_0} \cdot \ln\left(\frac{1}{1 - X_{CM}}\right)$$

where K' ($\text{NL} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$) is the pseudo-first order rate constant, $[CM]_0$ ($\text{mol} \cdot \text{NL}^{-1}$) the initial CM concentration and X_{CM} the conversion at space-time τ . Since a large excess of H_2 was used in all the experiments, the H_2 concentration can be considered constant, being included in the apparent rate constant, K' .

The LHHW model considers three sequential steps: adsorption of reactants on the catalyst surface, chemical reaction on the active sites of the catalyst and desorption of the reaction products.



Eqs 1, 2 and 3 show the chemical reaction steps considered and Table 1 summarizes the resulting expressions, where $[CM]$ and $[P]$ are the concentrations of CM and reaction products,

respectively, k_{ads} , k_r and k_{des} ($\text{NL}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$) the kinetic constants for the LHHW model with adsorption, chemical reaction or desorption control respectively, K_s and K_z ($\text{NL}\cdot\text{mol}^{-1}$) the lumped equilibrium constants for the LHHW model with adsorption or desorption control respectively, K_{ads} ($\text{NL}\cdot\text{mol}^{-1}$) is the CM adsorption equilibrium constant for the LHHW model with chemical reaction control and K'_{des} ($\text{NL}\cdot\text{mol}^{-1}$) is the product desorption equilibrium constant for the LHHW model with chemical reaction control. These equations were fitted to the experimental data by means of a non-linear least squares minimization. These mathematical tools are included in the commercial software Scientist 3.0 (Micromath Research). The quality of the fit was evaluated from the correlation coefficient (r^2).

3. Results and discussion

3.1 Preliminary studies

Previous to the catalytic runs, the possible contribution of homogeneous reaction was checked within the 100 - 250 °C temperature range in the absence of catalyst (using glass beads). No significant CM conversion was observed.

External and internal mass-transfer resistances were experimentally evaluated within the ranges of 0.013-0.033 $\text{m}\cdot\text{s}^{-1}$ for gas velocity and 0.15-0.71 mm for catalyst particle size. The space-time and the reaction temperature were maintained at 0.8 $\text{kg}\cdot\text{h}\cdot\text{mol}^{-1}$ and 200 °C, respectively in all these experiments. No significant differences in CM conversion and product distribution were observed so that mass-transfer limitations were discarded. Additional theoretical calculations were done. The external diffusion mass-transfer was evaluated by the estimation of the $(C_{CM} - C_{CMs})$ differences (being C_{CM} and C_{CMs} the gas-phase CM concentration and the catalyst external surface CM concentration, respectively). The mass-transfer coefficient (k_c) were previously calculated²¹, for which Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) adimensional numbers were estimated. The influence of internal mass

transfer resistance was evaluated by the determination of the ratio between the reaction rate inside the catalyst particle and the reaction rate in its external surface (η), for what the estimation of the Thiele number (Φ) was necessary²². In the most unfavorable conditions, the values of $(C_{CM} - C_{CMs})$ are very low (lower than 0.002) and the values of η are close to 1, within the temperature range used in this study, thus allowing neglecting mass-transfer limitations in our experimental conditions.

In a previous study²⁰, we reported the values of apparent activation energy obtained from the Arrhenius plots of the initial reaction rates of DCM and TCM disappearance upon HDC within the 125-250 °C range with the four catalysts tested. Those values fall between 44 and 53 kJ·mol⁻¹ in the case of DCM being fairly similar to the reported in previous studies for the HDC of DCM with Pd/C (commercial)¹⁵ and Pt/C¹⁹. In the HDC of TCM significantly lower values were obtained (17-42 kJ·mol⁻¹), given its higher reactivity. The same trend was observed by Chen et al.¹⁶ in the HDC of MCM, DCM and TCM with a Pd/C commercial catalyst.

3.2 HDC with Pd/C and Pt/C catalysts

The pseudo first order model did not provide a good fitting of the experimental results of DCM and TCM conversion vs space-time. In general relatively poor values of the correlation coefficient were obtained and significant deviation were observed. Similar conclusions were obtained in a previous study with a commercial Pd/C catalyst¹⁵.

