

## Evaluation of $V_2O_5$ – $WO_3$ – $TiO_2$ and alternative SCR catalysts in the abatement of VOCs

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### Abstract

Two different commercial SCR catalysts belonging to the  $V_2O_5$ – $WO_3$ – $TiO_2$  system, and different alternative catalysts based on Mn, Fe, Cr, Al and Ti oxides have been tested in the conversion of VOCs in excess oxygen in a temperature range typical of the SCR process (500–700 K). Propane, propene, isopropanol, acetone, 2-chloropropane and 1,2-dichlorobenzene have been fed with excess oxygen and helium. The industrial catalysts are poorly active in the conversion of propane, giving mainly rise to propene by oxy-dehydrogenation. The conversion of propene is higher with CO as the predominant product. In any case, the oxidation activity depends on the vanadium content of the catalyst. Isopropanol is mainly converted into acetone and propene, while acetone is burnt predominantly to CO. Mn- and Fe- containing systems are definitely more active in the conversion of hydrocarbons and oxygenates, giving rise almost exclusively to  $CO_2$ . 2-Chloropropane is selectively dehydrochlorinated to propene and HCl starting from 350 K, propene being later burnt to CO on the industrial  $V_2O_5$ – $WO_3$ – $TiO_2$  catalysts, whose combustion activity is, apparently, not affected by chlorine. On the contrary, chlorine strongly affects the behavior of Mn-based catalysts, that are active in the dehydrochlorination of 2-chloropropane, but are simultaneously deactivated with respect to their combustion catalytic activity. The conversion of 1,2-dichlorobenzene gives rise to important amounts of heavy products in our experimental conditions with relatively high reactant concentration. ©1999 Elsevier Science B.V. All rights reserved.

**Keywords:** SCR catalysts; VOC;  $V_2O_5$ – $WO_3$ – $TiO_2$ ; Mn oxides; Chlorinated hydrocarbons

### 1. Introduction

The abatement of  $NO_x$  from waste gases from stationary sources is efficiently achieved with the SCR process, i.e. by reducing them with ammonia using monolithic catalysts [1,2]. Different variants of this process are applied to the emissions of different plants, such as oil, coal and natural gas power plants, ethylene

plants, nitric acid plants, stationary diesel engines, urban incinerators.

The industrial SCR catalysts are based on  $V_2O_5$ – $O_3(MoO_3)$ – $TiO_2$ , but they change significantly in composition and properties for different actual applications, in relation to the composition of the gas-phase effluents.

Gases from municipal solid waste incinerators [3,4] contain, besides  $NO_x$ , considerable amounts of many other pollutants, such as metal-containing

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Table 1  
Summary of catalyst characteristics

Notation	Composition		Origin	S (m <sup>2</sup> /g)
VWT1	V <sub>2</sub> O <sub>5</sub> –WO <sub>3</sub> /TiO <sub>2</sub>	0.5 : 9.9 : 89.6 wt/wt	commercial	70
VWT5	V <sub>2</sub> O <sub>5</sub> –WO <sub>3</sub> /TiO <sub>2</sub>	3.7 : 9.2 : 87.0 wt/wt	commercial	47
M1	Mn <sub>3</sub> O <sub>4</sub>		precipitation	12
M2	Mn <sub>2</sub> O <sub>3</sub>		precipitation	11
MF	Mn <sub>2</sub> O <sub>3</sub> –Fe <sub>2</sub> O <sub>3</sub>	entire range	coprecipitation	8–11
MA	Mn <sub>3</sub> O <sub>4</sub> –Al <sub>2</sub> O <sub>3</sub>	entire range	coprecipitation	20–200
MT	Mn <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	0–9.5% wt/wt Mn <sub>2</sub> O <sub>3</sub>	impregnation	77–84
MWA	Mn <sub>3</sub> O <sub>4</sub> –WO <sub>3</sub> /γ–Al <sub>2</sub> O <sub>3</sub>	10.5 : 30.5 : 59 wt/wt	impregnation	146
MFA	Mn <sub>3</sub> O <sub>4</sub> –Fe <sub>2</sub> O <sub>3</sub> –Al <sub>2</sub> O <sub>3</sub>	1 : 1 : 1 Mn : Fe : Al a.r. <sup>a</sup>	coprecipitation	20
FCA	Fe <sub>2</sub> O <sub>3</sub> –Cr <sub>2</sub> O <sub>3</sub> –Al <sub>2</sub> O <sub>3</sub>	1 : 1 : 1 Fe : Cr : Al a.r. <sup>a</sup>	coprecipitation	8

