

Catalytic combustion of carbon tetrachloride

Tamer Tanilmiş, Süheyda Atalay*, H. Erden Alpaya,
Ferhan Sami Atalay

Department of Chemical Engineering, Ege University, Bornova, 35100 İzmir, Turkey

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Abstract

The catalytic combustion of carbon tetrachloride (CCl_4) by metal oxide catalysts coated on the monolith support was investigated. The prepared catalysts were tested at temperatures between 300 and 800 °C and at varying gas hourly space velocity (GHSV) values with an excess air ratio of 3100%. The catalyst, whose composition was 18% Cr_2O_3 , 2% Ce_2O_3 and 80% $\gamma\text{-Al}_2\text{O}_3$, was found to almost completely oxidize CCl_4 . The operating conditions proposed are 5702 h^{-1} for GHSV, 3100% excess air and a temperature slightly higher than 800 °C. The reaction rate expression was found to be independent of oxygen partial pressure but strongly dependent on CCl_4 partial pressure. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorinated hydrocarbons are widely used chemicals in industry and wastes from them are classified as hazardous and toxic. The simplest subgroup of the chlorinated hydrocarbon family is composed of the chlorinated methanes, including methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform (CHCl_3) and carbon tetrachloride (CCl_4). These chemicals are generally used as industrial solvents. The difficulty in incinerating of these compounds (ranked from the most to the least) is CCl_4 , CHCl_3 , CH_2Cl_2 and CH_3Cl [1]. Although conventional incineration of the gaseous effluent containing these compounds presents several problems, catalytic combustion used successfully in the destruction of many organic compounds, could overcome these difficulties. Reports of catalytic combustion of chlorinated hydrocarbons are found both in open and patent literature [2–9]. For safe and complete combustion, more severe conditions are required than for VOCs. In addition to the active catalysts prepared utilizing noble metals such as platinum, rhodium and palladium, the metal oxide catalysts containing the metals in the II-B and III-B groups of the

* Corresponding author. Tel.: +90-232-388-7600; fax: +90-232-388-7776.

Nomenclature

a, b	constants in saturation growth curves
F	molar flow rate (mol/s)
k	reaction rate constant (mol/(kg catalyst s Pa ^{1.14}))
P	partial pressure (Pa)
r	reaction rate (mol/(kg catalyst s))
R	ideal gas constant (J/(mol K))
T	temperature (°C)
W	catalyst weight (kg)
x	conversion of carbon tetrachloride
x_{O_2}	conversion of oxygen

Subscripts

CCl ₄	carbon tetrachloride
O ₂	oxygen

periodic table are used. The oxides of cobalt, copper, manganese and chromium which are resistant to chlorinated compounds are often used as catalysts.

The alumina support is generally used as pellets of variable diameter or as a washcoat on monolith carriers. Since monolith carriers have some advantages over a conventional carrier, they have been preferred in the studies recently performed [9–11]. The commercial catalysts prepared on monolith carriers are also available in industry [12].

The thermal incineration of chlorinated hydrocarbons requires temperatures up to 1200 °C with energy consumption [7]. However, in the catalytic combustion of chlorinated hydrocarbons, mild conditions are required and these conditions change according to the hydrocarbon being incinerated.

In a study of the combustion of waste gases containing chlorinated hydrocarbons, a bimetallic Pd, Pt/Al₂O₃ catalyst has been used with pollutant concentrations of 0.1 vol.% [7]. For a GHSV value of 15,000 h⁻¹ and for a temperature range 350–680 °C, it was found that the waste gas could be oxidized totally and that the catalytic combustion had a significant economic and technical benefit compared to conventional thermal incineration.

In our previous study, an extensive summary of the studies on chlorinated hydrocarbons was presented [13]. In that study, catalytic combustion of methylene chloride was carried out at temperatures between 550 and 600 °C and a GHSV value of 78,000 h⁻¹. These conditions were suitable to combust methylene chloride completely over a ceria-doped chromic oxide gamma alumina monolith catalyst.