Figures 1 and 2 show the experimental data of the DCM and TCM conversion, respectively, vs. space time at different temperatures as well as the fitting curves with the LHHW model with reactant adsorption as the rate-controlling step. The values of the fitting parameters are collected in Tables 2 and 3. As can be seen, this model supplies a good prediction of the experimental results both in the case of DCM and TCM hydrodechlorination. The application

of the LHHW with the chemical reaction and desorption of products as rate-controlling steps yielded inconsistent results since negative values were obtained for K_{ads} , K'_{des} and K_z in some cases. The results obtained are in good agreement with those of a previous work ¹⁵ on the HDC of DCM with commercial Pd/C catalysts ¹⁶.

Dissociative adsorption of CMs as the rate-controlling step is consistent with the high reactivity shown by those compounds in HDC with Pd/C and Pt/C catalysts, which additionally increases with the chlorine content of the molecule (TCM > DCM), as demonstrated in a previous work ¹⁸. Thus, chemical reaction is a faster step than the previous adsorption. A theoretical study on the HDC of chloromethanes over Pd ²³ indicated that the exothermic character of the dissociative adsorption of those species increased with the number of chlorine atoms of the molecule, following the same trend than their reactivities and, therefore, in agreement with the assumption that the scission of the C-Cl bond involved in the dissociative adsorption is the rate-controlling step. This is also consistent with the mechanism proposed in previous studies ^{15,20,23}, based on the direct formation of carbene (CH_2^{**}) intermediate, which appeared to be the most energetically favored species in DCM adsorption on Pd surface, providing a parallel reaction scheme for CH_3Cl and CH_4 (or C_2 hydrocarbons) formation. This reaction scheme for the HDC of chloromethanes with Pd/C and Pt/C catalysts was supported by experimental results in previous studies ¹⁸⁻²⁰. The effective hydrogenation of the intermediates is confirmed by the high selectivity to non-chlorinated compounds yielded by those catalysts.

Activation energy values were calculated from the LHHW model with CM adsorption control. For DCM HDC, activation energies of 50 and 49 $\text{kJ}\cdot\text{mol}^{-1}$ were obtained using Pd/C and Pt/C catalysts, respectively. The activation energy values for the HDC of TCM were 52 $\text{kJ}\cdot\text{mol}^{-1}$ with Pd/C and 29 $\text{kJ}\cdot\text{mol}^{-1}$ with Pt/C. These results are in agreement with the results obtained by Chen et al. ¹⁶ who reported values of 58 $\text{kJ}\cdot\text{mol}^{-1}$ and 54 $\text{kJ}\cdot\text{mol}^{-1}$ for DCM and TCM

hydrodechlorination, respectively, with palladium catalysts. Slightly lower values were obtained in other studies (22-41 kJ·mol⁻¹) on DCM HDC with palladium catalysts ¹³⁻¹⁵. Activation energies values for the HDC of DCM and TCM with Pt catalyst have not been found in the existing literature.

3.3 HDC with Rh/C and Ru/C catalysts

As in the case of Pd/C and Pt/C catalysts, the experimental conversion vs space-time data showed significant deviations from the obtained using the pseudo-first order rate equation for the HDC of both, DCM and TCM, with the Rh/C and Ru/C catalysts. Those deviations were more pronounced at the lower temperature tested.

The three LHHW models served to fit reasonably well the experimental data. Nevertheless, in the HDC of DCM with Ru/C, K_s and K_z yielded some negative values and thus adsorption of reactants and desorption of products were discarded as rate-controlling steps. Therefore, the LHHW model with chemical reaction control can be postulated to describe the kinetics of DCM HDC with Ru/C. That was also the case with the Rh/C catalyst. Figure 3 depicts the experimental results and the fitting curves. The values of the parameters are reported in Table 4. This difference with respect to the Pd/C and Pt/C catalysts, where the adsorption of reactants was the rate controlling step, can be attributed to a lower hydrogenolysis-hydrogenation ability of Rh/C and Ru/C, as it was found in previous studies ^{17,20}. Therefore, as the reaction of adsorbed chloride radicals with H₂ is slowed down, it becomes the controlling step. The lower hydrogenolysis-hydrogenation ability of Rh/C and Ru/C is consistent with their higher selectivity to hydrocarbons of more than one carbon atom. This is more remarkable in the case of Ru/C, where higher amounts of these compounds were observed and formation of olefins were also detected at low space-times as intermediate products, evidencing a different mechanism ²⁰. Moreover, the conversion obtained was considerably lower than with the other

catalysts. This is in agreement with the lower values of the rate constants obtained for Ru/C (Table 4).

