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A study of the abatement of VOC over V_2O_5–WO_3–TiO_2 and alternative SCR catalysts

E. Finocchio[a], M. Baldi[b], G. Busca[a,*], C. Pistarino[a], G. Romezzano[a], F. Bregani[c], G.P. Toledo[c]

[a] Dipartimento di Ingegneria Chimica e di Processo, Università di Genova, P. le J.F. Kennedy, I-16129 Genova, Italy
[b] Dipartimento di Ingegneria Idraulica e Ambientale, Università, via Ferrata 1, I-27100 Pavia, Italy
[c] ENEL-SRI, PDM, via Reggio Emilia 39, I-20134 Segrate, Milano, Italy

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Abstract

The conversion of C3 organic compounds (propane, propene, 1- and 2-propanol, allyl alcohol, propanal, acrolein, acetone and 1- and 2-chloropropane) in the presence of excess oxygen has been investigated over two V–W–TiO_2 commercial SCR catalysts differing in the V content and over Mn–TiO_2 alternative SCR catalysts. V–W–Ti catalysts show poor activity in the oxidation of hydrocarbons and oxygenates and give significant amounts of partial oxidation products. Moreover they give rise to CO in excess of CO_2. The sample higher in V is more active. Mn–TiO_2 is definitely more active in oxidation of hydrocarbons and oxygenates, and produces, at total conversion, CO_2 as the only detectable product.

V–W–Ti catalysts are very active in dehydrochlorination of the two 2-chloropropane isomers and retain the same oxidation activity also in the presence of HCl. On the contrary, Mn-based catalysts in the presence of chlorocarbons convert into dehydrochlorination catalysts but lose their catalytic activity in oxidation. V–W–Ti catalysts can be used in Cl-containing atmospheres while Mn–TiO_2 can be proposed for DeNO$_x$ and VOC abatement in Cl-free atmospheres such as for diesel engine exhaust gas purification.

Keywords: VOC; SCR catalysts; V_2O_5–WO_3–TiO_2

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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 [1–3]. 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–WO_3 (MoO_3)–TiO_2 [4,5] 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 can contain, besides NO_x, considerable amounts of many other pollutants, such as metal-containing volatile inorganic compounds that can poison the SCR catalysts and volatile organic compounds (hydrocarbons, oxygenates, nitrogen-containing compounds, chlorocarbons, etc.). Among these, variable amounts of PCDD

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[*] Corresponding author. Fax: +39-010-3536028.
E-mail addresses: mbaldi@iol.it (M. Baldi), icibusca@csita.unige.it (G. Busca), toledo@alpha1.cram.enel.it (G.P. Toledo)

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(polychloro-dibenzodioxins, or simply “dioxins”) and PCDF (polychloro-dibenzofurans) can also be present. On the other hand, the SCR reactors for incinerators work in the presence of oxygen, VOC and chlorine compounds in the temperature range of 473–673 K which could result in the “de novo” synthesis of dioxins [6]. Producers of SCR catalysts and processes claim that “modified” catalytic systems allow the simultaneous abatement of dioxins and NO_x in the SCR reactors [7]. These materials are monoliths based on TiO_2. However, detailed data on the actual composition and properties of such modified catalysts, to our knowledge, have not been described in the open literature.

Another potential application of SCR catalysts is the purification of waste gases from stationary or mobile diesel engines, using urea as the source of ammonia [8]. In this case, the SCR catalyst can stay in contact with unburnt hydrocarbons and soot, and possibly oxygenated compounds. On the other hand, these waste gases are virtually chlorine-free but can contain significant amounts of sulphur compounds.

The present paper reports the evaluation of two industrial V–W–Ti SCR catalysts and of some alternative preparations active in SCR catalysis, in the conversion of different types of model volatile organic compounds, such as aliphatic hydrocarbons, oxygenates and chloroalkanes.

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 the catalyst was loaded in the 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^3.

