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Catalytic abatement of dichloromethane over transition metal oxide catalysts: Thermodynamic modelling and experimental studies

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Abstract

Dichloromethane (DCM) is a noxious chemical that is widely used in industry. The current work focuses on the catalytic abatement of DCM from industrial effluents to minimize its harmful effects to the environment and human wellbeing. Three transition metal oxide catalysts (V, Cu and Mn) supported on γ -Al₂O₃ were synthesized for total oxidation of DCM in presence of steam. Thermodynamic modelling was used to reveal information related to the stability of the used transition metal oxides in the abatement conditions. The results showed that with 10 wt-% CuO and 10 wt-% V₂O₅ containing catalysts 100% conversion of DCM together with 90% HCl yield and insignificant by-product formation can be achieved at temperature around 500°C. According to modelling, V₂O₅ should be stable at the conditions of DCM oxidation, while CuO would be more stable at higher temperature level (decomposition of CuCl₂ starts at 300°C). MnCl₂ remains stable until 800 °C, which leads to deactivation of MnO₂ catalyst. Presence of steam inhibits the poisoning

of the materials by chlorine based on thermodynamic calculation. XRF analysis supports the results of thermodynamic modelling – used MnO_2 and CuO catalysts contain chlorine, which was not detected in case of $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$. $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ seems to be a good alternative to noble metal catalysts for the total oxidation of dichloromethane when used in the presence of steam and the temperatures above $300\text{ }^\circ\text{C}$ to minimize Cl-poisoning. The outcomes of this study showed that the prepared metal oxides are promising catalysts for to minimize pollution caused by chlorinated volatile organic compounds.

Keywords: Copper oxide, CVOC, Elimination of toxic substances, Environmental catalysis, Total oxidation, Vanadium oxide,

1 Introduction

Dichloromethane (DCM) is widely used in several applications, such as a cleaning and degreasing agents, in pharmaceuticals and electronics manufacturing, film coatings, aerosol, automotive products and decaffeination of coffee (Aranzabal et al., 2014; EPA, 2011). The diverse use of DCM leads to its high emissions to the atmosphere, which cause many problems impacting human wellbeing, as described in ref. (Wexler et al., 2005), and which may even lead to consequences as serious as death (OSHA-NIOSH, 2013). The DCM carcinogenicity to humans is still under debate, since it was reported earlier that DCM might be a carcinogen (IARC, 2016). However, in 2017 the European Chlorinated Solvent Association (ECSA) stated that there is no real proof concerning the carcinogenicity of DCM to humans (ECSA, 2017). The exposure limit set by the European Union for DCM is 100 ppm for 8 h and 200 ppm in 15 min (European Commission, 2009). Due to these reasons and increasingly stringent emission legislation, demands for efficient technologies to remove and /or minimize the DCM emissions have arisen (Ojala et al., 2011).

Catalytic oxidation is probably the most interesting method for destruction of chlorinated volatile organic compounds, CVOCs, since it presents certain advantages over other possible techniques, such as lower operating temperature hindering dioxin formation and reducing energy requirement as well as lower capital costs (Aranzabal et al., 2014). Catalytic oxidation is effective in the case of diluted CVOC concentrations without using additional fuel. Furthermore, catalytic materials can be designed to be more selective towards less harmful reaction products (such as HCl and CO₂) thus minimizing the production of harmful by-products. (Ojala et al., 2011)

Pt is frequently used active phase in catalytic oxidation of CVOCs. In the case of DCM, Pt catalysts supported on Al₂O₃, HFAU, Ce_{0.5}Zr_{0.5}O₂ and Al₂O₃ modified by TiO₂ and CeO₂ have been investigated.. (Matějová et al., 2013; Pinard et al., 2004; Pitkäaho et al., 2013) Despite the fact that noble metal containing catalysts show high activities and selectivities in the catalytic oxidation of

CVOCs, these types of catalysts present also some disadvantages, since they might be poisoned by chlorinated reaction products, such as HCl and Cl₂. Another disadvantage is the higher costs of noble metals compared to metal oxides. (Aranzabal et al., 2014) Recently, the studies have been focused on the transition metal oxide catalysts, even if their activities and selectivities are typically less than those observed for the noble metals. They might, however, resist the poisoning by chlorine better than noble metals, even though it has been reported that in some cases chlorine could form volatile compounds with metal oxides (Saqr et al., 2011; Tseng et al., 2010). The most used transition metal oxide catalysts in CVOC oxidation are Co, Cr, Fe, Mn, Cu, V, and Cr. These oxides show rather high activities and selectivities. (Aranzabal et al., 2014; Yang et al., 2019; Zhang et al., 2018)

In the current work, we studied CuO, MnO₂ and V₂O₅ as an alternative to Pt in DCM oxidation. CuO supported on ceria and/or titania has shown its potential in DCM, 1,2-dichloroethane and trichloroethylene oxidation (Cao et al., 2016; Yang et al., 2019). One benefit of CuO is that it can be reduced at less than 200°C, which may be beneficial for the DCM complete oxidation reaction. (Huang et al., 2011) In addition, Cu-Mn mixed oxides supported on TiO₂ have been studied in chlorobenzene oxidation (Vu et al., 2009). Suitability of Mn oxide alone in oxidation of DCM, trichloroethylene chlorobenzene and o-dichlorobenzene has been proven earlier as well (Gutiérrez-Ortiz et al., 2003; Tian et al., 2010; Tseng et al., 2010). Both CuO and Mn containing catalysts lead to high selectivity towards CO₂ (Gutiérrez-Ortiz et al., 2003). Vanadium oxide is well-known active phase in CVOC oxidation. It has been applied in the cases of chlorobenzene, DCM, perchloroethylene, trichloroethylene and dichlorobenzene total oxidation (Gallastegi-Villa et al., 2015; Pitkäaho et al., 2012; Wu et al., 2012). It also changes the oxidation state easily similarly to copper (Weckhuysen and Keller, 2003). Compared to Copper and manganese oxides, vanadium oxide is more stable against deactivation by chlorine (Bertinchamps et al., 2008).

In the present work, the selected metal oxides were supported on γ -Al₂O₃, because our earlier studies showed γ -Al₂O₃ to have certain advantageous properties for DCM oxidation (El Assal et al., 2017). Since we also know that especially Cu(I) oxide might deactivate in presence of HCl, the stability of the selected oxides under the used reaction conditions was investigated by modelling.

2 Experimental

2.1 Catalysts' preparation

Aluminium oxide (Al₂O₃) support was prepared by the sol-gel method proposed by Yoldas (Yoldas, 1975). Aluminium-tri-sec-butoxide and ultrapure water were kept under stirring at 60°C for 60 min. Then, the mixture was hydrolysed by HCl to smooth the progress of the condensation process. Afterwards, temperature was increased to 80°C where the reaction was allowed to continue for 120 min. The white viscous sol was formed at the end of the stirring. The molar ratio of aluminium precursor, water and HCl, used during the preparation was 1:100:0.1, respectively.

The prepared support was dried on a sand bath at 60 °C overnight followed by drying in a ventilated oven at 120 °C in order to eliminate the solvent from the gel. The prepared material was then heated from room temperature to 500 °C with 5 °C min⁻¹ as the heating rate, and calcined at this temperature for 6 h to reach the wanted final oxide form of Al₂O₃.

The calcined support (Al₂O₃) was wet impregnated by 30 wt-% of metal oxides (Mn, V and Cu). Sodium permanganate monohydrate (NaMnO₄ · H₂O, Sigma Aldrich, 99.9%), copper nitrate (Cu(NO₃)₂ · 4 H₂O, Sigma Aldrich, 99.9%) and vanadium acetylacetonate (V(C₁₀H₁₄O₅), Merck, > 98%) were the precursors used in catalyst preparations. In addition, 10 wt-% of V₂O₅ and 10 wt-% of CuO catalysts supported on alumina were also prepared. The required amount of support was immersed in the solution of dissolved precursor and kept under mechanical stirring at room temperature overnight. The thermal treatment was the same as used in the support treatment. The

catalysts are later denoted as xCuAl for CuO/ γ -Al₂O₃, xVAl for V₂O₅/ γ -Al₂O₃ and xMnAl meaning MnO_x/ γ -Al₂O₃, where x is the loading of the impregnated phase.

2.2. Catalyst characterization

The specific surface areas and pore volumes of the samples were determined by physisorption of nitrogen at -196 °C using a Micromeritics ASAP 2020 instrument. The specific surface area was calculated using the BET method and pore size distribution was obtained by using the BJH method. Prior to adsorption experiments, the samples were degassed under vacuum at 250 °C during 2 h.

The XRD spectra were obtained by a BRUKER-5500 diffractometer using Cu radiation with a wavelength of $\lambda_{\text{Cu}} = 0.15406$ nm and by Rigaku SmartLab 9 kW using Co radiation with a wavelength of $\lambda_{\text{Co}} = 0.178901$ nm and a graphite monochromator for eliminating K β radiation and fluorescence. The samples were scanned in a range of 2θ from 5° to 90° with the rate of measurement of 0.04 °/2s. The diffraction patterns obtained were compared with the library data from JCPDS.

XRF analyses were done using a PANalytical Axios-MAX apparatus equipped with a rhodium anode as a standard. To enhance the sensitivity, the power was fixed at 3 kW (60 kV, 50 mA). The analysis was done for samples in powder form (loose-powder method).

Temperature programmed desorption of ammonia (NH₃-TPD) was carried out with an AutoChem II 2920 device. Prior the analysis, the sample was pre-treated under He flow from room temperature to 500 °C with a heating rate of 10 °C min⁻¹, kept at this temperature for 30 min, and then cooled down to room temperature. The adsorption of 15%NH₃/He was done during 60 min at room temperature, after which the sample was flushed with He for 30 min. The NH₃ desorption was done from room temperature to 500 °C with heating rate of 5 °C min⁻¹. The flow rate of the gases during analysis was fixed to 50 mL min⁻¹. The concentration of desorbed NH₃ was analysed by a TCD detector. The total quantity of acid sites was determined by integration of the observed peaks between 40 and 500 °C.

A Timegated® 532 Raman spectrometer was used for collecting the Raman spectra of fresh and used 10 wt-% CuO, V₂O₅ and MnO₂ catalysts and alumina support. The TG-Raman device uses a 532 nm pulsed laser and CMOS SPAD detector. The analysis was done in the range from 200 to 1200 cm⁻¹ with a spectral resolution of 10 cm⁻¹.

2.3 Catalytic oxidation of dichloromethane

DCM oxidation experiments were carried out in a fixed-bed tubular reactor operating under atmospheric pressure. The DCM (Sigma Aldrich and Algal, 99.0 %) concentration used was 500 ppm and the experiments were carried out in presence 1.5 vol-% of water to ensure sufficient selectivity towards HCl. The total flow of the reaction mixture was set to be 1 L min⁻¹ through the catalyst bed. The temperature range used in the light-off test was from 100 to 500 °C with heating rate of 5 °C min⁻¹. The tests were repeated at least once to verify the results. More details of the experimental set-up are described elsewhere (Pitkäaho et al., 2012).