In the HDC of TCM, although the fitting of the three models to the experimental data provided very good values of the correlation coefficient ($r^2 > 0.996$) in all cases, some negative values were obtained for K_S , K_{ads} and K'_{des} , so that the LHHW model with desorption of products as the rate-controlling step can be postulated. Figure 4 shows the experimental values of the TCM conversion vs. space time and the fitting curves with that model. The values of the parameters are reported in Table 5. Desorption of products being the rate-controlling step is supported by the results of a previous study²⁰. Since chloroform is significantly more reactive than dichloromethane, the effect of the lower hydrogenation ability of Rh/C and Ru/C in the rate of the process compared to Pd/C and Pt/C is more remarkable. That lower hydrogenation ability of Rh and Ru catalysts is evidenced in the HDC of TCM since a high selectivity to chlorinated products and higher amounts of hydrocarbons different to methane were obtained²⁰. Moreover, the catalysts showed different mechanisms in the HDC of TCM. In the case of Pd/C and Pt/C the process appeared to take place through a parallel reaction scheme²⁰, where all the products are primary, suggesting the formation of methane through a concerted mechanism¹⁸. In contrast, the HDC of TCM with Rh/C and Ru/C proceeds through the hydrodechlorination of DCM and formation of olefins as intermediate products²⁰. The lower hydrogenolysis-hydrogenation rate and the presence of chloride and olefin radicals, which are very reactive, favor the oligomerization of the intermediates. This leads to the formation of larger molecules whose exit from the micropores of the catalyst is the rate-limiting phenomenon. This is supported by the characterization results of the spent catalysts²⁰. A great loss of activity was observed upon time on stream. It appears to be associated with the accumulation of carbonaceous deposits on the catalyst surface, leading to a severe drop of the BET area. The formation of carbonaceous deposits on these catalysts is consistent with the thermogravimetric results, under nitrogen

flow. Figure 5 shows the TG-DTG profiles obtained for the four catalysts before and after TCM HDC. A similar weight loss, within the temperature range 200-500 °C, can be observed for the fresh and used Pd and Pt catalysts, whereas in the case of Rh/C and Ru/C, a more remarkable loss of weight was observed for the used catalyst. This supports the presence of carbonaceous deposits over these catalysts after their use in the HDC of TCM ²⁴. On the other hand, significant amounts of organic chloride were observed, mainly in Ru/C catalysts, after used in the HDC of TCM by XPS ¹⁷. The erratic values of the kinetic constant k_{des} decreased as the temperature increased except at the highest temperature tested. This can be explained by the formation of oligomeric coke-like deposits, whose composition may significantly change depending on the reaction temperature, and that would affect to the rate of products desorption through the constricted micropores. At the highest temperature (250 °C) a change of the controlling mechanism may be occurring.

Furthermore, a significant change in products distribution occurred when modifying the reaction temperature ²⁰, showing different trends in the evolution of selectivity. Therefore, the contribution of every reaction to the overall reaction rate varies significantly depending on the reaction temperature and that may contribute to the erratic values of the kinetic constant k_{des} . Activation energies of 39 and 64 kJ·mol⁻¹ were obtained for the HDC of DCM with Rh/C and Ru/C catalysts, respectively. As in the case of Pt/C, activation energies for the HDC of DCM and TCM with Rh/C and Ru/C were not found in the literature.