<sup>a</sup> Atomic ratio.

volatile inorganic compounds that can poison the SCR catalysts [5,6] and volatile organic compounds (VOC), namely hydrocarbons, oxygenates, nitrogen-containing compounds, chlorocarbons, etc.. Among these, it is possible to find variable amounts of polychloro-dibenzodioxins (PCDD), or simply ‘dioxins’) and polychloro-dibenzofurans (PCDF). On the other hand, the SCR reactors for incinerators work in the presence of oxygen, VOC and chlorine compounds in the temperature range of 520–620 K, which could result in the ‘de-novo’ synthesis of dioxins [4,7,8]. Producers of SCR catalysts and processes claim that ‘modified’ catalytic systems allow the simultaneous abatement of dioxins and NO<sub>x</sub> in the SCR reactors [9,10,11]. These materials are monoliths based on TiO<sub>2</sub> [12]. According to Jones and Ross [13] they should contain vanadia. However, detailed data on the actual composition and properties of such modified catalysts, to our knowledge, have not been described in the open literature. Combinations of conventional SCR catalysts with noble metal catalysts can also be used [14].

Similarly, the use of alternative low-price and low-quality fuels in power stations can cause the contact of the SCR catalysts with volatile organic and inorganic compounds, that must be also abated before waste-gases venting.

Several alternative catalysts formulations have been proposed in the open literature for the SCR process [15]. In particular, Mn oxide on alumina [16] and MnO<sub>x</sub>–WO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts [17] have been proposed as low-temperature SCR catalysts at least for application to SO<sub>2</sub>-free waste gases. Fe oxides and

Fe<sub>2</sub>O<sub>3</sub>–Cr<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts have also been the object of several previous investigations [18,19].

The present paper reports the evaluation of two types of industrial V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub> SCR catalysts and of some alternative preparations (Table 1) active in SCR catalysis, in the conversion of different types of model VOCs.

## 2. Experimental

Catalytic tests were carried out at atmospheric pressure in a continuous fixed bed flow tubular glass reactor with an external co-axial tube filled with glass spheres to have a pre-heated homogeneous gas phase. 0.10 g of catalyst were loaded in form of fine powder (60–70 mesh) mechanically mixed with 0.4 g of inert, low surface-area, material (quartz) to avoid preferential gas flow paths and hot spots in the catalytic bed, whose total volume was ca 0.3 cm<sup>3</sup>.

The total gas flow varied from 100 to 370 ml/min and the feed composition changed from 0.1% to 2% of VOC in oxygen-containing helium. VOC/oxygen molar ratios in the feed were varied from 1 : 6 to 1 : 10.

The reactants and the reaction products were analysed using two on-line gas chromatographs (HP 5890). A six-port valve with a 0.5 cm<sup>3</sup> loop has been used for the gas sampling. Permanent gases (O<sub>2</sub>, CO and CO<sub>2</sub>) were separated using a 3-m Carbosieve S-II (Supelco) packed column (100–120 mesh) connected to a TCD detector. Other reaction products, as well as the organic reactant, were analysed employing a 50-m PLOT fused silica column with Al<sub>2</sub>O<sub>3</sub>/KCl as

stationary phase (Chromopack), connected to a FID detector. The detection of oxygenate compounds, possibly formed, had required a 50-m glass wide-bore VOCOL column (Supelco) that was connected to the FID detector instead of PLOT column. Occasionally, a GC-MS analysis of products has been performed using a HP GCD1800D instrument with an HP-VOC column.

In order to analyze HCl and Cl<sub>2</sub> the effluents were contacted with aqueous NaOH solution, later analyzed by titration. The production of Cl<sub>2</sub> (giving rise to NaClO by reacting with soda) was found always to be negligible. Blank experiments showed negligible reaction in the reactor filled with the quartz spheres only. The results will be presented as conversions (*C*) and selectivities (*S*), both calculated on molar bases.