A few of the studies on catalytic combustion explored the kinetics of chlorinated hydrocarbons. The kinetics of catalytic oxidation of CH₃Cl on a Cr₂O₃ catalyst obeyed a non-linear second order rate model and the reaction rate was independent of the concentration of oxygen [6]. In the destruction of chlorinated hydrocarbons from soil venting and groundwater remediation on the commercial halohydrocarbon destruction catalyst (HDC) catalyst developed by Allied Signal, a negative order with respect to 1,1,2-trichloroethane was reported [12]. In our earlier work, the kinetics of the catalytic combustion of methylene

chloride was searched by using the model proposed by Downie based on the Mars and van Krevelen mechanism and it was found that the reaction was weakly dependent on methylene chloride partial pressure and strongly on oxygen partial pressure [13].

From the literature survey one can conclude that catalytic combustion is being used as a successful technique to treat the gas effluents containing chlorinated and non-chlorinated hydrocarbons. The treatment of chlorinated hydrocarbons is generally performed on noble metals. This study was focused on the investigation of the process parameters affecting catalytic combustion of CCl_4 on metal oxide catalysts on a monolith carrier. In addition, derivation of the kinetic expression of the combustion reaction was one of the goals of the study.

2. Experimental

The experimental system consisted primarily of a vaporizer, a preheater and a fixed bed reactor. The procedures utilized are discussed in detail elsewhere [13,14]. A brief description is included below.

The catalysts used in the experiments were prepared as mixed metal oxides by an impregnation method utilizing a cordierite type ceramic monolith supplied by Corning. The compositions of the two catalysts on the monolith carrier of square cell shape are given in Table 1. The catalyst support was initially treated with distilled water overnight to remove any trapped air from the pores. Then they were dried at 120°C . A known weight of metal salts was dissolved in water and the solution mixed with alumina. The supports were dipped into the solution and then they were dried and the uniformity in coverage of the channels were controlled. The blocked channels were opened mechanically. The coating and drying cycles were repeated many times. Generally, the same method was used in the preparation of the catalysts. However, in the preparation of some monolith catalysts $\gamma\text{-Al}_2\text{O}_3$ and active material were coated in separate steps. The monolith catalysts were calcinated at 600°C for 4 h in a high-temperature muffle furnace (HTC 1400, Carbolite).

The reactant, CCl_4 and the solvent used in the absorbers, *n*-hexane, were supplied by UPARC and ATABAY, local chemical producers in Turkey. The reagents used in the preparation of the catalysts were purchased from Aldrich and Merck.

The oxidative agent, air and the carrier gas, nitrogen were used directly from the cylinders as supplied. Individual gas flow rates were measured by Cole Palmer rotameters. The oxygen concentration varied between 1418 and 7377 vpm (0.14–0.74%). The experiments were performed at atmospheric pressure.

The catalysts prepared on monolith pieces or uncoated monolith pieces (for homogeneous reactions), were placed into the reactor. Gas leakage of the system was checked, if any.

Table 1
Composition of the catalysts

Catalyst no.	Components (wt.%)		
	$\gamma\text{-Al}_2\text{O}_3$	Cr_2O_3	Ce_2O_3
1	80	15	5
2	80	18	2

The reactor was insulated and the feed tank was filled with CCl_4 . The flow rates of air and nitrogen were adjusted utilizing the rotameters with valves to the desired values. The scrubbers on the steady state and unsteady state lines were filled with a NaOH solution. The absorbers were charged with *n*-hexane. The temperatures of the vaporizer and preheater were set to the desired temperatures. The outer surface temperature of the reactor was set to obtain the desired bed temperature by utilizing the monolith catalyst temperature. The temperature of the 21 mm ID reactor was monitored by a chromel–alumel thermocouple that was inserted into a thermowell extended axially in the reactor.

Cooling water was circulated through the condensers. The pump was activated and its speed adjusted to obtain the desired flow rate of CCl_4 . The temperature of the monolith catalyst was recorded. When the system attained steady state, the gas stream leaving the reactor was directed to the steady state line. The time was recorded. At the end of 90 min period, the run was ended. The undestructed CCl_4 was absorbed in hexane and was analyzed using a gas chromatograph with flame ionization detector. A polar capillary column (HP-FFAP) gave an adequate separation.