4. Conclusions

The kinetics of DCM and TCM hydrodechlorination with activated carbon-supported metallic catalysts has been studied in a fixed bed reactor in the absence of mass-transfer limitations. The reaction rate of the HDC of DCM and TCM with Pd/C and Pt/C catalysts is well described by the Langmuir-Hinshelwood-Hougen-Watson model with reactant adsorption as the rate-

controlling step, in accordance with the high reactivity of these compounds. The same model but with chemical reaction as the rate-controlling step fits well the experimental results obtained in the HDC of DCM with Rh/C and Ru/C, due to lower hydrogenolysis-hydrogenation ability of these catalysts. In contrast, desorption of reaction products appears to control the reaction rate for the HDC of TCM with Rh/C and Ru/C, but erratic values of the kinetic constants are obtained. This can be attributed to the formation of oligomeric coke-like deposits that would affect to the rate of products desorption through the constricted micropores, as suggested by the characterization results, and the important loss of activity suffered by these catalysts upon time on stream.

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FIGURES

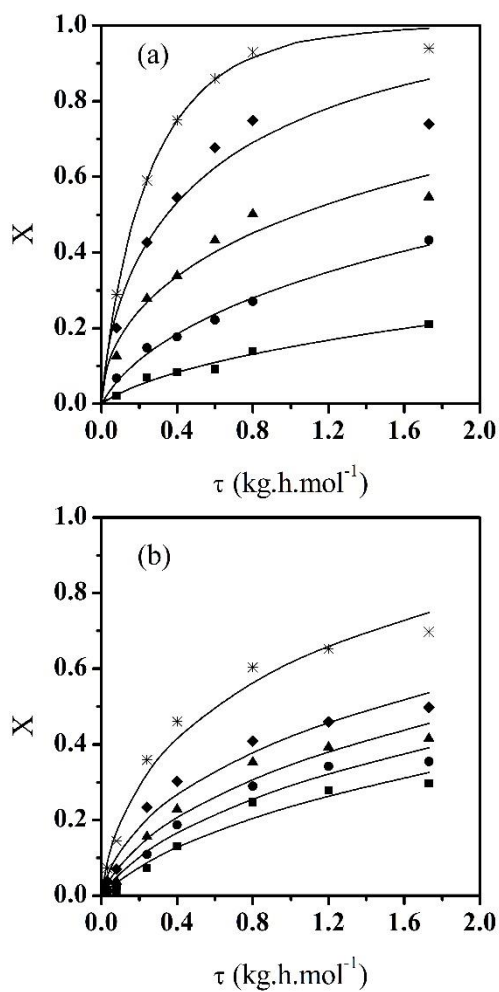


Figure 1. DCM conversion vs. space time at different temperatures: (■) 150 °C; (●) 175 °C; (▲) 200 °C; (◆) 225 °C; (*) 250 °C with the Pd/C (a) and Pt/C (b). Experimental values (symbols) and predicted curves with the LHHW model with DCM adsorption as rate-controlling step.

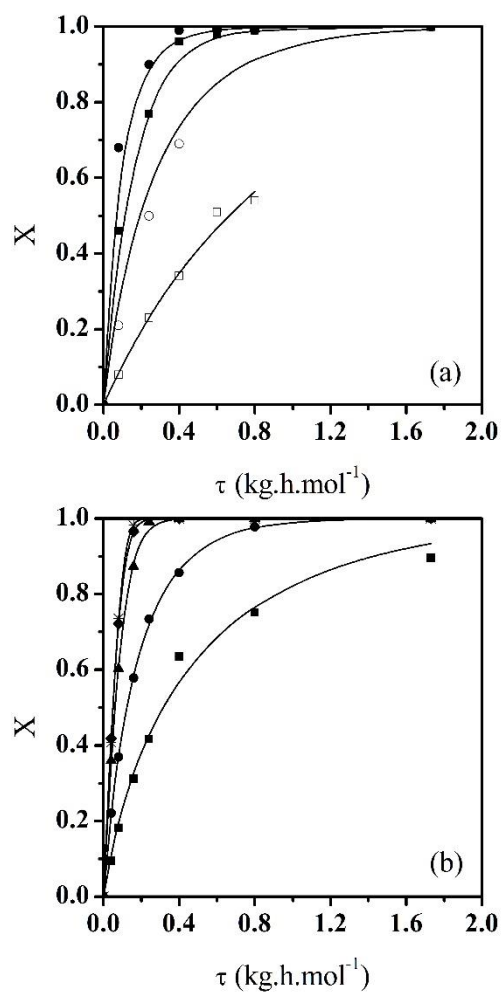


Figure 2. TCM conversion vs. space time at different temperatures: (\square) 100 °C; (\circ) 125 °C; (\blacksquare) 150 °C; (\bullet) 175 °C; (\blacktriangle) 200 °C; (\blacklozenge) 225 °C; ($*$) 250 °C with the Pd/C (a) and Pt/C (b). Experimental values (symbols) and predicted curves with the LHHW model with TCM adsorption as rate-controlling step.