Selected DCM oxidation tests were done with 100 mg of catalyst sample giving a high gas hourly space velocity (GHSV) equivalent to 704 867 h⁻¹ during the experiments. The second set of the tests for studying the amount of active phase were done with 400 mg, which gives GHSV of 143 793 h⁻¹. The catalysts were sieved to obtain a 0.25–0.5 mm granule size in order to avoid the effect of diffusion during DCM oxidation (more details related to this issue can be found from (El Assal et al., 2017)).

2.4 Modelling

The formation and the stability of Mn, Cu and V chlorides in the used reaction conditions were evaluated by modelling with HSC Chemistry 6 software. The equilibrium compositions versus temperature have been calculated by the Gibbs energy minimization method. The input concentrations corresponded to our real experimental mixture. The total concentration of the compounds was fixed

to 1000 mol and the pressure used in the modelling was 1 bar. Solid phase as oxides was introduced in the modelling as input and the amounts corresponded 10 and 30 wt-%. The different cases studied are summarized in Table 1. An additional modelling was done to check the situation also when the by-products are present in the reaction mixture. However, this did not change the results of the modelling related to metal chlorides and thus they are not presented in more detail.

Table 1.

3 Results

3.1 Performance of 30 wt-% catalysts in DCM oxidation

The first comparison of the performance of the prepared catalysts in DCM oxidation was done over 30CuAl, 30MnAl and 30VAl. The high loading of active phases was chosen in order to have an excess of transition metal oxide on the alumina support and to minimize the effect of chlorine-induced poisoning of the active phases. The results (Fig. 1) show that the conversion of DCM started at about 300°C for all the catalysts, and the maximum conversion achieved at 500 °C was about 65, 55 and 15 % over 30VAl, 30CuAl and 30MnAl, respectively. The light-off temperatures (T_{50} , temperature needed for 50 % of DCM conversion) were about 480°C for 30VAl and 490 °C for 30CuAl. 30MnAl never reached the light-off point in the used temperature range. From the final reaction products, HCl, H₂O and CO₂ are those wanted. The yields of HCl observed for 30VAl and 30CuAl catalysts at 500 °C were practically the same. The Mn-containing catalyst presented an insignificant formation of HCl that was less than 2 %.

Fig. 1.

Fig. 2.

The main observed by-products were CO and CH₂O over 30 wt-% of Mn-, Cu- and V-containing catalysts (Fig. 2). 30VAl produced higher amount of by-products than other catalysts: 185 ppm and 25 ppm for CO and CH₂O, respectively. These undesired products were observed with low amounts over 30 MnAl, but it was only able to reach 15 % conversion of DCM. In addition, the 30 CuAl catalyst presented the lowest amounts of by-products formation even though the observed DCM conversion was about 55%.

3.2 Formation and stability of metal chlorides in the used experimental conditions

Even though the transition metal oxide catalysts are active for DCM oxidation, copper and manganese oxide catalysts might be deactivated in the presence of Cl-containing compounds as reported by Gu *et al.* (Gu *et al.*, 2010) and Bertinchamps *et al.* (Bertinchamps *et al.*, 2008). The deactivation of Cu and Mn oxides might occur, since they are also active in Deacon reaction to form Cl₂ from HCl. Cl₂ and HCl may both cause formation of CuCl and MnCl₂, which are not active in the DCM oxidation reaction. In order to check this issue, we used thermodynamic modelling. The conditions for the modelling were selected to represent the complete conversion of DCM in presence and absence of H₂O and considering the production of HCl, H₂O and CO₂. In addition, by-products such as CH₂O, CH₃Cl as well as CO and Cl₂ were included in a separate modelling study. The cases are summarized in Table 1 in connection with the experimental section.

Fig. 3 and 4 show the modelling results for 30 wt-% Cu-containing catalysts. Results for 10 wt-% of Cu are presented in supplementary information (Figs. 1S and 2S). The catalysts containing 10 and 30 wt-% of Cu present similar profiles regarding the CuCl₂ decomposition and CuO formation in presence of water (Fig. 3(a) and (b)) that started at around 300 °C, at the same time with formation

of HCl. CuCl_2 was no longer present after about 850 °C. No significant changes concerning the results were observed after addition of by-products and Cl_2 .

In absence of water in the input (Fig. 4), the start of CuCl_2 decomposition was shifted to a slightly higher temperature (350 °C) in the case of 30 wt-% CuO , and more than half of the initial amount of CuCl_2 still existed at 800 °C with both loadings of CuO . In the case when by-products and Cl_2 were added to the input (See supplementary information Figs. 3S, 4S and 5S), a small formation of Cl_2 started at around 500 °C. Presence of H_2O in the feed stream seems to lead to decomposition of CuCl_2 at a lower temperature range thus improving the stability of CuO catalyst.

Fig. 3.

Fig. 4.

The modelling results related to the 30 wt-% MnO_2 are shown in supplementary material Figures 6S and 7S, and for 10 wt-% MnO_2 catalysts in Figures 8S and 9s. The results showed in the presence of water (Fig. 6S(a)), that amount of MnCl_2 starts to decrease from the beginning up to 650 °C where it reaches the minimum and starts to increase again. At the same time, maxima in HCl and MnO_2 formation are observed. Similar results were observed for 10 wt-% MnO_2 with only difference in amounts of the produced MnCl_2 and reacted MnO_2 . According to the thermodynamic modelling, some amount of MnCl_2 is always present in equilibrium conditions. In absence of water (Fig. 7S(a)), similar results were obtained as in the presence of water. However, the amount of MnCl_2 was higher in absence of water in the studied temperature range.

In presence of water in the input and when Cl_2 was added to the output (Fig. 6S(b)), we observed a different situation. Cl_2 is present from the beginning (at low temperature) and starts to decrease after 100 °C. MnCl_2 formation starts at 150 °C and is still present after 850 °C. The HCl amount starts to increase at 100 °C and reaches the maximum at around 650 °C. Based on this information we assume that the poisoning of MnO_2 is possible even at high temperatures when Cl_2 is present. In absence of water in the input and in presence of Cl_2 in the output (Fig. 7S(b)), the formation of MnCl_2 is even more pronounced (about a double compared with situation when water is present). Moreover, at 800 °C 85% of initial of 10 wt-% MnO_2 can react to MnCl_2 according to the thermodynamics (see supplementary information). In the case of MnO_2 , it seems that water has an inhibiting effect against Cl-poisoning, which might be due to the reaction of MnCl_2 with H_2O to form $\text{Mn}(\text{OH})\text{Cl}$ at low temperature (230°C) or Mn_2O_4 at higher temperature (near 500°C). Based on these results, we expect that poisoning of MnO_2 might appear in our experimental conditions of DCM oxidation.

In the case of vanadium, the modelling did not show formation of VCl_2 even in the presence of Cl_2 . The absence of water in the input affected the formation of HCl. The maximum HCl formation in presence of water was observed at 600 °C. However, a similar maximum was never reached in the absence of water up to 850 °C. In presence of water, the Cl_2 amount went to zero at 600°C, whereas without water it remained in the equilibrium composition until 850 °C, which was the maximum temperature used in the modelling. The results of the modelling related to vanadia are presented in supplementary material (Figs. 10S and 11S). To conclude, vanadia-containing catalysts should be rather stable in our experimental conditions. Based on the modelling and preliminary testing results, we decided to continue with copper- and vanadium-containing catalysts and decrease the loading of the active phases. Copper- and vanadium- containing catalysts seem to have better stability in the used reaction conditions. In addition, these two catalysts show better performance in DCM oxidation.

3.3 Performance of 10 wt-% catalysts in DCM oxidation

Fig. 5 shows the results of the DCM oxidation for Al_2O_3 , 10VAl and 10CuAl. The observed activities are very good. Al_2O_3 alone is able to convert DCM fully at 475 °C. The addition of 10 wt-% of vanadia does not improve the catalyst performance in terms of DCM conversion. In the case of 10 wt-% of CuO, the DCM oxidation efficiency is reduced slightly (after 350 °C), since 100% conversion is reached at around 500 °C. The slight change after 350 °C might be due to the poisoning by chlorine.

The yield of HCl obtained during DCM oxidation is presented in the same Fig. 5. 10VAl present the highest yield of HCl, reaching almost 95% at 450 °C. The other catalysts reach almost the same yields (90%), but at higher temperature. At this point, 10VAl presents the highest DCM conversion, and also the highest yield of HCl as the wanted final product.

Fig. 5.

From the observed by-products, the highest formation was observed for CH_2O and CH_3Cl . The formation of the by-products is shown in Fig. 6. The major result is that 10CuAl presents the lowest by-product formation in the whole temperature range. The second remark is that Al_2O_3 presents lower yields of CO and CH_2O and a higher yield of CH_3Cl . The higher formation of CH_3Cl compared to CH_2O on alumina can be explained by the higher amount of Lewis acid sites (LAS) present on the surface compared with the amount of Brønsted ones (BAS). The relationship between the type of the acid sites and the by-products distribution with the same Al_2O_3 was observed in our previous work (El Assal et al., 2017). After addition of 10 wt-% of V_2O_5 on alumina, we observe a change in the distribution of by-products. In this case, higher formation of CH_2O is observed. This should indicate modification of the acidic properties on the material surface, and presence of a higher amount of BAS on the catalyst surface. Indeed, it has been reported before (Lin and Bai, 2003), that V_2O_5 has mainly

BAS. To conclude, CuO seems to be a very interesting catalytic material for DCM oxidation, since only small amounts of by-products are observed over the whole temperature range and quite similar conversions of DCM are achieved than with V₂O₅ catalyst.

Fig. 6.

3.4 Characterization

Since we characterized alumina used in this study in our previous work, we summarize here shortly our results reported in (El Assal et al., 2017) as background information. The XRD patterns observed for calcined Al₂O₃ were related to gamma (γ -) phase in addition to a presence of amorphous phase in majority. That allowed alumina to gain a high surface area of 225 m² g⁻¹. N₂ physisorption isotherm was of Type IV with hysteresis Type H2, which is characteristic of the mesoporous material with bottle-shaped pores. The observed pore size distribution was homogeneous, and the pore size was centred at around 6 nm. The thermal desorption of pyridine and lutidine over Al₂O₃ followed by FTIR analysis revealed the presence of both Lewis (LAS) and Brønsted (BAS) acid sites. The comparison between both existing acid sites showed that the prepared Al₂O₃ support has more LAS than BAS (Table 2) on the surface. As it can also be seen from the table, pyridine is more sensitive to LAS and it does not show the existence of BAS correctly. Thus, lutidine as more sensitive to BAS, was used in quantification of BAS. More discussion on this issue can be found in (El Assal et al., 2017).

Table 2.

The XRD pattern of calcined 10 wt-% Cu catalyst (at 500 °C) did not show the presence of CuO, and only γ -Al₂O₃ (JCPDS file 50-0741) and the amorphous phase were observed (Fig. 7; CuAl). The result indicates that the CuO is highly dispersed on the alumina surface, which is in agreement with the finding of Li *et al.* (Li et al., 2011). The EDS mapping (Fig. 8), proves the good dispersion of copper on the surface of γ -Al₂O₃. From the XRD diffractograms of 10VAl and 30VAl catalysts the following phases can be identified: shcherbinaite phase of V₂O₅ and γ -Al₂O₃ together with an amorphous phase (Fig. 7). From the XRD analysis, it is difficult to estimate accurately the crystallite size due to the presence of the amorphous phase.

Fig. 7.