### 3. Results and discussion

#### 3.1. Catalysts characterization

The VWT1 catalyst is a commercial catalyst with a typical composition for application to power plants DeNO<sub>x</sub>ing reactors. It has been the object of previous investigations [20,21]. The VWT5 catalyst is a typical commercial catalyst for application to the treatment of waste gases from urban incinerators. It has been investigated in the frame of the Eurocat SCR European Program [22]. In both cases, the TiO<sub>2</sub> support is in the form of anatase, and V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> are supported on it. M1, M2 and MF catalysts have been the object of a previous study [23]. M1 constitutes pure hausmannite (α-Mn<sub>3</sub>O<sub>4</sub>) while M2 constitutes pure bixbyite (α-Mn<sub>2</sub>O<sub>3</sub>). MF catalysts are mixtures of the two saturated solid solutions of bixbyite and haematite (α-Fe<sub>2</sub>O<sub>3</sub>). MT catalysts are obtained by impregnating Mn acetate over TiO<sub>2</sub>-anatase from Ti oxide, followed by calcination. The maximum Mn oxide loading (9.5% Mn<sub>2</sub>O<sub>3</sub> wt/wt) was calculated to correspond to the theoretical monolayer coverage of the support surface. The MWA catalyst contains MnWO<sub>4</sub> supported on alumina, according to XRD analysis. MA, MFA and FCA catalysts are polyphasic materials containing corundum-type and spinel-type phases. The preparation chemistry of FCA materials has been discussed elsewhere [24].

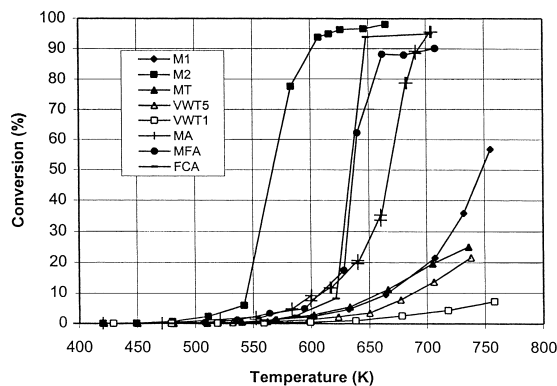


Fig. 1. Conversion of propane over different catalysts (see Table 1 for notation) (He:O<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> 87.75:11:1.25, total flow 350 ml/min).

#### 3.2. Oxidation of aliphatic hydrocarbons: propane and propene

In Fig. 1 the conversion of propane obtained on the commercial V–W–Ti catalysts is compared with that obtained with other SCR catalysts in the same conditions. The two commercial SCR catalysts are very poorly active in converting propane in the temperature range typical for the SCR process. The catalytic activity of the VWT5 catalyst is higher by far than that of VWT1, in agreement with the current idea that V is the active site for oxidation. Note that, here, we work in the absence of ammonia (as a first step in this research) which is usually recognized as an inhibiting agent for oxidation over oxide catalysts and that could also react with VOC molecules.

The supported ‘monolayer-type’ Mn–Ti catalyst is more active than both commercial SCR materials, and is nearly as active as the spinel type phase Mn<sub>3</sub>O<sub>4</sub> hausmannite. The Mn–Al, Mn–Al–Fe and Fe–Cr–Al catalysts are even more active than Mn<sub>3</sub>O<sub>4</sub>, but the sesquioxide Mn<sub>2</sub>O<sub>3</sub> bixbyite is the most active catalyst, allowing the total conversion of propane not far from 600 K, i.e. in the overall temperature window of the SCR process. As shown elsewhere [23], the presence of small amounts of iron oxide, as in MF catalysts, gives rise to a higher activity with respect to that on M2.

Comparing the product selectivities, it is possible to notice that the two Mn oxides, at total conversion of propane, give rise to a 100% selectivity to CO<sub>2</sub>,

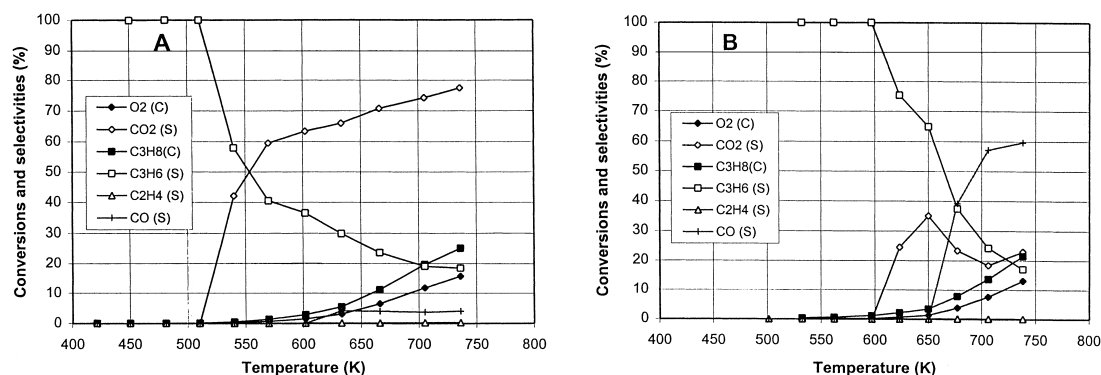


Fig. 2. Conversion of propane and selectivity to products on monolayer-type MT (A) and on VWT5 (B) (He : O<sub>2</sub> : C<sub>3</sub>H<sub>8</sub> 87.75 : 11 : 1.25, total flow 350 ml/min).