A few runs were conducted to determine the potential for reactions between the gas reactants in the absence of the catalyst. In these experiments, the reactor temperature range was between 300 and 700 °C and excess air was 3100% (4357 vpm). Pieces of bare monolith were placed into the reactor and the GHSV value was maintained at 7603 h^{-1} .

Before the kinetic experiments, the performance of the prepared catalysts were evaluated at temperatures from 300 to 800 °C and at constant GHSV values between 4701 and 7603 h^{-1} . The first set of the kinetic experiments was carried out with a constant partial pressure of oxygen and the second set was carried out with a constant partial pressure of CCl_4 to investigate the dependency of the reaction rate on partial pressures of the reactants.

3. Results and discussion

The homogeneous reactions between 300 and 700 °C were evaluated by calculating the conversions with the help of calibration experiments performed at 100 °C. In these experiments the flow rate of CCl_4 was varied by keeping excess air at 3100%. The conversion of CCl_4 , which was the measure of combustion efficiency, for homogeneous and catalytic reactions, gas hourly space velocity (GHSV) and residence time were defined as:

$$\text{conversion, } (x) = \frac{\text{moles of } \text{CCl}_4 \text{ absorbed in the calibration experiment} - \text{moles of } \text{CCl}_4 \text{ absorbed in the experiment}}{\text{moles of } \text{CCl}_4 \text{ absorbed in the calibration experiment}} \times 100 \quad (1)$$

$$\text{GHSV} = \frac{\text{total volumetric flow rate of the gas at STP}}{\text{volume of the catalytic bed}} \quad (2)$$

$$\text{residence time} = \frac{\text{volume of the catalytic bed}}{\text{total volumetric flow rate of the gas at the bed temperature}} \quad (3)$$

The calculated conversions in the homogeneous reactions are given in Table 2.

Table 2
Conversions in homogeneous reactions^a

Reactor temperature (°C)	Residence time (s)	Conversion (%)
300	0.245	28.5
400	0.209	29.8
450	0.194	36.9
500	0.182	42.9
650	0.152	51.9
700	0.144	54.0

^a CCl₄ mole fraction in the feed = 0.43%, excess air ratio = 3100%, GHSV = 7603 h⁻¹.

The gas phase reactions in the absence of a catalyst were significant. Even at a temperature of 300 °C, approximately 30% of CCl₄ was destroyed.

The experiments to determine the performance of the catalysts were carried out in the same manner. Catalyst 1 was tested at different preheater and reactor temperatures. The results are presented in Fig. 1. As can be seen in the figure, reactor temperature proportionally affects the combustion efficiency. Additionally, the temperature of the preheater also affects the combustion efficiency. If the conversion values obtained at the preheater temperature of 350 °C are compared to that of the homogeneous reactions, the fractional increase in the combustion efficiency can be as high as 47%. To attempt to increase the combustion efficiency, catalyst 1 was tested at changing GHSV values. The results are given in Fig. 2. As expected, the combustion efficiency increases as GHSV value decreases. Due to the set-up limitations, it was not possible to decrease the GHSV further.