The total gas flow varied from 300 to 350 ml min^{-1} (with a GHSV of 60.000 h^{-1} and more) 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 analyzed using two on-line gas chromatographs (HP 5890). A six-port valve with a 0.5 cm^3 loop was used for the gas sampling. Permanent gases (O_2, CO and CO_2) 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 analyzed employing a 50 m PLOT fused silica column with Al_2O_3/KCl as the stationary phase (Chromopack), connected to an FID detector. The detection of oxygenated compounds, possibly formed, required a 50 m glass wide-bore VOCOL column (Supelco), which was connected to the FID detector instead of the PLOT column. Occasionally a GC–MS analysis of products was performed using an HP GCD1800D instrument with an HP-VOC column.

To analyze HCl and Cl_2, the effluents were brought into contact with NaOH water solution, and then analyzed by titration. The production of Cl_2 (giving rise to NaClO by reacting with soda) was always found to be negligible. The chlorine balance was generally approximately fulfilled. 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

In Table 1 some characteristics of the catalysts investigated in the present study are reported. The

Table 1
Summary of catalyst characteristics

Notation	Composition		Origin	S (m^2/g)
VWT1	V_2O_5–WO_3/TiO_2	0.5:9.9:89.6 wt./wt.	Commercial	70
VWT5	V_2O_5–WO_3/TiO_2	3.7:9.2:87.0 wt./wt.	Commercial	47
MT	Mn_2O_3/TiO_2	0–9.5% wt./wt. Mn_2O_3	Impregnation	77–84

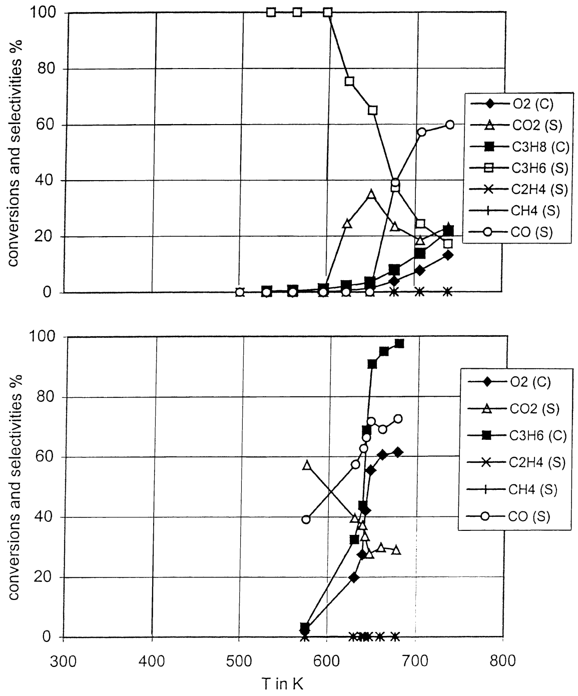

Fig. 1. Conversion (*C*) of propane (top) and propene (bottom) and selectivities (*S*) to products over VWT5 catalyst.

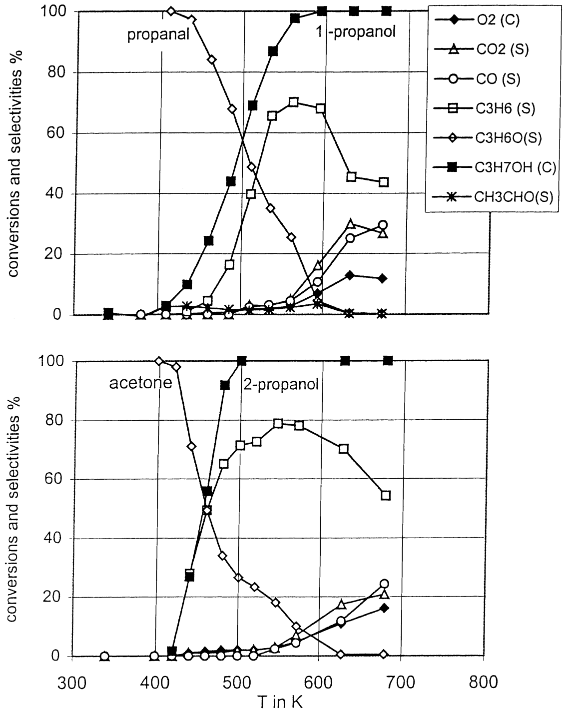

Fig. 2. Conversion (*C*) of 1-propanol (top) and 2-propanol (bottom) and selectivities (*S*) to products over VWT1 catalyst.