with propene and CO as additional products only when conversion is still incomplete. The other catalytic materials, in the same conditions, convert uncompletely propane and give rise to relevant amounts of propene and CO, together with CO<sub>2</sub>.

This difference is shown in Fig. 2, where the product selectivities obtained on Mn<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> and VWT5 are compared. On VWT5 the selectivity to propene is initially 100% and decreases progressively, while the selectivity to CO<sub>2</sub> increases. However, when conversion exceeds 5%, CO starts to be the predominant product. On Mn-Ti when conversion exceeds a few percents, CO<sub>2</sub> is, by and large, the main product. This behavior is parallel to that of the other Mn-containing catalysts, where CO<sub>2</sub> is selectively produced at total propane conversion. On the FCA catalyst propane is totally converted to CO<sub>2</sub> above 650 K.

The activity trend concerning propene oxidation is not exactly the same as previously observed from propane oxidation (Fig. 3). Again, the Mn-Ti catalyst shows similar activity to that of the VWT1 catalyst, but is definitely less active than the VWT5 catalyst. Mn-oxides and Mn-Al-based catalysts are definitely more active than VWT5. In all cases, the selectivity to CO + CO<sub>2</sub> approaches 100% in these conditions, although CO is produced in big amounts over both VWT catalysts, while CO<sub>2</sub> is almost exclusively formed in the other cases. Additionally, trace amounts of ethylene, methane and higher hydrocarbons and oxygenated compounds can be found over VWT catalysts. In particular, maleic and phthalic anhydride were observed as non-negligible products. The forma-

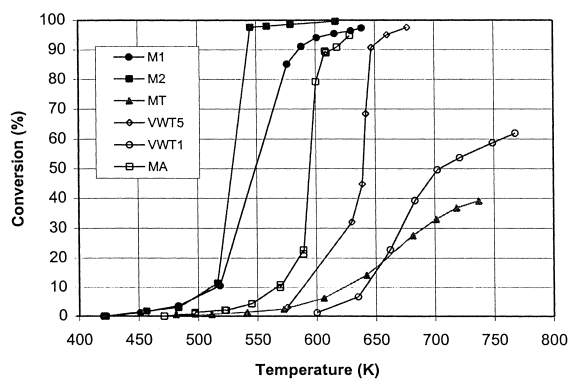


Fig. 3. Conversion of propene over different catalysts (see Table 1 for notation) (He : O<sub>2</sub> : C<sub>3</sub>H<sub>6</sub> 87.75 : 11 : 1.25, total flow 350 ml/min).

tion of these compounds (with 4 and 8 carbon atoms, respectively) provides evidence of the oligomerization of propene and the selective oxidation of oligomers. Studies performed with lower oxygen concentrations on supported vanadia catalysts allowed to detect several hydrocarbons, both aliphatic and aromatic, and oxygenates from propene. This behavior is likely to be associated with the Brønsted acidity detected over these catalysts [20,21,22] allowing the cationic oligomerization of olefins [25,26], and the well-known typical catalytic activity of vanadia-based catalysts in the selective oxidation of C<sub>4</sub>-C<sub>10</sub> hydrocarbons in producing maleic and phthalic anhydrides [27].