The EDS mapping in Fig. 8 was done without crushing the prepared samples and the size of the granule was between 0.25–0.5 mm, which is the same size than that used in DCM oxidation experiments. Fig. 8 demonstrates that the prepared catalysts have good dispersion of vanadium and copper on the surface of alumina. According to the EDS mapping, copper seems to be slightly more homogeneously distributed on the surface of alumina than vanadium. The average amount determined by EDS is included in Table 3. The obtained amount was quite similar to the target value.

Fig. 8.

The elemental analysis results of the catalysts are shown in Table 3. The analysed and expected amounts are quite similar to each other. These results show the success of the impregnation of vanadium and copper on alumina.

Table 3.

The exhibited nitrogen adsorption-desorption isotherms of the prepared catalysts are all Type IV with an H2-type hysteresis loop (Fig. 9). These indicate the presence of mesoporous material and relatively large pores with a narrow opening (neck of bottle) or clusters of small spheroidal particles according to the International Union of Pure and Applied Chemistry (IUPAC) (Sing, 1982; Thommes, 2010). The obtained specific surface area of CuAl and VAl catalysts determined by the BET method are summarized in Table 3. The results show decreasing of the surface area after impregnation of the support, however, the pore sizes determined with the BJH method remain quite similar (Table 3). The decrease of the specific surface areas after impregnation is most probably due to the blockage of the pores in the support and quite expected after rather high loading of copper and vanadium oxides.

Fig. 9.

The thermal desorption of NH_3 was used in determination of total acidity of the materials and to estimate the strength of the acid sites. Based on the analysis, all the materials show the presence of weak (w), medium (m) and strong (s) acid sites in the temperature ranges of 50–250°C, 250–400°C and superior than 400 °C, respectively. In our case, The NH_3 -TPD experiment was done up to 500 °C, because it was the maximum temperature used in DCM oxidation experiments and started to approach the V_2O_5 melting temperature (690 °C). The total acidities of the materials were 0.145 mmol g^{-1} for Al_2O_3 , 0.150 mmol g^{-1} for 10VAl, 0.215 mmol g^{-1} for 30VAl and 0.160 mmol g^{-1} for 10CuAl. The total acidity of the material increased after addition of active phases.

4 Discussion

Opposite to our expectations based on the literature (Gutiérrez-Ortiz et al., 2003; Liu et al., 2001; Wang et al., 2009, 2008), we did not find good activity for Mn-containing catalyst. This is most probably due to the formation of an unexpected form of oxide, $\text{Na}_{0.7}\text{MnO}_{2.05}$, that seems to be less active in the studied reaction. The mixed oxide is formed due to the used Mn precursor and the temperature of the calcination. The same phase was observed earlier by Kappenstein *et al.* (Kappenstein et al., 2002) when using the same preparation procedure. Unfortunately, we did not notice the formation of the mixed oxide in the beginning, and it was observed only at the end when poor activity of Mn-containing catalyst was considered in more detail. Another reason for poor activity of the Mn-containing catalyst might be found from thermodynamic modelling. The formation of MnCl_2 seems to be evident in the used reaction conditions even though we do not have information on the kinetics of the formation. Additionally, the prepared 30MnAl catalyst has very low specific surface area that most probably affects the activity compared with other transition metal oxides.

10CuAl and 10VAl catalysts showed very good activity in DCM oxidation. In addition, by-product formation over 10CuAl was very small – at the level of detection of the used FTIR instrument. When we compare these results to Pt/ Al_2O_3 studied earlier, we observed that Pt/ Al_2O_3 was converting 100 % of DCM at around 450 °C with a high yield of HCl. The formation of the by-products, CO, CH_2O and CH_3Cl was higher than that for 10CuAl catalyst reaching maxima of 55, 35 and 20 ppm, respectively, in the temperature range between 350 and 400 °C. In the current work we observed that V_2O_5 addition on Al_2O_3 modifies the type of acid sites on the material based on the distribution of the by-products. The similar modification of surface acidity was observed also in the case of Pt/ Al_2O_3 (El Assal et al., 2017). Analogous observations were not made with CuO due to the very low by-product formation.

In our earlier research, we compared properties and performance of different support materials, and we observed that higher total acidity of a support leads to a better DCM conversion. In the current

study, we observed that when the acidity of the material is increased after addition of copper and vanadium oxides, the DCM conversions are rather decreased than improved. This may be due to decreased specific surface area due to the blockage of the pores of Al_2O_3 after impregnation of rather high loading of used metal oxides. The relation of the total acidity of the catalysts with DCM conversion, as well as relation of the type of acid sites to by-product distribution should be studied in more detail by using *in-situ* techniques, for example.

To go further in the study the presence of chlorine on the catalysts, a TG Raman measurement was done for 10CuAl, 30MnAl and Al_2O_3 . The spectra of used Al_2O_3 showed the vibrations in the area of Al-Cl stretching vibration that did not exist for fresh Al_2O_3 indicating the presence of the chlorine on the material. For the used 10CuAl, in addition to Al-Cl stretching vibrations, also bands related to Cu(II) – Cl stretching vibration were observed. In the case of spent manganese containing catalyst, no bands in addition to Al-Cl stretching vibration were observed. In the case of 30MnAl catalyst, the signal-to-noise ratio for the measurement was rather low, complicating the interpretation of the spectra. The observations related to the presence of chlorine species on the used materials support the results of the modelling. However, based on the modelling, we expected to see more chlorine compounds on 30MnAl catalyst. This is why, we did additional XRF analysis, and as a result we observed that used 30MnAl catalyst contained significantly more chlorine than the used 10CuAl catalyst. Furthermore, the used 10VAl or 30VAl practically did not contain chlorine. These results, as well as Raman results related to 10VAl and 10CuAl, are well in line with the results of thermodynamic modelling.

Spivey *et al.* (Spivey and Butt, 1992) have concluded in their review, that chlorine may form volatile compounds with transition metal oxides. Thus, during the XRF analysis of the used catalysts, the amounts of metal oxides were also checked. It was found that the transition metal oxide amounts in 10CuAl and 30CuAl catalysts were kept well. In contrast, the amount of MnO_2 in 30MnAl was

reduced by 25% and vanadium in 10VAl catalyst to about a half. Based on these results, we can state that the loss of MnO_2 and even V_2O_5 might occur in the used reaction conditions. Loss of CuO was not observed, which is an interesting result. However, to study this issue more, a long-duration stability test with the used catalytic materials should be conducted.

5 Conclusion

The objective of this work was to study the performance of transition metal oxides (Cu, Mn and V) in total oxidation of dichloromethane. The aim was to find alternative catalysts to often used noble metals, since noble metals are expensive and they have been reported to deactivate in the presence of chlorine-containing compounds. The selected transition metals were supported on $\gamma\text{-Al}_2\text{O}_3$ that was found to be a good support in our earlier studies. It was found that $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ are very good alternatives for $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$. Both of these transition metal oxides give good DCM conversion and HCl yields. In addition, the formation of by-products over $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ during the whole temperature range tested is almost insignificant. The results of the thermodynamic modelling showed that in the used DCM oxidation conditions, MnO_2 catalyst can be expected to deactivate with time due to formation of MnCl_2 . V_2O_5 and CuO are more stable. However, some chlorine was observed on spent CuO -containing catalyst based on XRF results. The reaction conditions containing water vapour are favourable for avoiding the formation of corresponding chlorides at higher temperature (after 300°C), which is the starting temperature of DCM oxidation. Loss of V_2O_5 may occur during the reaction conditions based on XRF analysis. For this reason, and the fact that CuO produced significantly less by-products, it seems to be the best option to replace Pt among the tested materials.

Acknowledgements

The authors are grateful to Kaisu Ainassaari and Markus Riihimäki for their help in the samples characterization. The staff of the Center of Microscopy and Nanotechnology (University of Oulu, Finland) and Institute of Chemistry of Poitiers, Materials and Natural Resources (University of Poitiers, France) are acknowledged for characterizations as well.

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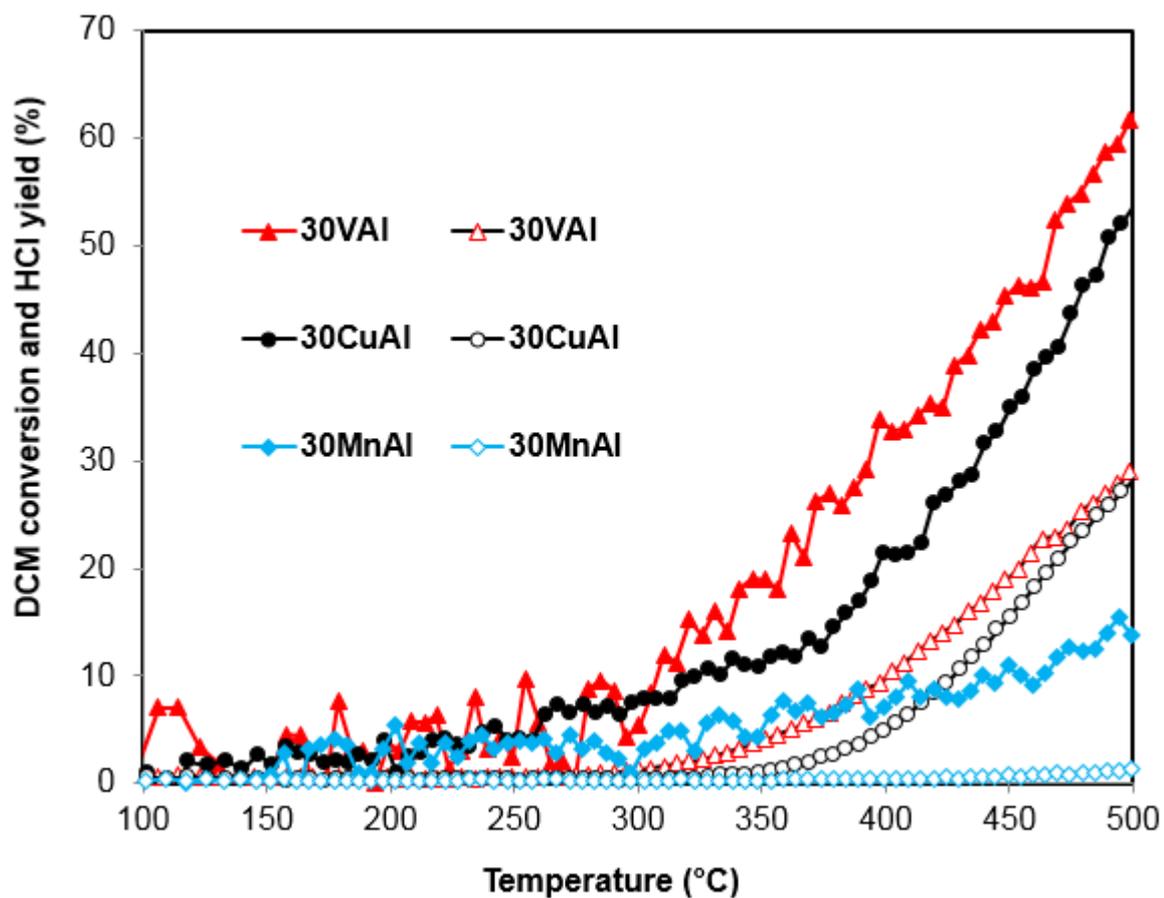


Fig. 1. Light-off curves of DCM over the different catalysts with 30 wt-% of loading (catalyst mass 100 mg, DCM 500 ppm, H₂O 1.5 vol-%, 1 L min⁻¹, GHSV 704 867 h⁻¹). Filled symbols indicate DCM conversion and open symbols show the yield of HCl.