VWT1 catalyst is a commercial catalyst with a typical composition for application in power plants deNO$_x$ing reactors, which has been the object of previous investigations [9]. The VWT5 catalyst is a typical commercial catalyst for application in the treatment of waste gases from urban incinerators. It has been investigated in the frame of the Eurocat SCR European program [10]. In both cases the TiO_2 support is in the form of anatase, and V_2O_5 and WO_3 are supported on it. The typical temperature range for the SCR process over these catalysts is 523–673 K.

Fig. 1 shows the behavior of the VWT5 catalyst in the oxidation of propane and propene as model paraffin and olefin hydrocarbons. The conversion of propane is very limited in the typical temperature range of the SCR process, and propene is the main product, although the selectivity to it decreases in favor of CO_x with increasing temperature. On the contrary, propene is almost totally converted at the higher temperature side of the SCR temperature window, but is almost unconverted below 573 K. The oxidation of propene gives rise mostly to CO, with lower amounts of CO_2 and traces of oxygenated compounds. This shows that the industrial SCR catalysts, even those richer in vanadium oxide, are poor catalysts for the combustion of aliphatic hydrocarbons in the typical temperature range of the SCR process, and can give rise to even more poisonous products such as olefins from alkanes and oxygenated compounds.

Fig. 2 shows the behavior of VWT1 in the conversion of the two isomeric alcohols 1-propanol (top) and 2-propanol (bottom). Both the alcohols are totally converted at the higher temperature side of the SCR temperature range. However, the conversion of 2-propanol is definitely higher than that of 1-propanol at lower temperatures (above 450 K). On the other hand, the main product at the lowest conversions is the oxydehydrogenation product in both cases, i.e. acetone from 2-propanol and propanal from 1-propanol. At the highest conversion, instead, the main product is in both cases propene, produced by the acid-catalyzed dehydration. Propene is not completely oxidized on this low-V-content SCR catalyst, so that it is still the predominant product up to approximately 700 K. CO

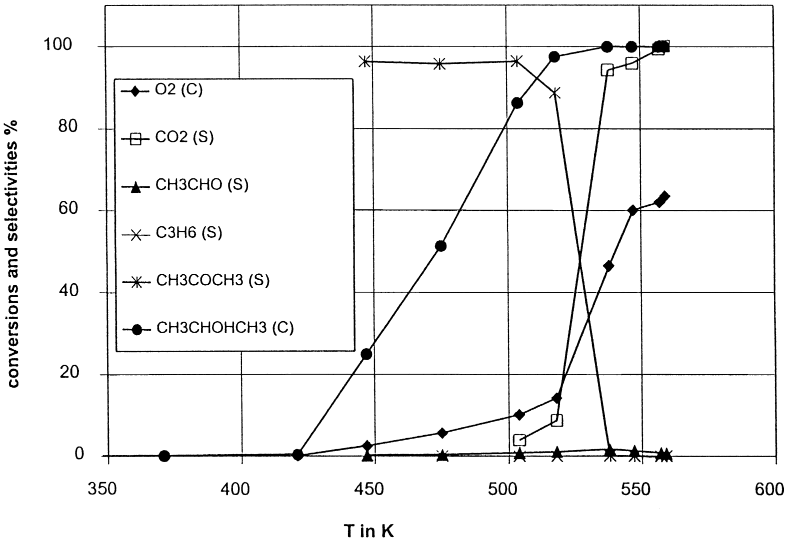

Fig. 3. Conversion (*C*) of 2-propanol and selectivities (*S*) to products over MT (9.5% Mn_2O_3) catalyst.

and CO_2 are produced in small but nearly equivalent amounts, but other oxygenated compounds such as acetaldehyde are also detected, even in relevant amounts.