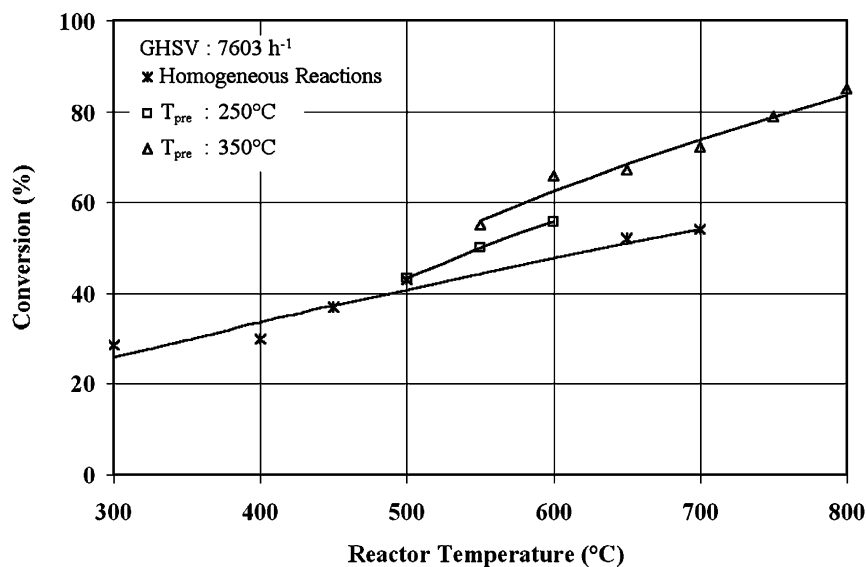


Fig. 1. Results for catalyst 1 at different preheater temperatures.

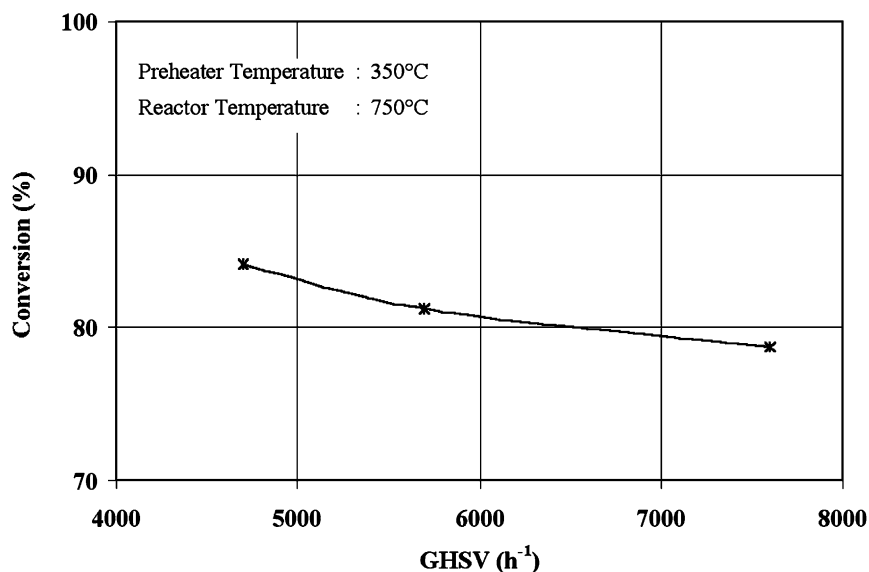


Fig. 2. Results for catalyst 1 at different GHSV values.

The observed combustion efficiencies at the studied conditions were poor. Thus, it was decided to prepare a second catalyst containing more chromium. The second catalyst was tested at a preheater temperature of 350 °C and a GHSV value of 5702 h^{-1} utilizing the experience obtained with the catalyst 1. The combustion efficiencies obtained using this catalyst are shown in Fig. 3. The benefit of using this catalyst is seen from the figure. The second catalyst gave a higher combustion efficiency than the first catalyst, resulting in 94.5% conversion at 800 °C. Although this conversion could be increased by increasing the temperature or by decreasing GHSV value, no further experiments were performed and it was decided that total combustion could be obtained by using the second catalyst and by controlling operating conditions.

The kinetic experiments were studied utilizing the second catalyst and two sets of experiments were performed as mentioned previously. These experiments were evaluated using other calibration experiments performed at 100 °C. In the kinetic experiments, the temperature of the reactor was varied between 350 and 500 °C.

3.1. Reaction rates

The conversion values in the kinetic experiments were greater than 10%. It was not possible to operate the reactor in differential mode at the studied conditions. For that reason, the reaction rates could not be calculated directly.