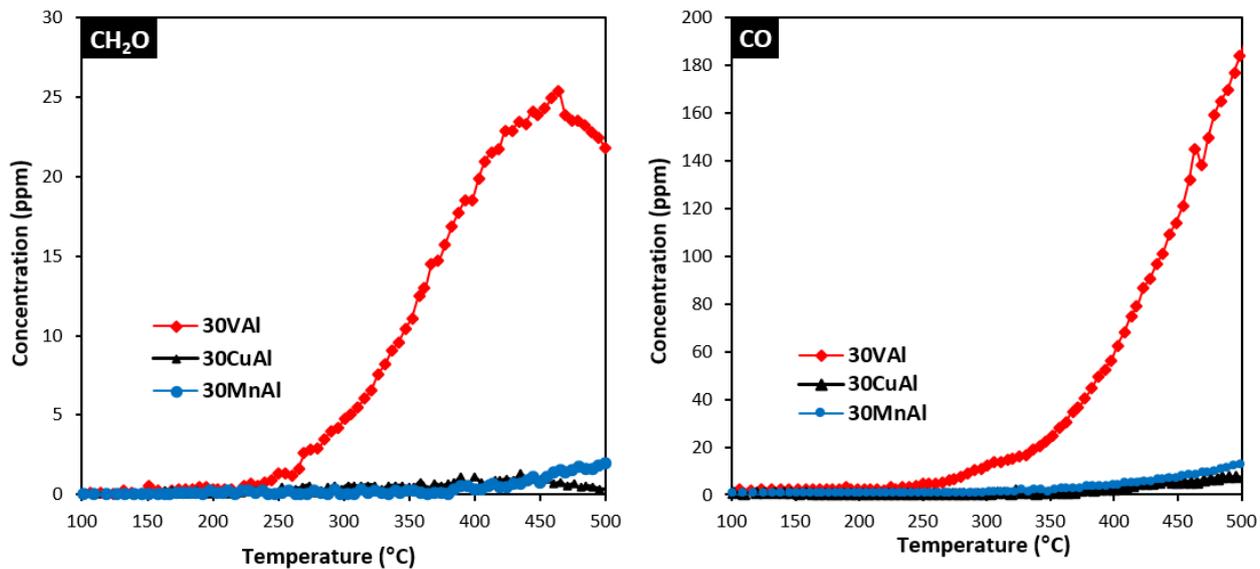


Fig. 2. Amount of major by-products over 30VAI, 30CuAl and 30MnAl. The same experimental conditions were used as in Fig. 1.

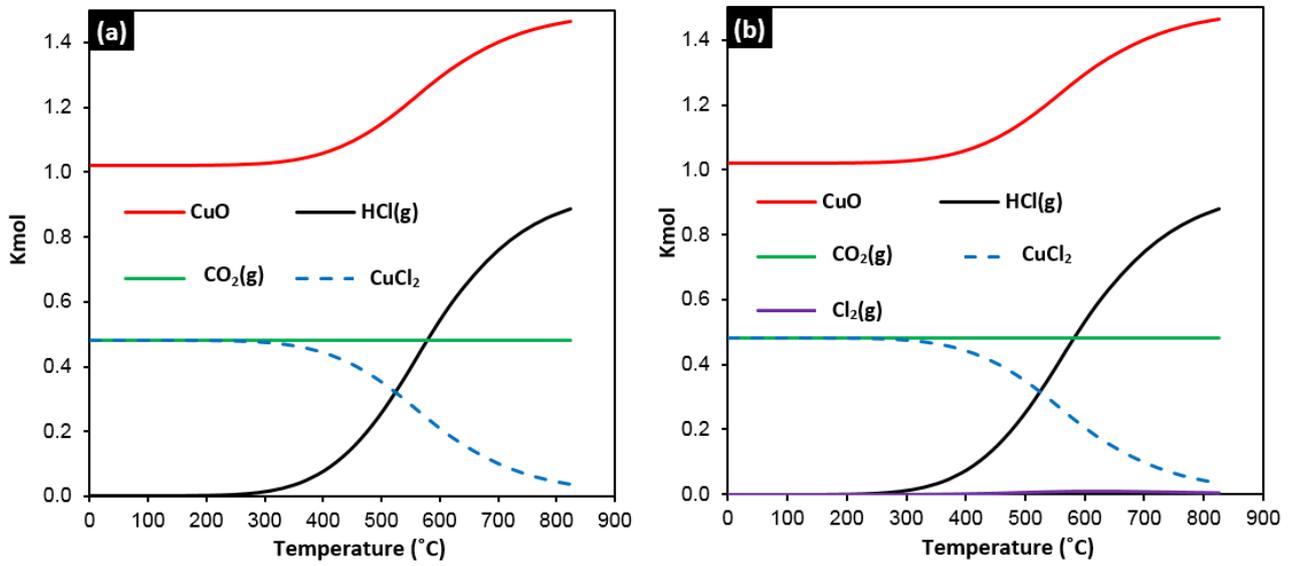


Fig. 3. Results of thermodynamic modelling for 30% CuO in the presence of water in the input (Cases 1 and 2; Table 1) a) without Cl₂ in the output and b) with Cl₂ in the output.

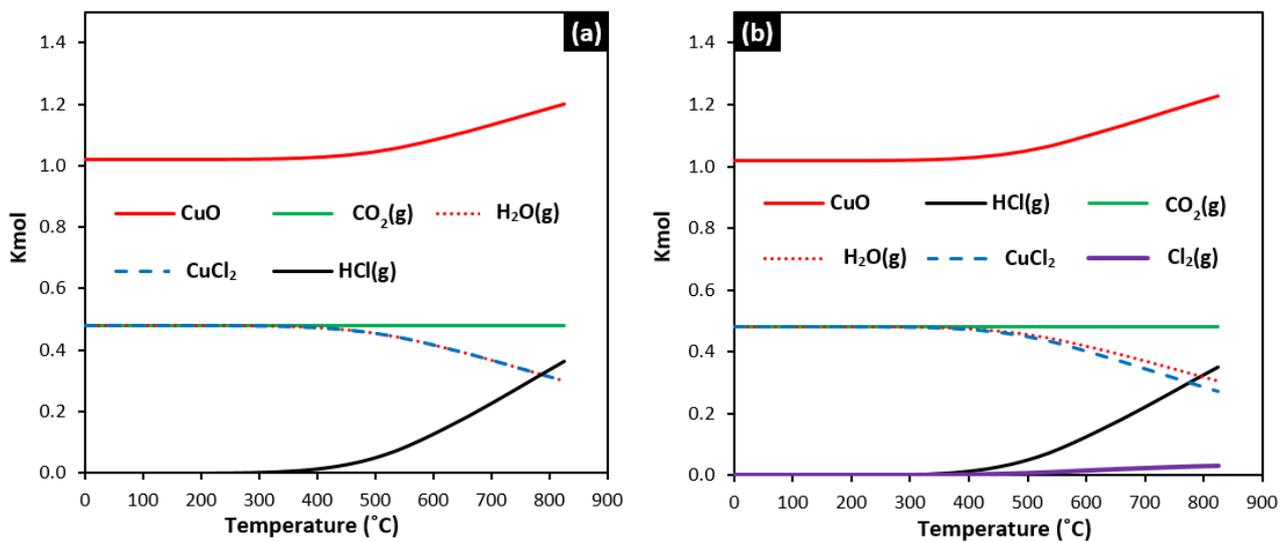


Fig. 4. Results of thermodynamic modelling for 30%CuO in the absence of water in the input (Cases 4 and 5; Table 1) a) without Cl₂ in the output and b) with Cl₂ in the output.

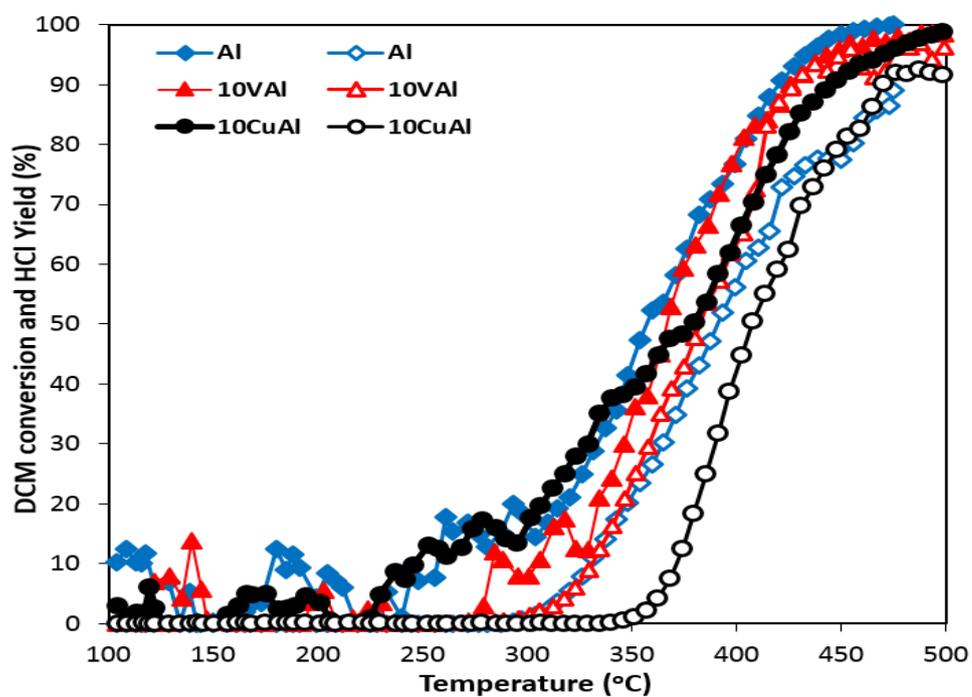


Fig. 5. Light-off curves of DCM over the different catalysts (catalyst mass 400 mg, DCM 500 ppm, H₂O 1.5 vol-%, 1 l min⁻¹, GHSV 143790 h⁻¹). Filled symbols are related to DCM conversion and open symbols indicate the yield of HCl.