As previously discussed [11], alternative Mn-based catalysts are more active than industrial V–W–Ti catalysts in oxidizing hydrocarbon and oxygenated compounds. Fig. 3 shows the behavior of an impregnated Mn–Ti catalyst in the conversion of 1-propanol. This material was found to act as an excellent SCR catalyst, particularly in the presence of water [12]. Actually this catalyst, which is only weakly acidic [13], converts 2-propanol less than the very acidic [4] VWT1 catalyst. However, over Mn–Ti catalyst, at total conversion, is obtained an almost total selec-

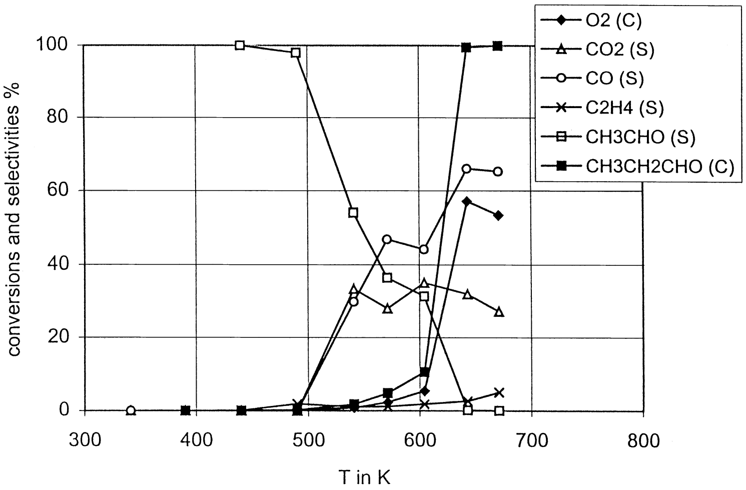

Fig. 4. Conversion (*C*) of propanal and selectivities (*S*) to products over VWT1 catalyst.

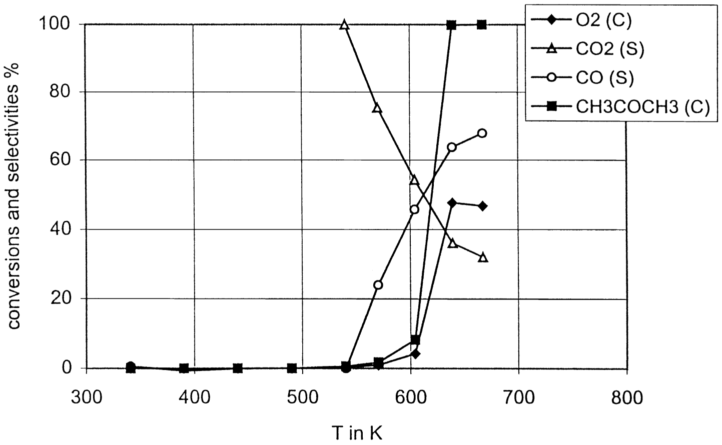

Fig. 5. Conversion (*C*) of acetone and selectivities (*S*) to products over VWT1 catalyst.

tivity to CO_2, acetone being produced as the main product only during incomplete conversion. This shows that Mn–Ti alternative SCR catalysts are more active in oxidation and more selective to CO_2 than V–W–Ti-based industrial SCR catalysts.

We have also investigated the conversion of the corresponding carbonyl compounds propanal (Fig. 4) and acetone (Fig. 5). Also, these compounds are totally converted almost exclusively to CO_x only at the higher temperature side of the SCR temperature range. CO is produced in bigger amounts than CO_2 and relevant amounts of ethylene are produced from propanal. Acetaldehyde is the main product of the conversion of propanal at low temperatures and is still produced in significant amounts up to near 650 K. On the contrary the oxidation of acetone gives CO_x as the only detectable products.