The better combustion of hydrocarbons on catalysts based on Mn and Fe oxides agrees with previous data that showed these oxides to be among the most active

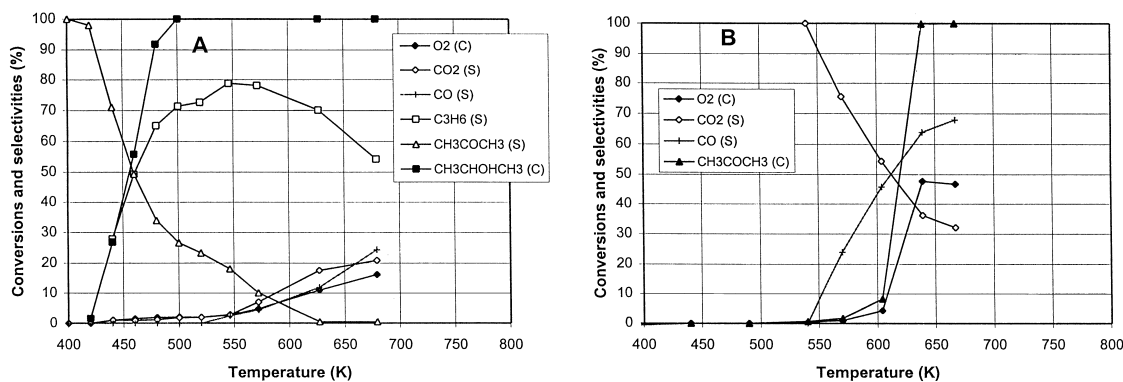


Fig. 4. Conversion of isopropanol (A) and of acetone (B) and selectivities to products over VWT1 (He:O<sub>2</sub>:C<sub>3</sub>H<sub>7</sub>OH or C<sub>3</sub>H<sub>6</sub>O88:10.3:1.7, total flow 350 ml/min).

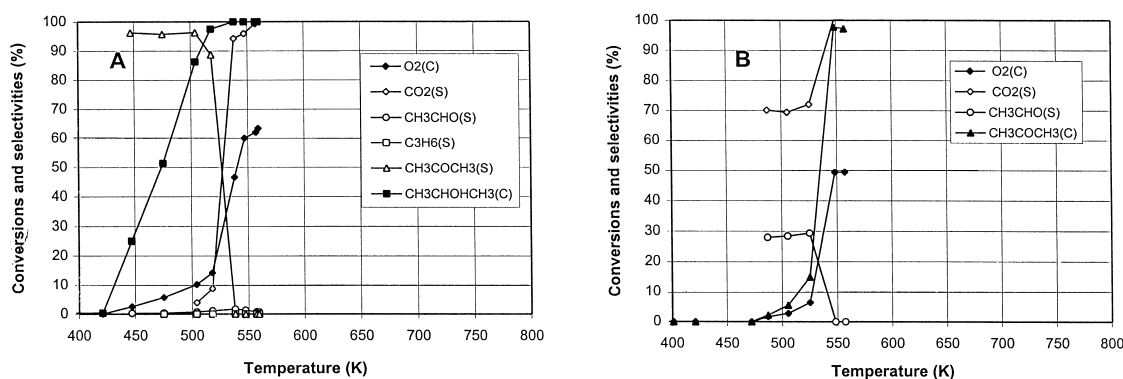


Fig. 5. Conversion of isopropanol (A) and of acetone (B) and selectivities to products over M1 (He:O<sub>2</sub>:C<sub>3</sub>H<sub>7</sub>OH or C<sub>3</sub>H<sub>6</sub>O88:10.3:1.7, total flow 350 ml/min).

base metal oxides for total oxidation of hydrocarbons [28] and for the oxidation of CO to CO<sub>2</sub> [29].

### 3.3. Oxidation of oxygenated aliphatic compounds: 2-propanol and acetone

The behavior of the VWT1 catalyst upon conversion of 2-propanol and of acetone is described in Fig. 4. It is evident that the selective oxy-dehydrogenation of 2-propanol to acetone at low temperature and its dehydration to propene at higher temperature are observed as the predominant reactions. This agrees with the high activity and selectivity reported for V<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub> catalysts in converting isopropanol to acetone [30], to the very high acidity of WO<sub>3</sub> [31,32] and WO<sub>3</sub>–TiO<sub>2</sub> [33] and to their ability to convert isopropanol into propene at very low temperature [30,31]. Combustion to CO

and CO<sub>2</sub> (nearly 1 : 1 product ratio) starts very late and is still very small at 680 K. Additionally, small but not negligible amounts of acetaldehyde are observed in the effluent from the reactor. The combustion activity is only in part improved on VWT5 catalyst.

On the contrary, total conversion of acetone is obtained on the same catalyst at 650 K giving rise to CO and CO<sub>2</sub> (nearly 65 : 35 product ratio). Again, it is possible to observe very small amounts of acetaldehyde. The only partial combustion of isopropanol corresponds to the faster dehydration of the alcohol with respect to its oxy-dehydrogenation, and to the limited conversion of propene in this temperature range, as shown above.