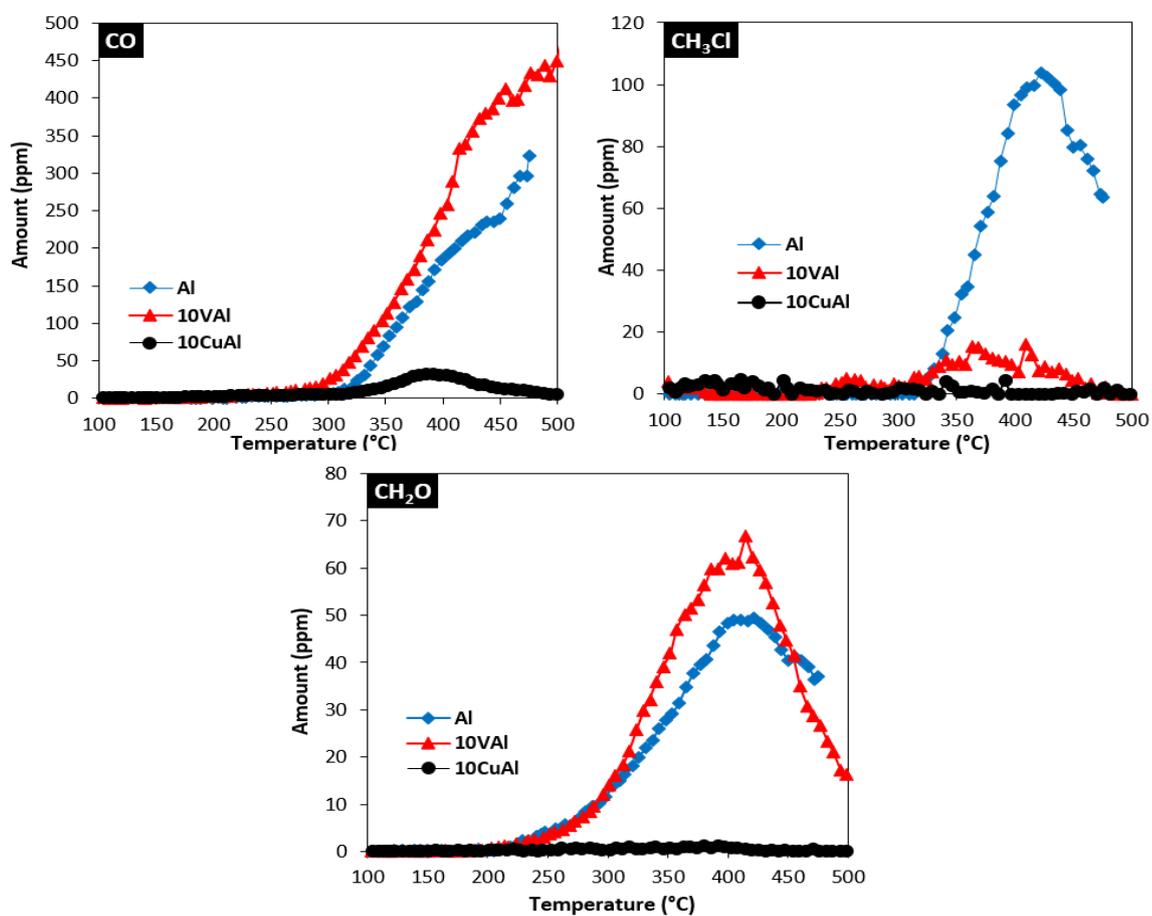


Fig. 6. Amount of major by-products over 10VAl, 10CuAl and Al₂O₃. The same experimental conditions were used as in Fig. 5.

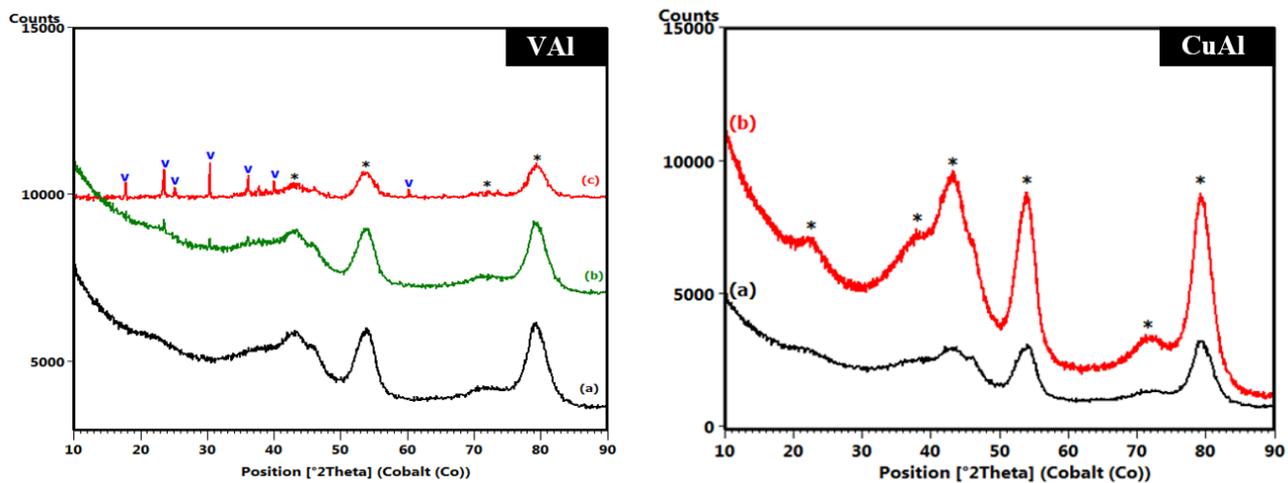


Fig. 7. XRD patterns of VAl catalysts: Al₂O₃ (a), 10VAl (b) and 30VAl (d) and CuAl catalysts: Al₂O₃ (a), 10CuAl (b).

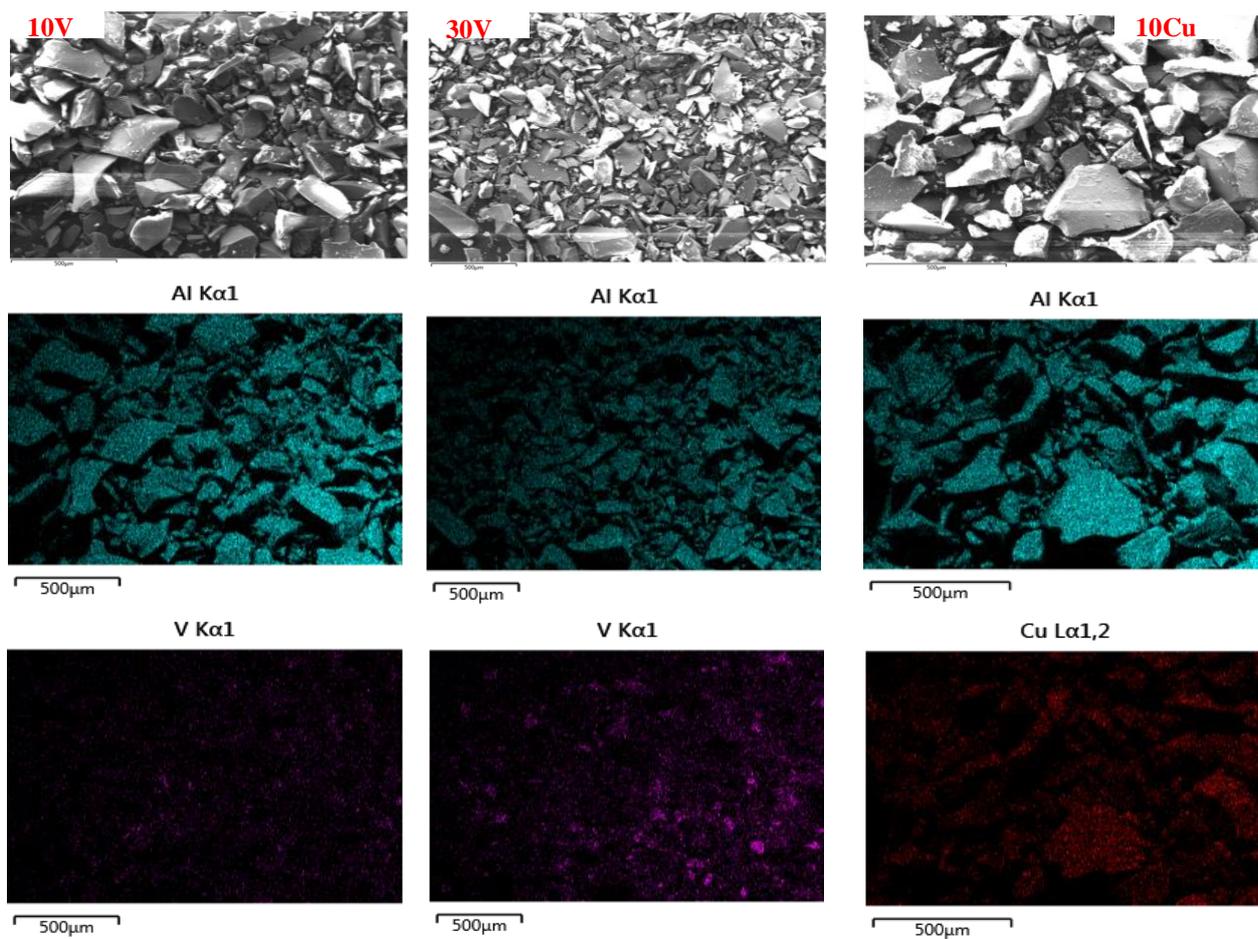


Fig. 8 EDS mapping of V- and Cu- containing catalysts. Images taken by FESEM.

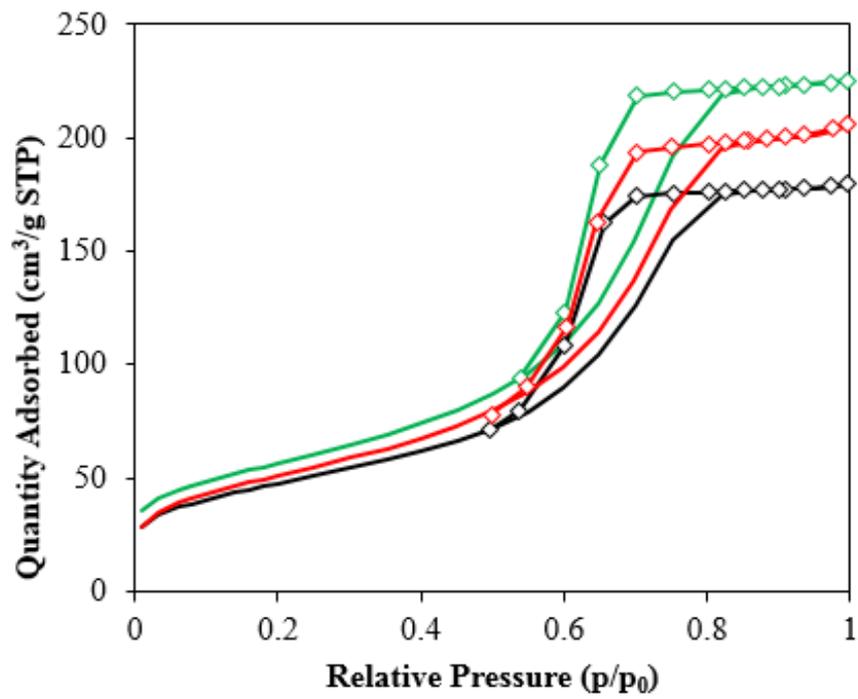


Fig. 9. Isotherm of N₂-physorption of different catalysts: green is 10VAI, black is 30VAI and red is 10CuAl, open symbols indicate desorption.

Table 1. Studied modelling cases and used molar amounts of the compounds, (+) indicates a situation where the compound is included in calculation and (-) means not included in the output.