Figs. 6 and 7 show the behavior of the VWT1 catalyst in the oxidation of the unsaturated oxygenated compounds: allylic alcohol (Fig. 6) and acrolein (Fig. 7). The main conversion product from allyl alcohol at low temperature is, as expected, the oxydehydro-

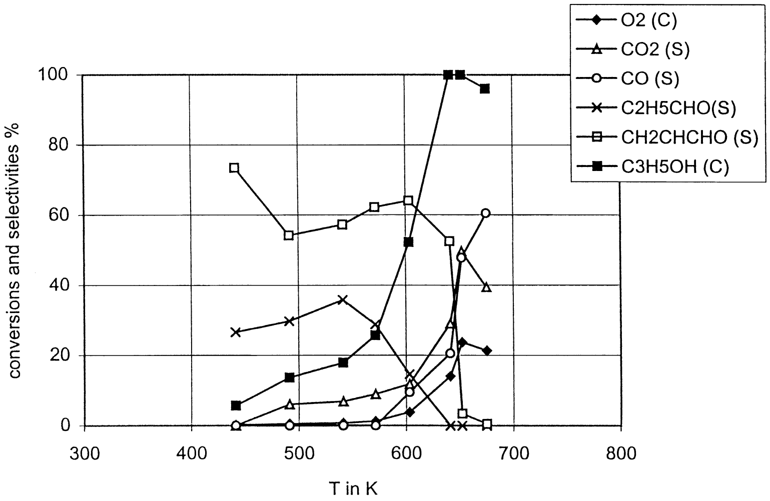

Fig. 6. Conversion (*C*) of allylic alcohol and selectivities (*S*) to products over VWT1 catalyst.

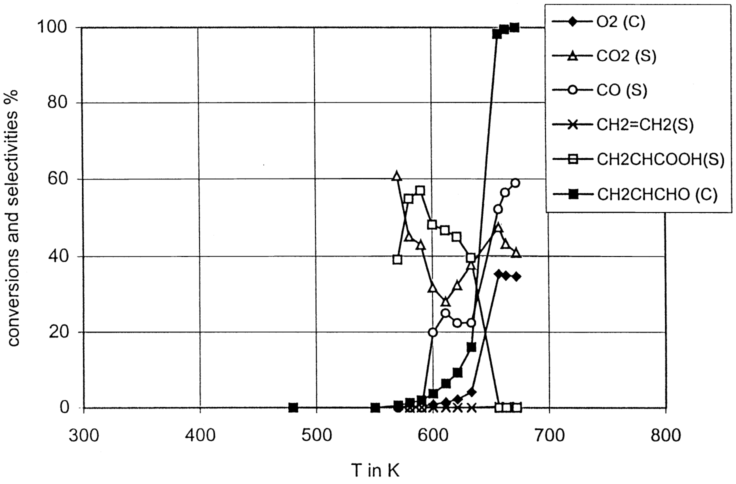

Fig. 7. Conversion (*C*) of acrolein and selectivities (*S*) to products over VWT1 catalyst.

genation product acrolein, but significant amounts of propanal (an isomer of allyl alcohol) are also observed. This unexpected reaction can arise from an internal redox mechanism, where the hydrogen produced by the conversion of the primary alcohol grouped to aldehyde hydrogenates the double bond. In any case, total conversion of allyl alcohol to CO_x is actually obtained just above 650 K. Acrolein (Fig. 7) is also burnt in this temperature range to CO_x (in both cases CO predominates), but acrylic acid is also a relevant product at the lower temperature side.

As previously reported, Mn-based catalysts are deactivated as combustion catalysts in the presence of chlorine, but their reactivity is partially recovered in the presence of water [11]. We have investigated the conversion of 1- and 2-chloropropane over the V–W–Ti industrial catalysts both in the presence and in the absence of water. Fig. 8 shows the behavior of the VWT5 catalyst in the conversion of both chloropropanes. The 2-chloropropane isomer is clearly converted more than the 1-chloropropane isomer at low temperature. In both cases the products are propene and HCl (not shown) at low temperature and CO_x+HCl at higher temperatures. No Cl_2 was found. Interestingly, the propene selectivity curves are nearly coincident in the two cases. This behavior can be interpreted assuming an E1 elimination mechanism giving rise to the more stable 2-propyl carbenium ion from the secondary chloropropane and