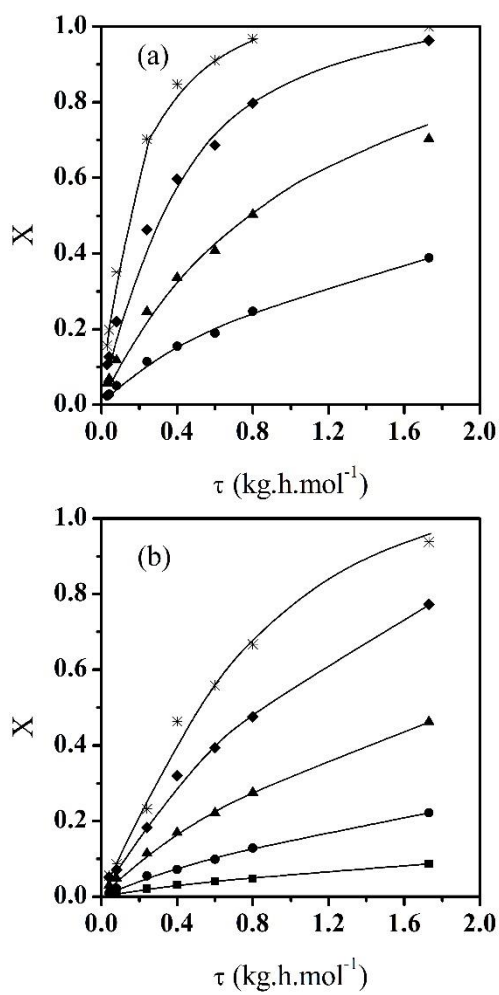


Figure 3. DCM conversion vs. space time at different temperatures: (■) 150 °C; (●) 175 °C; (▲) 200 °C; (◆) 225 °C; (*) 250 °C with the Rh/C (a) and Ru/C (b). Experimental values (symbols) and predicted curves with the LHHW model with chemical reaction as rate-controlling step.

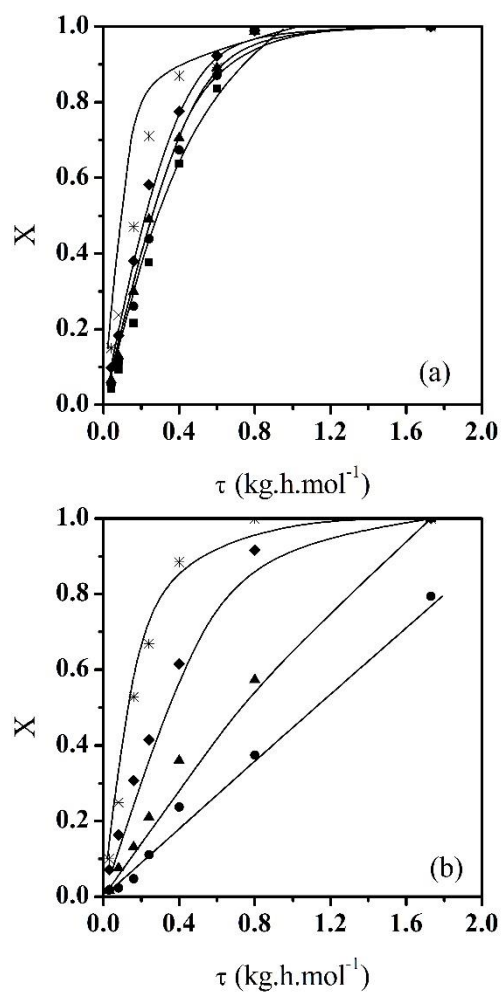


Figure 4. TCM conversion vs. space time at different temperatures: (■) 150 °C; (●) 175 °C; (▲) 200 °C; (◆) 225 °C; (*) 250 °C with the Rh/C (a) and Ru/C (b). Experimental values (symbols) and predicted curves with the LHHW model with desorption as rate-controlling.