Mn-based catalysts behave differently, as shown in Figs. 5 and 6. On both, Mn<sub>3</sub>O<sub>4</sub> (Fig. 5(A)) and the monolayer-type MnO<sub>x</sub>–TiO<sub>2</sub> (Fig. 6(B)) the

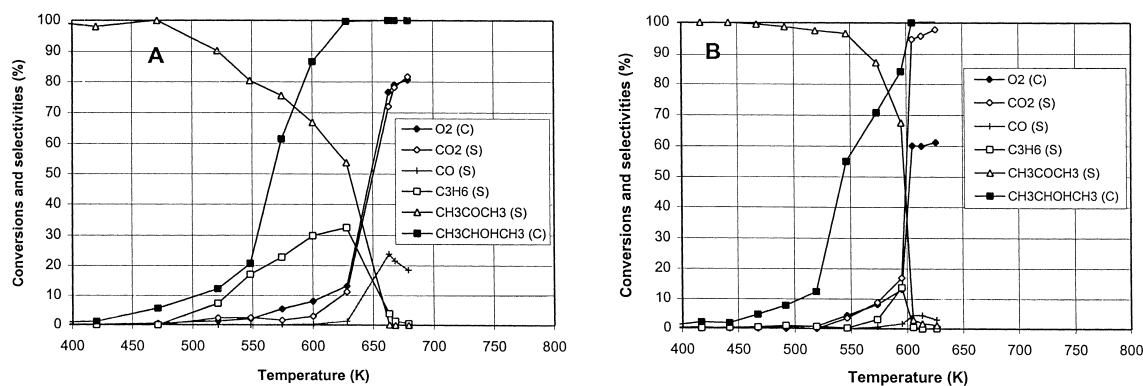


Fig. 6. Conversion of isopropanol and selectivities to products over 2.4%MT (A) and 9.5%MT (B) ( $He:O_2:C_3H_7OH$  88:10.3:1.7, total flow 350 ml/min).

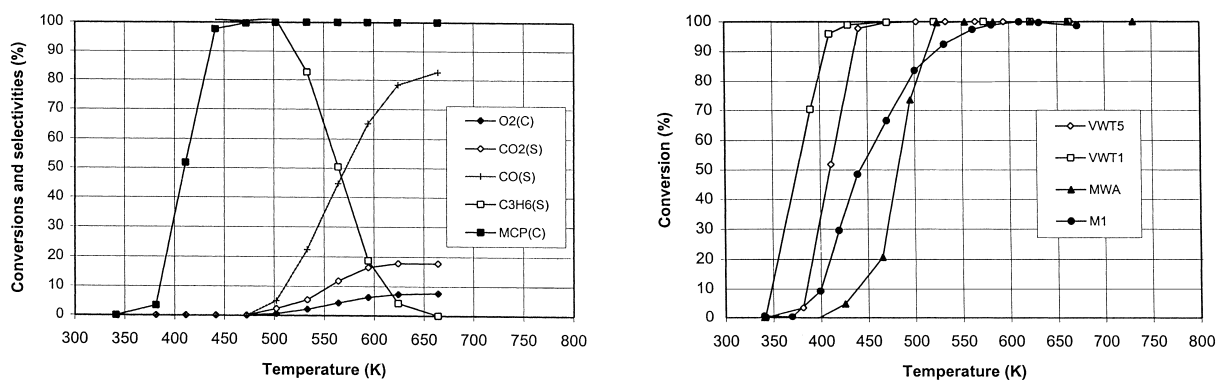


Fig. 7. Conversion of 2-chloropropane and selectivities to products over VWT5 ( $He:O_2:C_3H_7Cl$  94.9:5:0.1, total flow 370 ml/min).

Fig. 8. Conversion of 2-chloropropane over different catalysts (see Table 1 for notation) ( $He:O_2:C_3H_7Cl$  94.9:5:0.1, total flow 370 ml/min).

dehydration and the partial oxidation of 2-propanol occur significantly only at low temperatures, where conversion is still incomplete. Above 530 K (for M1) or 600 K (for MT) 2-propanol conversion approaches 100%, and  $CO_2$  is the only product. On sub-monolayer MT (Fig. 6(A)), the total conversion of the alcohol is shifted at higher temperatures and CO is formed in high amounts (near 20% selectivity).