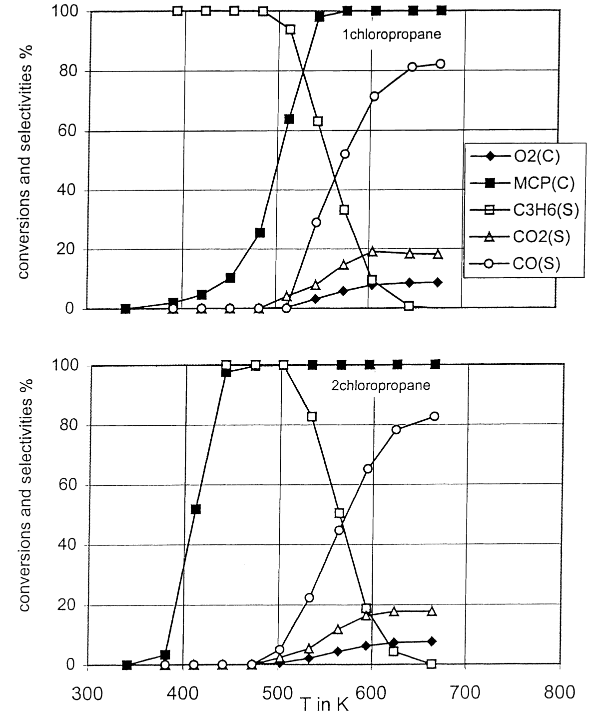

Fig. 8. Conversion (*C*) of 1-chloropropane (top) and 2-chloropropane (bottom) and selectivities (*S*) to products over VWT5 catalyst.

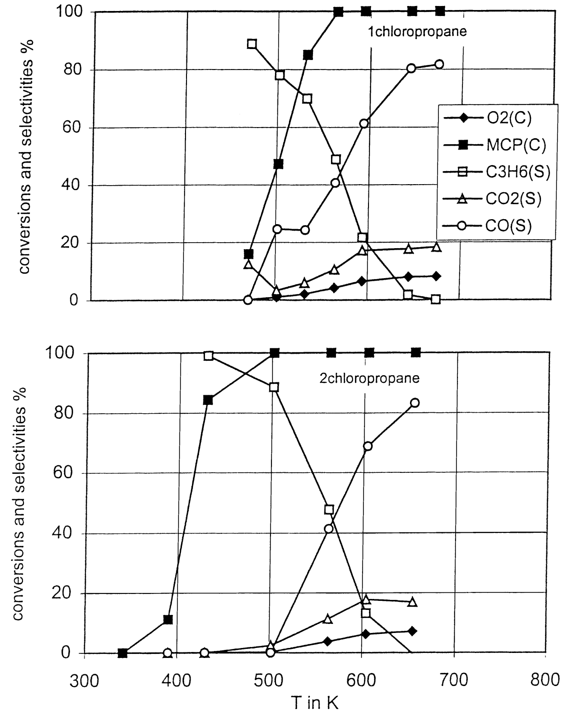

Fig. 9. Conversion (*C*) of 1-chloropropane (top) and 2-chloropropane (bottom) and selectivities (*S*) to products over VWT5 catalyst in the presence of water vapor.