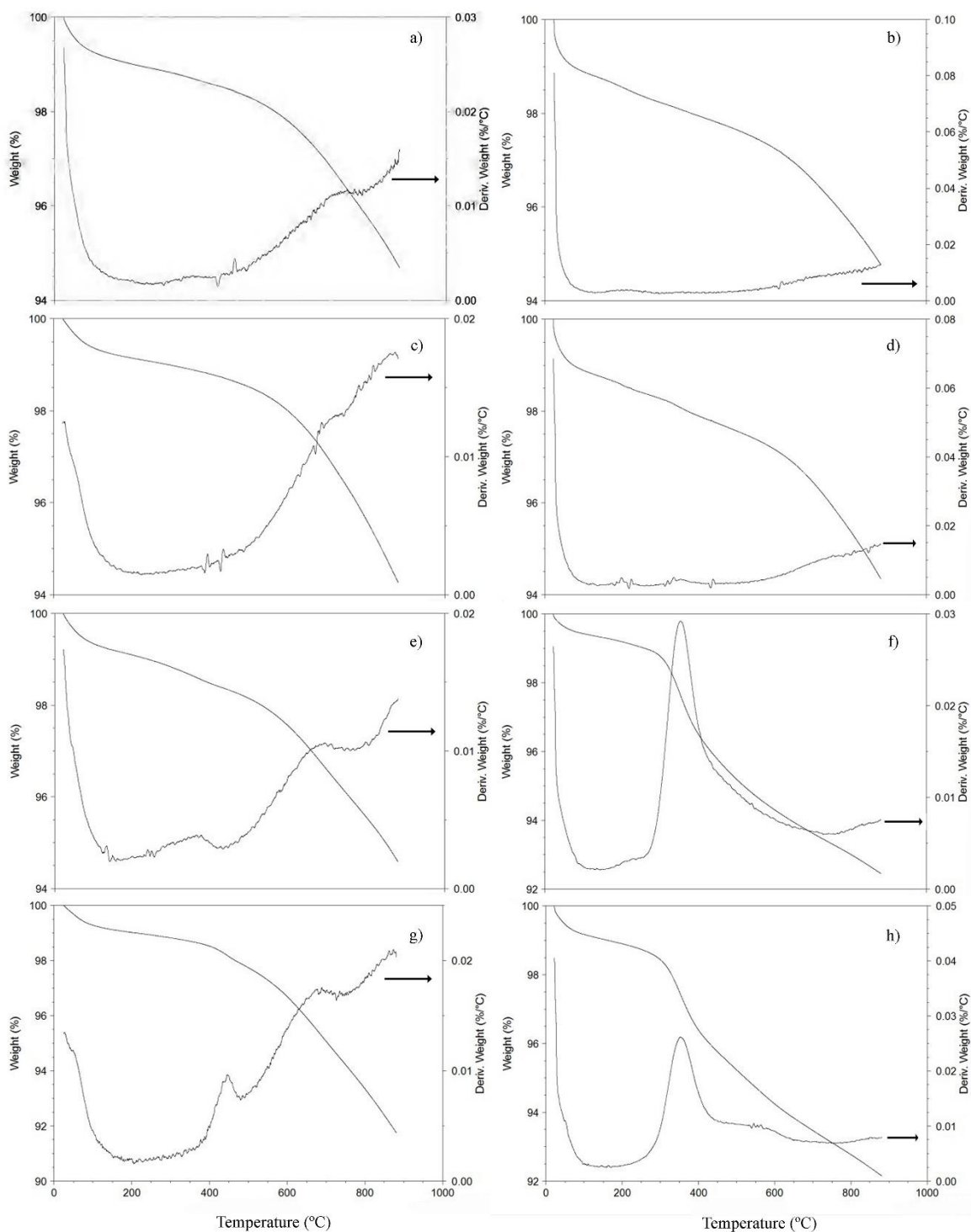


Figure 5. TG-DTG profiles for the catalysts before and after used in the HDC of TCM: a) Pd/C fresh; b) Pd/C used ; c) Pt/C fresh; d) Pt/C used; e) Rh/C fresh; f) Rh/C used; g) Ru/C fresh; h) Ru/C used.