### 3.4. Oxidation of chlorinated aliphatic compounds: 2-chloropropane

In Fig. 7 is described the behavior of the catalyst VWT5 in converting 2-chloropropane. The reactant is fully converted already at 440 K, but the only C-containing product in these conditions is

propene. Propene is converted later to CO (predominant) and  $CO_2$  starting from 500 K, total combustion being obtained starting from 650 K. The curve of propene produced by 2-chloropropane parallels perfectly that obtained by conversion of pure propene, as shown above. This fact shows that the combustion of 2-chloropropane is obtained through a sequence of dehydrochlorination to propene and HCl, followed by combustion of propene. Additionally, the data indicate that the HCl produced in the first step has no effect on the following propene burning step. The behavior on VWT1 is similar, but with higher conversion of chloropropane (Fig. 8) and lower selectivity to  $CO_x$ . This indicates that the dehydrochlorination activity is higher on VWT1 than on VWT5, while the propene

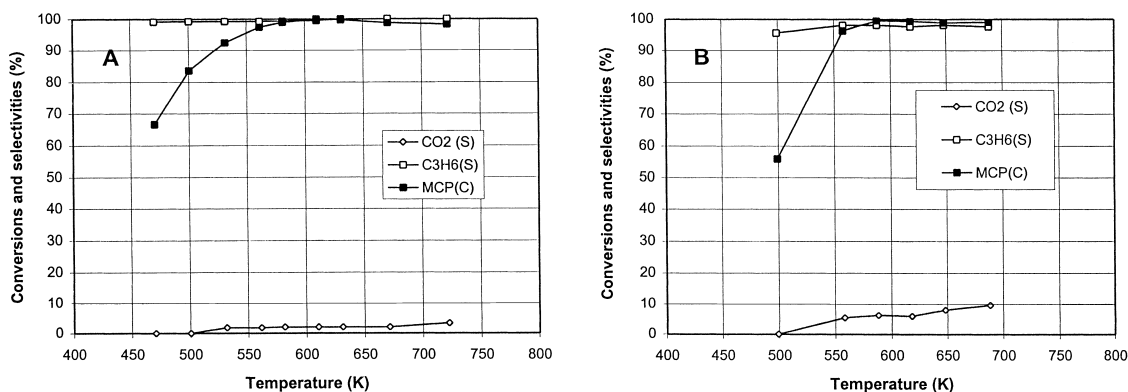


Fig. 9. Conversion of 2-chloropropane and selectivities to products over M1 without steam (A) and with steam (B) (He:O<sub>2</sub>:C<sub>3</sub>H<sub>7</sub>Cl 94.9:5:0.1, total flow 370 ml/min).

combustion activity is reversed, as shown above. The C balance is nearly fulfilled on both VWT1 and VWT5, although the GC-MS analysis shows the presence of trace amounts of heavier products, in particular, in the case of the VWT1 catalyst. Experiments performed co-feeding steam showed that steam has no significant effect on 2-chloropropane total oxidation on VWT catalysts. The data concerning conversion of 2-chloropropane are in good agreement with results reported by Jones and Ross [13] showing the conversion of ethylchloride on a commercial V–W–Ti catalyst in a similar temperature range. Surprisingly, however, these authors report about the complete combustion of ethylchloride in these conditions without formation of the dehydrochlorination product ethylene. These authors showed that an industrial catalyst is more active in converting ethylchloride than other supported vanadia catalysts [13].

Alternative catalysts are less active in converting 2-chloropropane than the commercial ones. (Fig. 8). 2-chloropropane is totally converted on Mn<sub>3</sub>O<sub>4</sub> (Fig. 9(A)) starting from above 600 K, but propene is the only product observed. This disagrees with the ability of Mn<sub>3</sub>O<sub>4</sub> to give rise to total oxidation of a propene feed in this temperature range, as shown above. This indicates that Mn<sub>3</sub>O<sub>4</sub> deactivates as a combustion catalyst upon chloroalkane conversion. This is reasonably due to the effect of HCl, produced during the dehydrochlorination step, in deactivating Mn oxide towards combustion catalysis. In this case, the addition of steam (Fig. 9(B)) in the feed causes a significant although small shift of the product selec-

tivities towards CO<sub>2</sub>. On the other hand, the catalyst during conversion of 2-chloropropane has been deactivated, as shown by its lack of activity when the fed hydrocarbon has been changed from chloropropane to propene: after the change of reactant, it has been impossible to obtain any significant conversion of propene. Only partial reactivation is obtained by feeding water vapor.