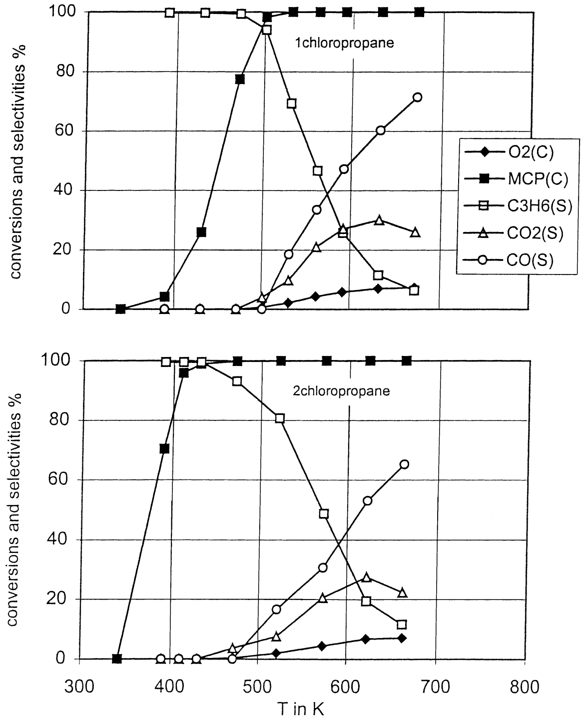

Fig. 10. Conversion (*C*) of 1-chloropropane (top) and 2-chloropropane (bottom) and selectivities (*S*) to products over VWT1 catalyst in presence of water vapor.

the less stable 1-propyl carbenium ion from the primary chloropropane. Thus, propene is formed faster from the secondary than from the primary halocarbon in the first acid-catalyzed step. The later step, i.e. the oxidation of propene, is the same in the two cases. On the other hand, the comparison between Figs. 1 and 8, where the conversion of propene over the same catalyst is reported, shows that the presence of HCl in the environment does not detectably perturb the oxidation catalytic activity of the catalyst, in contrast to what has been shown for Mn-based catalysts. Fig. 9 shows the results of the same experiment carried out in the presence of water vapor (0.2 vol.%/vol.). It seems evident that the effect of water vapor is very less if at all.

Fig. 10 shows the behavior of the low-vanadium content VWT1 catalyst in the same conditions (conversion of both chloropropanes in the presence of oxygen and water vapor). The behavior is qualitatively similar, but the first elimination step (dehydrochlorination of chloropropanes to propene+HCl) is clearly shifted to lower temperatures. This is likely to occur due to the more abundant acid sites present on this catalyst [4], characterized by stronger amounts of the acid component WO_3 with respect to V–W–Ti5 catalyst [10]. On the contrary, the successive conversion curves of propene to CO_x is shifted to higher temperatures, in agreement with the lower catalytic activity of this material for oxidation associated to the lower V content. This confirms that the first step is acid-catalyzed probably by the W oxide sites while the second one is an oxidation step involving the vanadium oxide sites.

It is worth mentioning that, in our reaction conditions (i.e. one tenth of the working hours), we did not find evidence of the loss of volatile vanadium chloride or oxychloride compounds from both vanadia-based catalysts. On the other hand, in our laboratory time scale, the catalytic activity appears to be stable. This contrasts with the behavior observed over Mn-based catalysts where the loss in the oxidative activity associated to the presence of chlorine is evident since the very beginning of each reactivity test.

4. Conclusions

The results reported here show that industrial V–W–Ti SCR catalysts are poorly active in converting hydrocarbons and oxygenates in the presence of oxygen, and give rise to significant amounts of partial oxidation products. Moreover, they produce relevant amounts of CO in oxidation reactions. However, they appear (after short-time experiments) to be very active in dehydrochlorination of chloroalkanes and to retain their oxidation catalytic activity in the presence of chlorine compounds. This is in agreement with the supposed V–W–Ti composition of catalysts claimed to allow the simultaneous abatement of NO_x, PCDD and PCDF in the SCR reactors applied to incineration plants. In any case, this suggests that these materials can be applied to Cl-containing waste gases. We have to, however, remark that, in our experimental conditions, we found relevant amounts of heavy products in the combustion of chlorobenzenes as reported previously [11].

On the other hand, our data show that Mn-based materials (in particular Mn–Ti oxides) have, in the presence of water, comparable or even better behavior than V–W–Ti catalysts in the SCR reaction [12]. These materials are also more active in burning hydrocarbons and oxygenates and give almost exclusively CO_2 at least in the 600–700 K temperature range. Thus, the Mn-based materials appear to be suitable choice for the simultaneous abatement of NO_x (with ammonia) and of non-chlorided VOC such as for application to diesel engine exhaust gases.

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