Case	Input				Output							
	DCM	H ₂ O	O ₂	N ₂	HCl	CO ₂	CO	CH ₂ O	CH ₃ Cl	Cl ₂	H ₂ O	
1	0.48	15	200	784.52	+	+	-	-	-	-	+	
2	0.48	15	200	784.52	+	+	-	-	-	+	+	
3	0.48	15	200	784.52	+	+	+	+	+	+	+	
4	0.48	0	200	799.52	+	+	-	-	-	-	+	
5	0.48	0	200	799.52	+	+	-	-	-	+	+	
6	0.48	0	200	799.52	+	+	+	+	+	+	+	

Table 2. The amounts of different acid sites on γ -Al₂O₃ obtained by thermal desorption of pyridine and lutidine.

Acidity	Probe molecule	150 °C		200 °C		250 °C		300 °C		350 °C		400 °C	
		LAS	BAS										
Al ₂ O ₃ (μ mol g ⁻¹)	Pyridine	318	0	266	0	204	0	138	0	98	0	69	0
	Lutidine	40	13	31	6	23	3	13	0	8	0	5	0

Table 3. Physicochemical properties of the catalysts: S_{BET} is the specific surface area, D_p means pore size and am. means amorphous phase

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	D_p (nm)	Metal amount* (%)			Identified phases (XRD)
			ICP	XRF	EDS	
** Al_2O_3	255	6	-	-	-	$\gamma\text{-Al}_2\text{O}_3 + \text{am}$
10VAI	200	6.9	-	12	11	$\text{V}_2\text{O}_5 + \gamma\text{-Al}_2\text{O}_3 + \text{am}$
30VAI	169	6.6	-	27	30	$\text{V}_2\text{O}_5 + \gamma\text{-Al}_2\text{O}_3 + \text{am}$
10CuAl	184	6.9	-	10	12	$\gamma\text{-Al}_2\text{O}_3 + \text{am}$
*** Al_2O_3	338	5.6	-	-	-	$\gamma\text{-Al}_2\text{O}_3 + \text{am}$
30VAI	184	4.5	23	-	-	$\text{V}_2\text{O}_5 + \gamma\text{-Al}_2\text{O}_3 + \text{am}$
30CuAl	177	5.6	27	-	-	$\text{CuO} + \gamma\text{-Al}_2\text{O}_3 + \text{am}$
30MnAl	12	3.7	28	-	-	$\text{Na}_{0.7}\text{MnO}_{2.05} + \gamma\text{-Al}_2\text{O}_3 + \text{am}$

*Calculated based on MnO_2 , CuO , V_2O_5 oxides

** Adapted from our previous work [29]

*** Different set of preparation used with catalysts below

SUPPLEMENTARY INFORMATION

Catalytic oxidation of dichloromethane over transition metal catalysts: Thermodynamic Modelling and Experimental studies

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Preparation of the catalysts

Aluminium oxide (Al_2O_3) support was prepared by the sol-gel method. Aluminium-tri-sec-butoxide and ultrapure water were kept under stirring at 60°C for 60 min. Then, the mixture was hydrolysed by HCl to smooth the progress of the condensation process. Afterwards, temperature was increased to 80°C where the reaction was allowed to continue for 120 min. The white viscous sol was formed at the end of the stirring. The molar ratio of aluminium precursor, water and HCl, used during the preparation was 1:100:0.1, respectively.

The prepared support was dried on a sand bath at 60°C overnight followed by drying in a ventilated oven at 120°C in order to eliminate the solvent from the gel. The prepared material was then heated from room temperature to 500°C with 5°C min^{-1} as the heating rate and calcined at this temperature for 6 h to reach the wanted final oxide form of Al_2O_3 .

The calcined support (Al_2O_3) was wet impregnated by 30 wt-% of metal oxides (Mn, V and Cu). Sodium permanganate monohydrate ($\text{NaMnO}_4\cdot\text{H}_2\text{O}$, Sigma Aldrich, 99.9%), copper nitrate ($\text{Cu}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, Sigma Aldrich, 99.9%) and vanadium acetylacetonate ($\text{V}(\text{C}_{10}\text{H}_{14}\text{O}_5)$, Merck, > 98%) were the precursors used in catalyst preparations. In addition, 10 wt-% of V_2O_5 and 10 wt-% of CuO catalysts supported on alumina were also prepared. The required amount of support was immersed in the solution of dissolved precursor and kept under mechanical stirring overnight at room temperature. The thermal treatment was the same as used in the support treatment. The catalysts are later denoted as xCuAl for $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$, xVAl for $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and xMnAl meaning $\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$ where x is the loading of the impregnated phase.

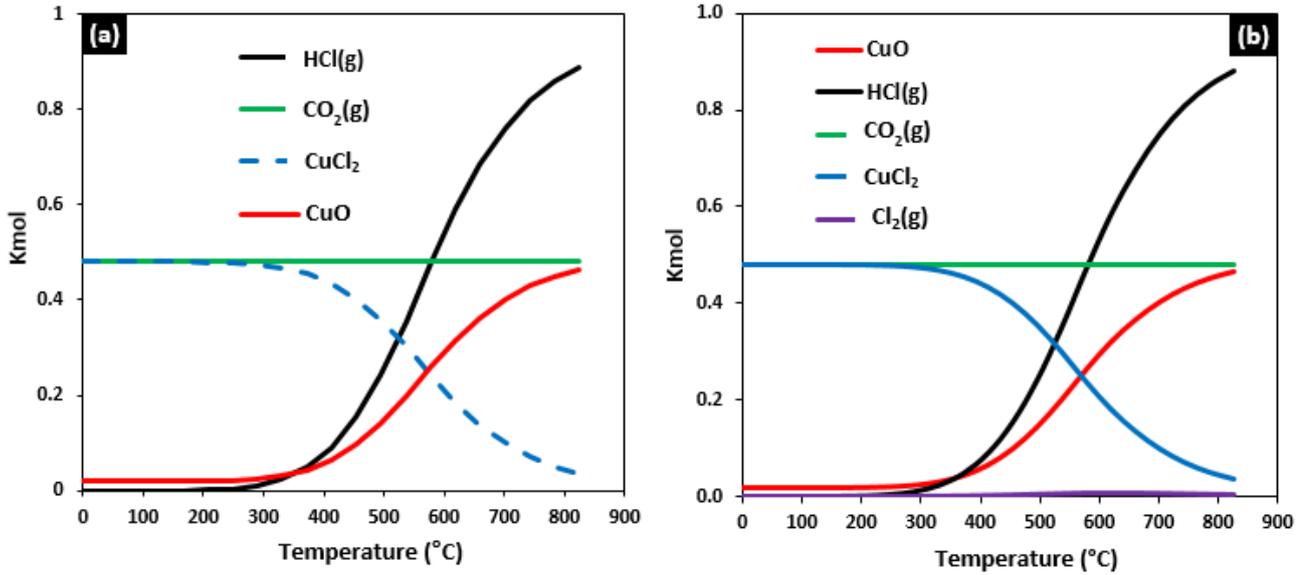


Fig. 1S. Results of thermodynamic modelling for 10%CuO in the presence of water in the input (Cases 1 and 2; Table 1) a) without Cl₂ in the output and b) with Cl₂ in the output

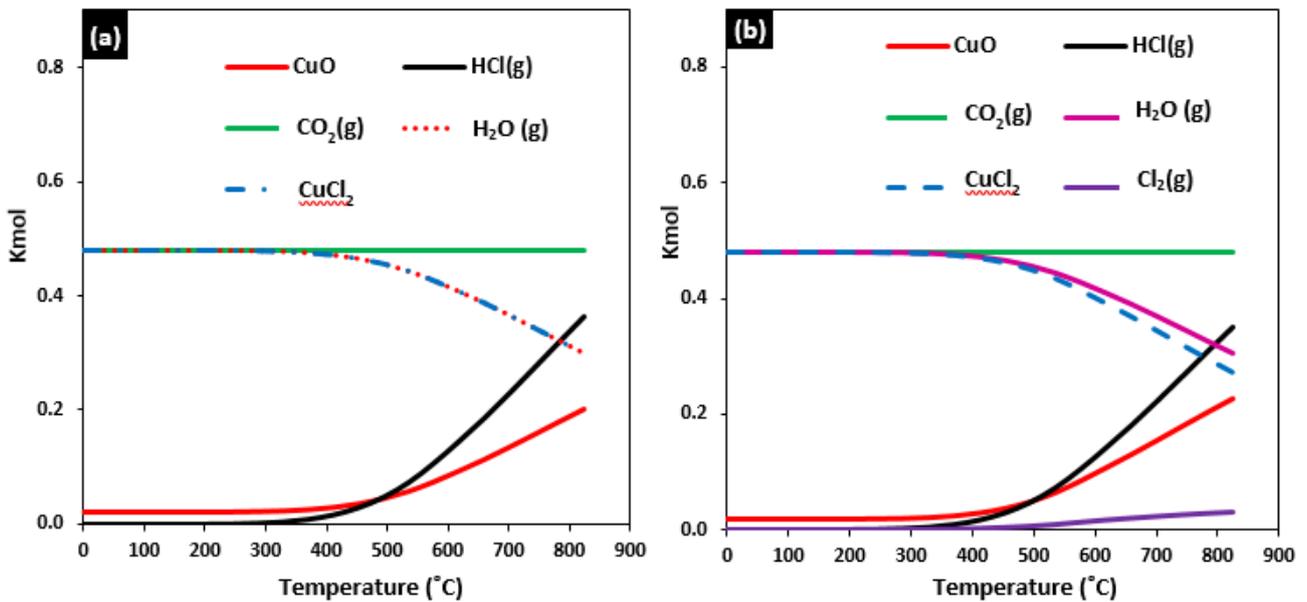


Fig. 2S. Results of thermodynamic modelling for 10%CuO in the absence of water in the input (Cases 4 and 5; Table 1) a) without Cl₂ in the output and b) with Cl₂ in the output

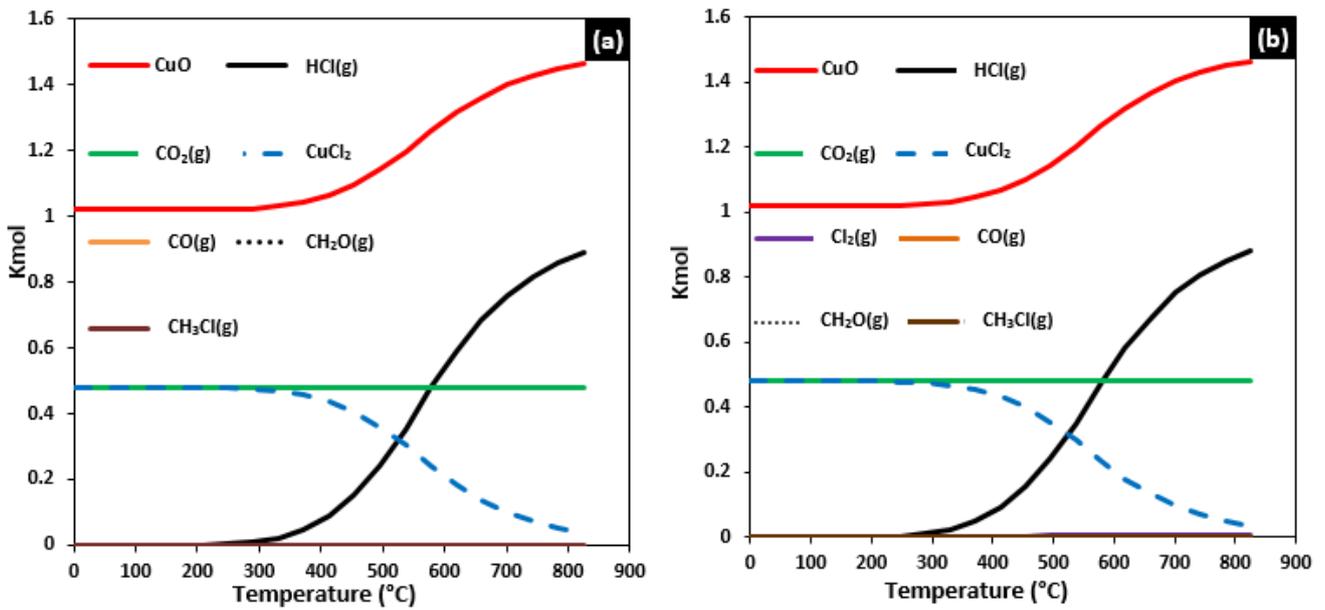


Fig. 3S. Results of thermodynamic modelling for 30%CuO in the presence of water in the input and by-products in output (Cases 3; Table 1) a) without Cl₂ in the output and b) with Cl₂ in the output.