The MWA catalyst is apparently even less active than the M1 catalyst and also gives rise to dehydro-chlorination with high selectivity to propene. Heavier byproducts are certainly formed among which we could identify several aliphatic chloro- and polychloroolefins and acetylchloride.

### 3.5. Oxidation of chlorinated aromatic compounds: 1,2-dichlorobenzene

The conversion of 1,2-dichlorobenzene over VWT1 is much higher than over Mn oxide and MnWA catalysts (Fig. 10). The data for VWT1 agree with those reported, for similar catalysts, by Krishnamoorthy et al. [34]. The conversion takes place starting from near 400 K and is complete near 600 K. CO and CO<sub>2</sub> were the only C-containing light products observed, in agreement with the data of Krishnamoorthy et al. [34]. However, the carbon balance is largely unfulfilled. The product analysis shows that several heavy organics, both chlorinated and not, are produced and dark organic products were formed and observed immediately after the catalyst bed. We expect that

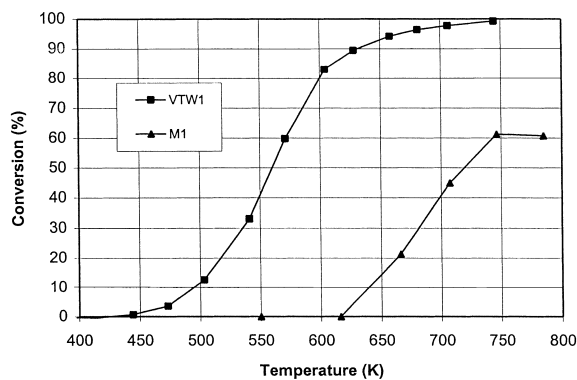


Fig. 10. Conversion of 1,2-dichlorobenzene over different catalysts (see Table 1 for notation) (He:O<sub>2</sub>:C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> 94.95:5:0.05, total flow 360 ml/min).

dioxins could be formed among the products. The catalyst appears to be coked, already after short-period experiments at low temperatures.

Interestingly, several authors confirm that the conversion of polychlorobenzenes is, on VWT SCR catalysts, lower than that of PCDD which are also converted less efficiently than PCDF [35]. Chlorobenzenes are also converted less efficiently than phenols [36,37] on similar catalysts.

#### 4. Conclusions

The data reported above show that the commercial SCR catalyst intended for application to power plants waste gases, VWT1, is poorly active as combustion catalyst for aliphatic hydrocarbons and oxygenated compounds, in the conditions used here. In fact, in the temperature range typical for SCR reactors, it only partially converts such compounds. The combustion of these VOCs gives rise to CO/CO<sub>2</sub> mixture generally rich in CO. Additionally, over this catalyst the selective oxidation of alkanes to alkenes, of alcohols to carbonyl compounds, the possibility of performing acid-catalyzed oligomerization of olefins and the selective oxidation of the higher hydrocarbons thus produced to oxygenated compounds give rise to effluent gases containing several dangerous and toxic compounds (such as aldehydes and anhydrides), although in traces.

The commercial SCR catalyst intended for application to incineration plants waste gases, VWT5,

is definitely more active as combustion catalyst for aliphatic hydrocarbons and oxygenated compounds. This is certainly related to its higher concentration of vanadium, in agreement with the key role of the vanadium oxide as the active component in SCR catalysts [15] for oxidation catalysis.

Alternative catalytic materials, based on manganese and iron oxides, which have been found to be very active, even at low temperatures, for SCR (although being possibly less selective to N<sub>2</sub> in the SCR reaction and more sensitive to SO<sub>2</sub> contained in the flow gases) allow the destruction of hydrocarbons and oxygenates at very low temperatures and with the almost exclusive production of CO<sub>2</sub>.

The picture is very different, however, when taking into consideration the behavior towards chlorinated VOCs. In fact, Mn- and Fe-based oxides are evidently poisoned by chlorine, losing their ability to burn organic compounds. On the other hand, they convert into good dehydrochlorination catalysts giving rise to elimination of HCl from aliphatic chlorinated compounds. VWT catalysts are also good dehydrochlorination catalysts for chloropropane, although they do not appear to be deactivated as combustion catalysts by chlorine, at least at the time scale of the laboratory experiment conducted so far (few tenths of hours). The behavior of both kinds of catalysts towards 1,2-dichlorobenzene suggests that, at least at the concentrations used here (evidently much higher than those that can be found in waste gases) dangerous heavier organic compounds are formed at the catalyst surface and are released with the effluent.

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