The conversion values in the experiments with variable partial pressure of CCl_4 were plotted versus space-time W/F_{CCl_4} values at each reactor temperature studied. The experimental points given in Fig. 4 were fit to saturation growth curves, which were in the

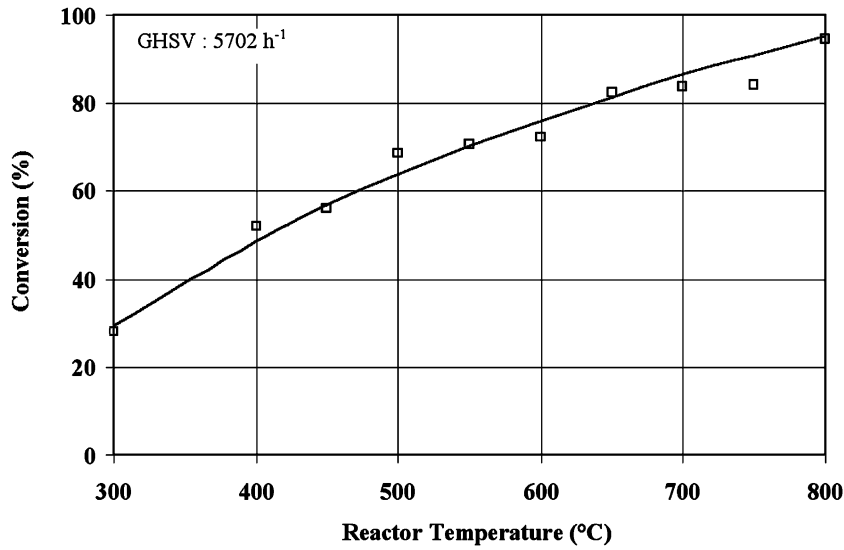


Fig. 3. Results for catalyst 2 at varying reactor temperatures.

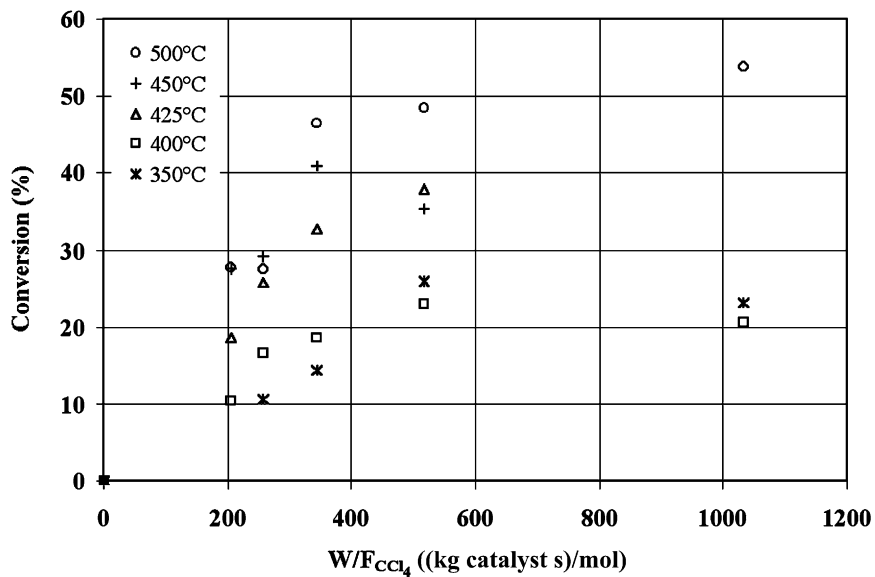


Fig. 4. Conversion values vs. space-time varied by CCl₄.

Table 3
Saturation growth curve constants in variable CCl_4 partial pressure experiments

	Reaction temperature ($^{\circ}\text{C}$)				
	350	400	425	450	500
a	0.32729	0.37603	0.45169	0.48398	0.64555
b	7301.3	5911.3	3251.7	2625.7	3445.2

form of

$$x = \frac{aW/F_{\text{CCl}_4}}{(b + W)/F_{\text{CCl}_4}} \quad (4)$$

where a and b are constants. By taking the inverse of both sides in the equation, saturation growth curves were easily linearized. The a and b values determined at each temperature are given in Table 3. By using these a and b values, the reaction rates were calculated and presented in Fig. 5.