TABLES

Table 1. Kinetic equations from the application of LHHW model in a catalytic fixed bed reactor

Rate-controlling step	Kinetic expression
$CM + I \rightarrow CMI$ Adsorption	$\frac{dx_{CM}}{d\tau} = \frac{k_{ads} \cdot [CM]}{1 + K_S \cdot [P]}$
$CMI \rightarrow PI$ Chemical reaction	$\frac{dx_{CM}}{d\tau} = \frac{k_r \cdot [CM]}{1 + K_{ads} \cdot [CM] + K'_{des} \cdot [P]}$
$PI \rightarrow P$ Desorption	$\frac{dx_{CM}}{d\tau} = \frac{k_{des} \cdot [CM]}{1 + K_Z \cdot [CM]}$

Table 2. Fitting parameters for the HDC of DCM with the Pd/C and Pt/C catalysts as obtained from the LHHW model with DCM adsorption control

Catalyst	T (°C)	$k_{\text{ads}} \times 10^{-3}$ (NL·kg ⁻¹ ·h ⁻¹)	$K_s \times 10^{-3}$ (NL·mol ⁻¹)	r^2
Pd/C	150	7.88	333.55	0.994
	175	20.45	186.08	0.998
	200	65.72	255.64	0.989
	225	91.69	87.11	0.988
	250	107.96	19.47	0.999
Pt/C	150	11.50	162.03	0.986
	175	18.27	195.56	0.989
	200	28.56	236.16	0.990
	225	62.70	393.03	0.993
	250	119.16	277.50	0.995

Table 3. Fitting parameters for the HDC of TCM with the Pd/C and Pt/C catalysts as obtained from the LHHW model with TCM adsorption control

Catalyst	T (°C)	$k_{ads} \times 10^{-3}$ (NL·kg ⁻¹ ·h ⁻¹)	$K_s \times 10^{-3}$ (NL·mol ⁻¹)	r^2
Pd/C	100	25.83	8.29	0.997
	125	93.83	13.40	0.990
	150	185.02	10.10	0.999
	175	1196.60	154.52	0.999
Pt/C	150	69.66	33.78	0.997
	175	142.70	10.98	0.999
	200	219.90	9.88	0.999
	225	237.62	14.03	0.999
	250	242.91	16.92	0.999

Table 4. Fitting parameters for the HDC of DCM with the Rh/C and Ru/C catalysts as obtained from the LHHW model with chemical reaction control

Catalyst	T (°C)	$k_r \times 10^{-3}$ (NL·kg ⁻¹ ·h ⁻¹)	$K_{ads} \times 10^{-3}$ (NL·mol ⁻¹)	$K'_{des} \times 10^{-3}$ (NL·mol ⁻¹)	r ²
Rh/C	175	30.56	26.50	319.0	0.998
	200	43.30	14.50	138.0	0.999
	225	93.82	3.01	49.5	0.999
	250	127.00	1.09	10.6	0.999
Ru/C	150	1.61	5.93	330.0	0.998
	175	5.54	23.30	153.0	0.999
	200	16.61	8.60	72.9	0.999
	225	21.12	1.56	4.9	0.998
	250	61.60	27.20	11.7	0.998

Table 5. Fitting parameters for the HDC of TCM with the Rh/C and Ru/C catalysts as obtained from the LHHW model with desorption control in the HDC of TCM

Catalyst	T (°C)	$k_{des} \times 10^{-3}$ (NL·kg ⁻¹ h ⁻¹)	$K_z \times 10^{-3}$ (NL·mol ⁻¹)	r^2
Rh/C	150	426.59	249.4	0.999
	175	266.84	125.6	0.999
	200	197.92	74.2	0.999
	225	153.06	34.6	0.999
	250	205.09	36.6	0.999
Ru/C	175	145.72	273.7	0.996
	200	122.91	127.3	0.997
	225	95.95	26.1	0.999
	250	201.78	34.8	0.999