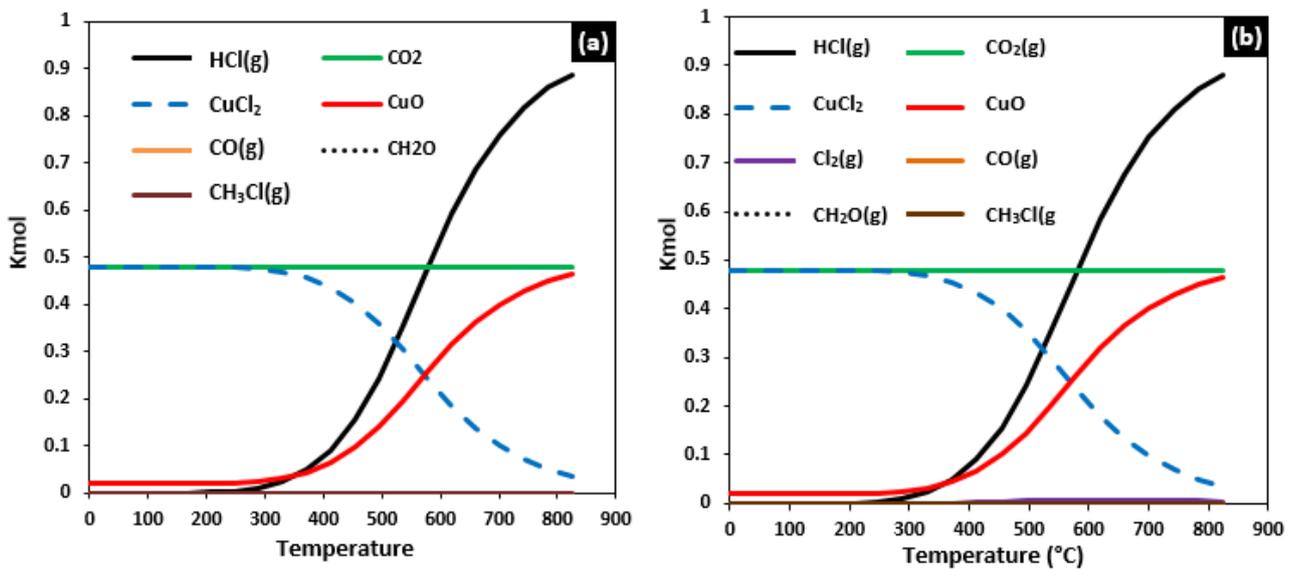


Fig. 4S. Results of thermodynamic modelling for 10%CuO in the presence of water in the input and by-products in output (Cases 3; Table 1) a) without Cl₂ in the output and b) with Cl₂ in the output.

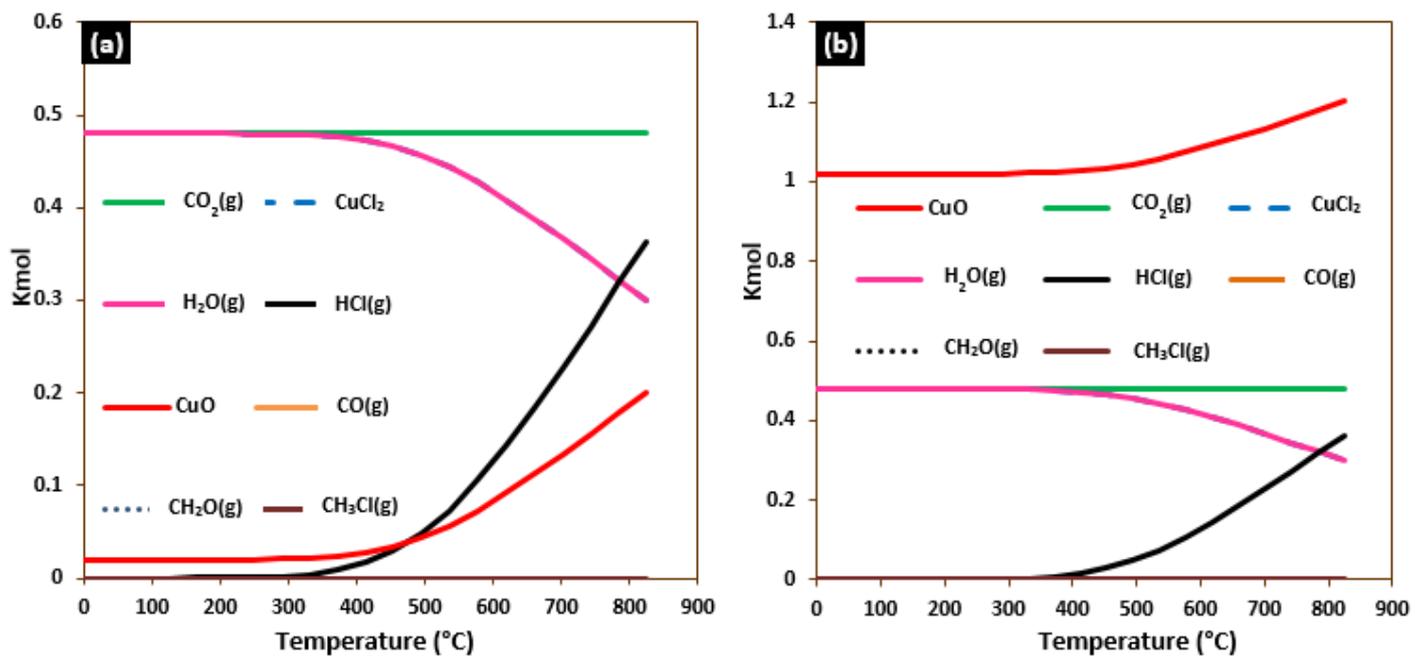


Fig. 5S. Results of thermodynamic modelling in the absence of water in the input and by-products in output (Cases 6; Table 1) a) 10% CuO, b) 30% CuO

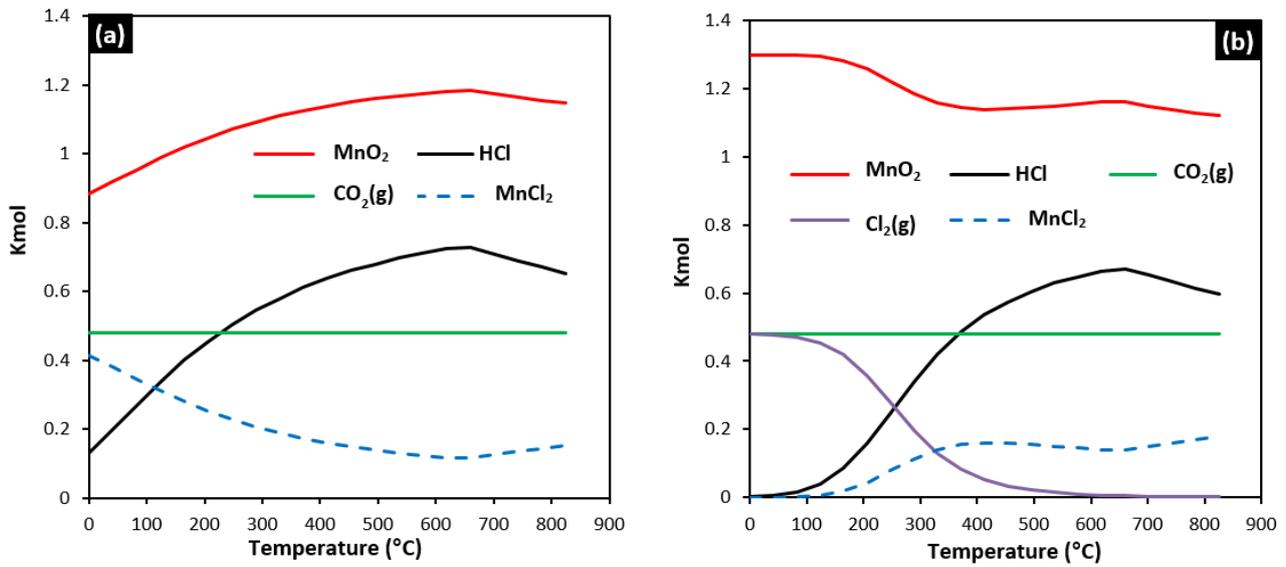


Fig. 6S. Results of thermodynamic modelling for 30% MnO_2 in the presence of water in the input (Cases 1 and 2 Table 1) a) without Cl_2 in output and b) with Cl_2 in output.