The experiments carried out at variable partial pressures of oxygen and at nearly constant partial pressure of CCl_4 were evaluated and then oxygen conversions were plotted versus space–time values based on oxygen (Fig. 6). In this evaluation the stoichiometry of the reaction was taken into consideration and oxygen conversion was defined as follows:

$$x_{\text{O}_2} = \frac{F_{\text{CCl}_4}}{F_{\text{O}_2}} x \quad (5)$$

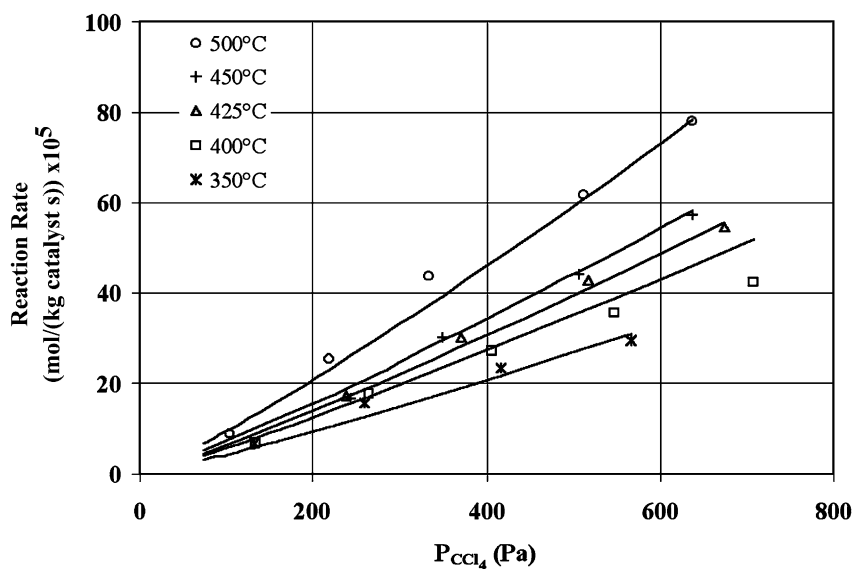


Fig. 5. Reaction rates vs. partial pressure of CCl_4 at different reactor temperatures.

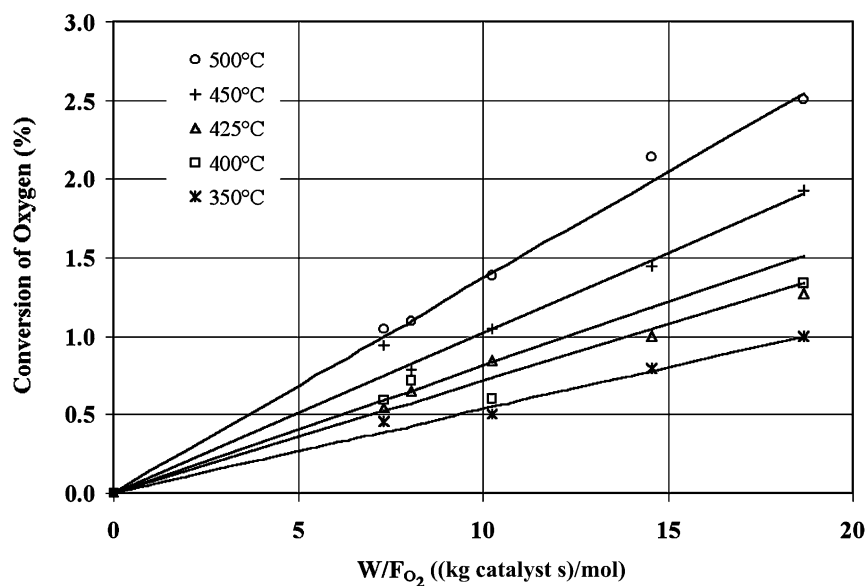


Fig. 6. Conversion of oxygen vs. space-time at different reactor temperatures.

Although the conversions calculated according to the CCl_4 were much higher than 10%, the calculated oxygen conversions were less than 10%.

The experimental points in Fig. 6 could be fitted by linear equations as the reaction rate was not affected by oxygen partial pressure at the studied conditions. By using the least squares method, equations were derived for each line and reaction rates were calculated utilizing the slopes of these lines. The calculated reaction rates are given in Table 4.

3.2. Kinetic model

The kinetic model proposed by Mars and van Krevelen [10] which depends on the reaction of the hydrocarbon from gas phase with adsorbed oxygen was derived and it was simplified by assuming the oxygen adsorption was a rapid process compared to the surface reactions.

Table 4
Reaction rates at different temperatures at varying partial pressure of oxygen

Reactor temperature (°C)	Log mean P_{O_2} (Pa)	Reaction rate (mol/(kg catalyst s)) $\times 10^5$
350	7350–18772	53.453
400	7337–18757	71.483
425	7340–18762	80.988
450	7314–18719	101.915
500	7290–18706	136.335

A kinetic expression derived according to mass of actions could yield the same equation due to the dependency of the reaction rates on partial pressures of the species. These results agree with Weldon and Senkan's study [6] for the catalytic oxidation of methyl chloride in air using a commercially available Cr_2O_3 catalyst in a packed bed reactor. In that study, the reaction rate was also found to be independent of the oxygen concentration. The values of apparent reaction rate constant k , at different temperatures and the reaction order satisfactorily representing the experimental data were determined. The reaction order was found to be 1.14. The change of k values with respect to temperature was tested by the Arrhenius equation and the following expression was found:

$$k = 8.75 \times 10^{-6} \exp\left(-\frac{18,930}{RT}\right) \quad (6)$$

The apparent activation energies were in the range reported in the literature for methylene chloride in a fluidized bed was 16,900 cal/mol and for CH_3Cl in a packed bed was 17,000 cal/mol [6,16]. The low value of the activation energy calculated in this study could be attributed to the high activity of the catalyst. The agreement between calculated and experimental reaction rates is shown in Fig. 7.

The role of external mass transfer effects was tested theoretically using correlations in the literature. The ratio of concentration difference between bulk and surface to bulk concentration was found to be one-tenth of the recommended value [15].

The reactor might be considered to operate isothermally even at integral reactor conditions since the very lean hydrocarbon was used.

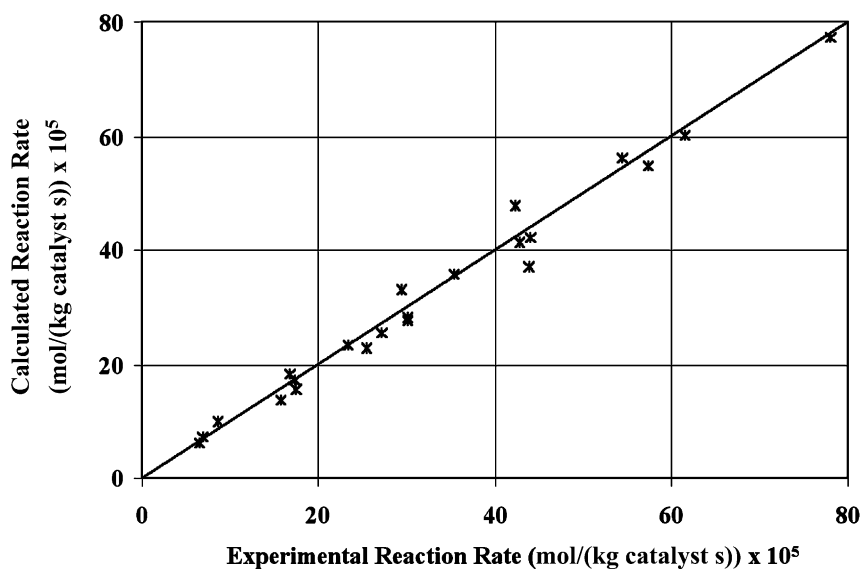


Fig. 7. Calculated vs. experimental reaction rates.

4. Conclusions

A bimetallic catalyst having Cr, Ce/Al₂O₃ on a monolithic support was able to combust CCl₄ almost completely. A temperature slightly higher than 800 °C and a GHSV value between 5000 and 6000 h⁻¹ are recommended. The reactions between the gas phase reactants were significant at these conditions.

The reaction rate was dependent on the hydrocarbon partial pressure but was independent of the partial pressure of the oxygen. Beginning with the Mars and van Krevelen mechanism, the reaction rate was simplified to a non-linear equation containing only CCl₄ partial pressure. The reaction rate order was found to be 1.14. The activation energy for the surface reaction was found to be around 19 kJ/mol.

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