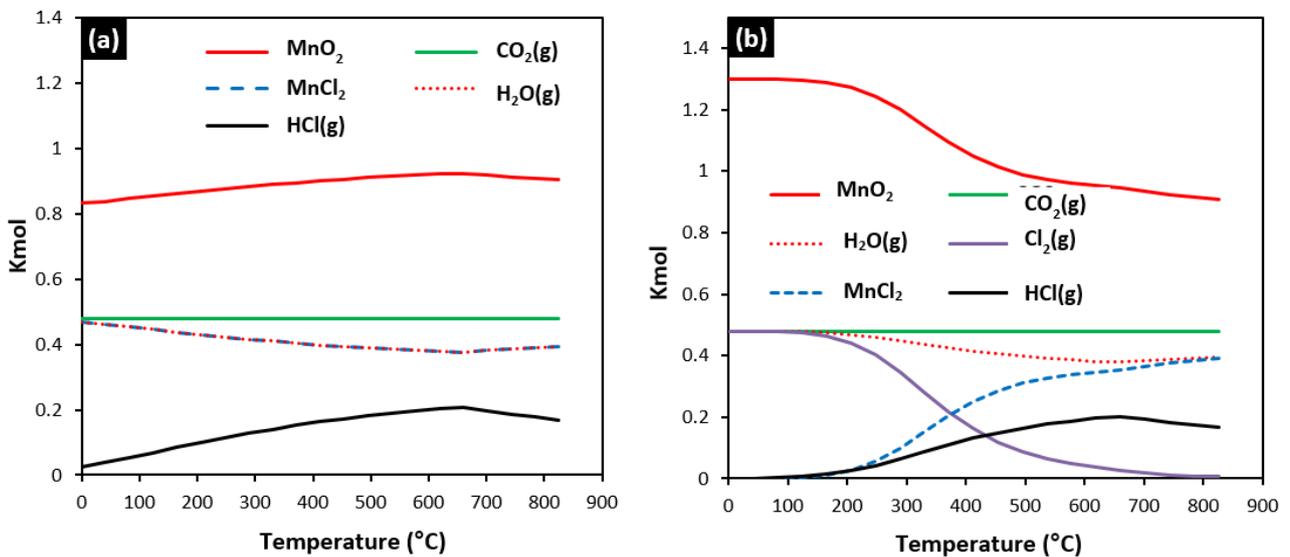


Fig. 7S. Results of thermodynamic modelling for 30% MnO_2 in the absence of water in the input (Cases 4 and 5; Table 1) a) without Cl_2 in output and b) with Cl_2 in output

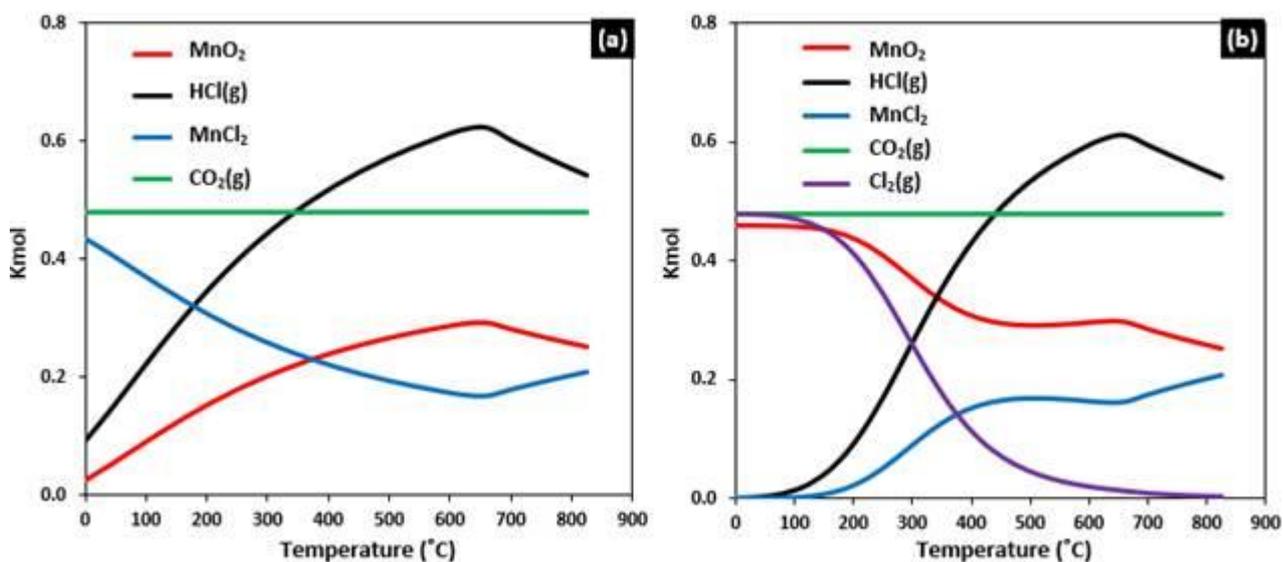


Fig. 8S. Results of thermodynamic modelling for 10% MnO₂ in the presence of water in the input (Cases 1 and 2

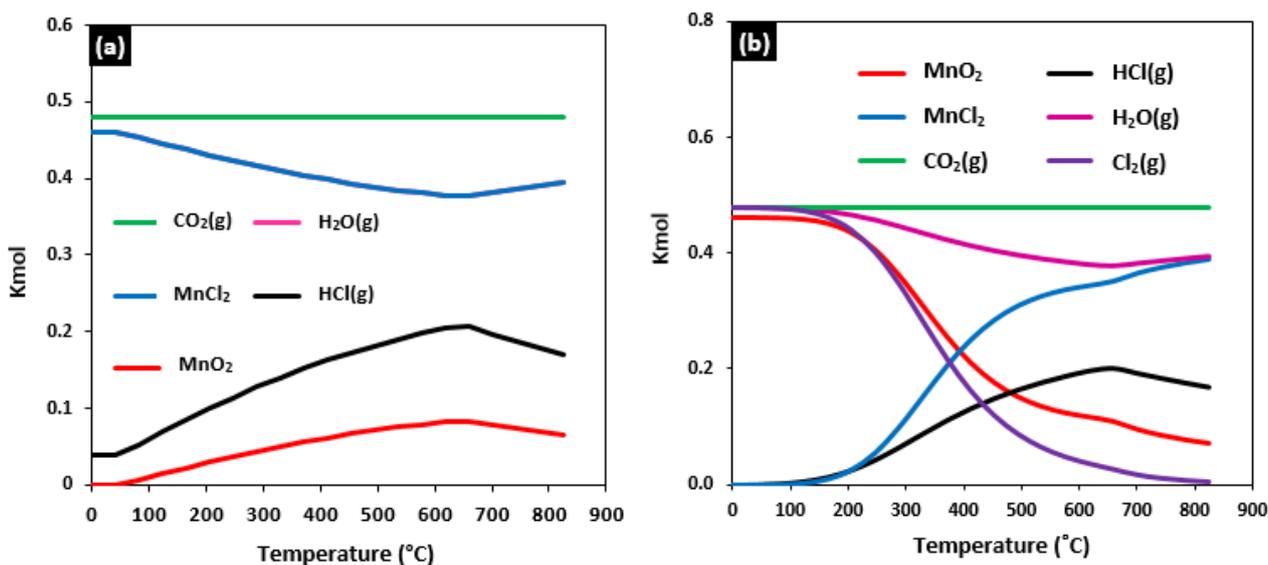


Table 1) a) without Cl₂ in output and b) with Cl₂ in output

Fig. 9S. Results of thermodynamic modelling for 10% MnO₂ in the absence of water in the input (Cases 1 and 2 Table

1) a) without Cl₂ in output and b) with Cl₂ in output

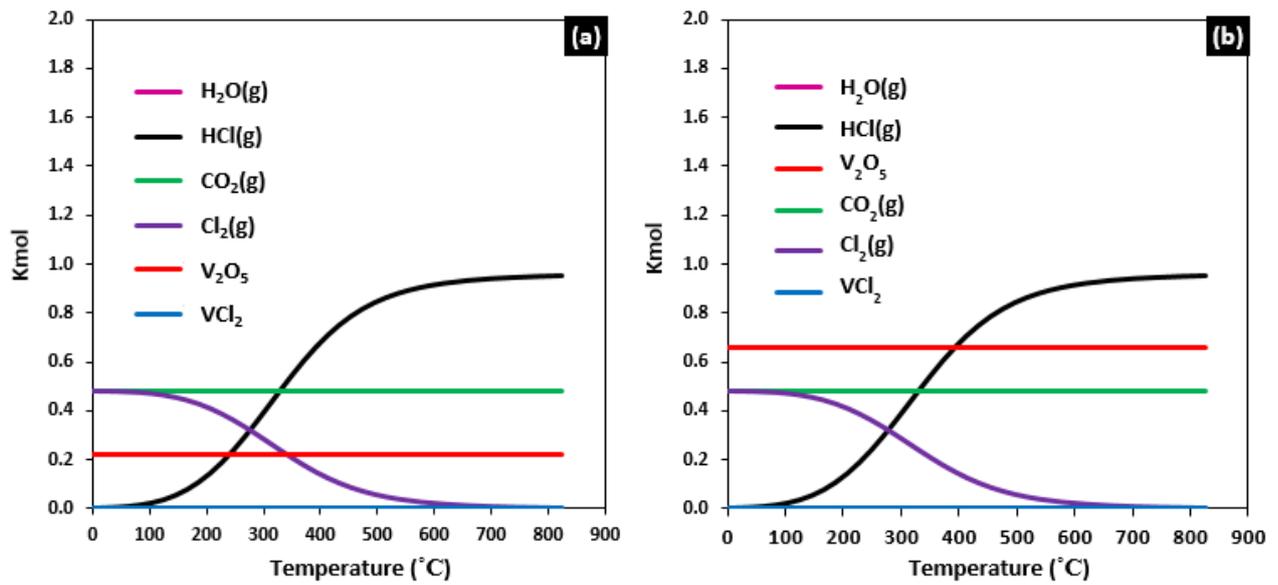


Fig. 10S. Results of thermodynamic modelling in the presence of water in the input and Cl_2 in output (Cases 2 Table

1) a) 10% V_2O_5 and b) 30% V_2O_5

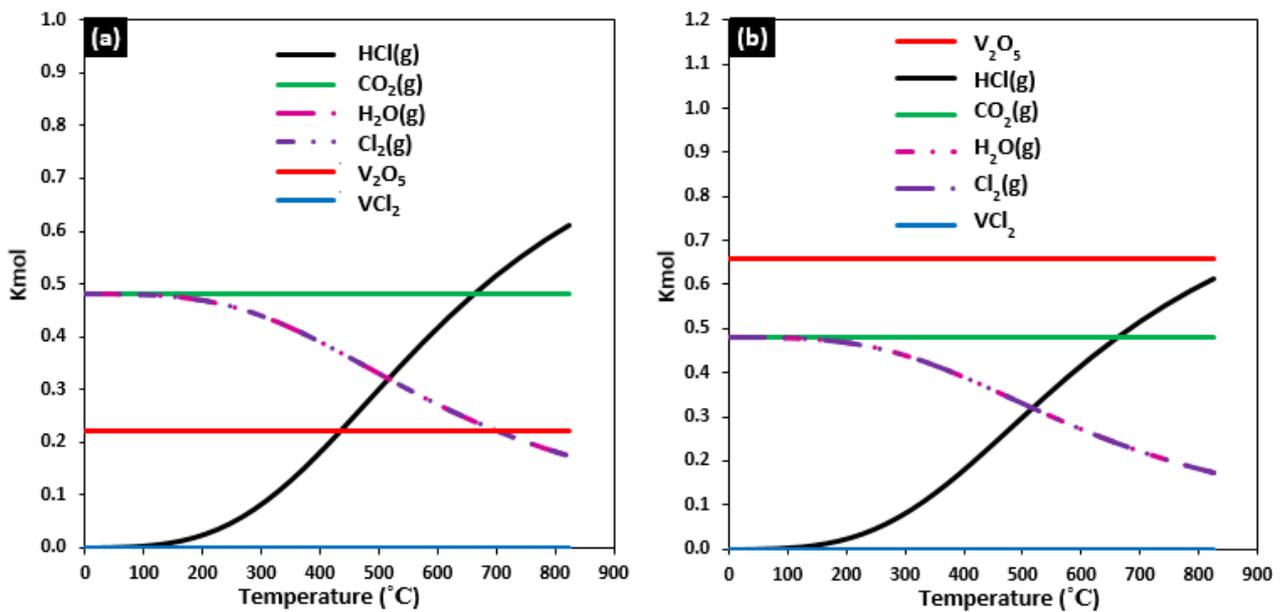


Fig. 11S. Results of thermodynamic modelling in the absence of water in the input and Cl_2 in output (Cases 2 Table

1) a) 10% V_2O_5 and b) 30% V_2O_5