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Catalytic Combustion of Trichloroethylene over Pd-Doped Ti-Pillared Montmorillonites[*]

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Palladium (0.8 wt.%) was introduced onto Ti-pillared montmorillonite samples by means of incipient wetness technique either before or after calcination of the pillared matrix. Combustion of trichloroethylene (TCE) has been chosen to test the catalytic properties of clay catalysts in deep oxidation of chlorinated volatile organics. The results were referred to the performance of a commercial catalyst. Both materials based on pillared clays were more active than the reference sample. The clay sample doped after calcination was better of the two and gave complete combustion of TCE at temperature by 100 K lower than the commercial catalyst. This material showed also the highest selectivity to HCl at maximum TCE conversion. Further improvement of the clay catalyst performance in terms of the HCl yield and suppression of chlorine evolution was achieved by addition of the methanol vapour to the reaction mixture. The results are discussed in terms of textural and acidic properties of the investigated catalysts.

Key words: pillared clay, montmorillonite, catalytic combustion, chlorinated volatile organics

Chlorinated volatile organic compounds (CVOCs) constitute a major portion of the hazardous solvent wastes released into the environment by industry. Catalytic combustion is one of the most promising technologies to control their emission. The main requirement is the total conversion of chlorine, contained in the organic molecule, into HCl, and oxidation of the organic part into H_2O and CO_2. It has been argued that the catalytic combustion of chlorinated volatile organics requires both acid and redox centres. Indeed, the catalytic systems found active in this process include supported noble metals, bulk or supported transition metal oxides, transition metal doped zeolites, pillared clays or mesoporous silicas, as well as classical acid catalysts such as Al_2O_3, zeolites and TiO_2/SiO_2 [1–16]. The microporous catalysts designed for the present study combine the acidic properties of Ti-pillared montmorillonite and redox properties of the Pd dopant.

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[*] Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

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EXPERIMENTAL

Materials. The montmorillonite used in this study was the sodium form of the less than 2 μm particle-size fraction extracted by sedimentation from Milowice bentonite (Poland), referred to as Na-mt. The cation exchange capacity of the clay is 84 meq per 100 g. Titania pillared clay was prepared following the procedure described by Sterte [17]. Titanium polycations were obtained by partial hydrolysis of $TiCl_4$ (Fluka, pract). In a typical experiment 6.5 cm^3 of 6 M HCl was added to cm^3 of $TiCl_4$ (0.082 M). This mixture was further diluted to 100 cm^3 by slow addition of distilled water under constant stirring. The resulting solution was aged for 3 h prior to its use. It was added dropwise to the vigorously stirred aqueous suspension containing 4 g/dm^3 of Na-mt in the amount corresponding to 10 mmol Ti^{4+} per gram of clay. The resulting product was stirred for 3 h at room temperature and then washed free of Cl^-. The air-dried product is described as Ti-mt, and after additional calcination in air at 673 K as Ti-PILC. Palladium was introduced onto Ti-mt or Ti-PILC by means of incipient wetness technique using aqueous solution of $PdCl_2$ in the amount corresponding to 0.8 wt.%. After drying at room temperature and calcination at 773 K for 2 h the samples obtained by impregnation of Ti-mt and Ti-PILC supports were referred to as Pd-Ti-mt(773) and Pd-Ti-PILC(773), respectively.

Methods. Chemical analysis was carried out on a Perkin Elmer ICP AES Plasma 40 spectrometer, after dissolution of the samples in a microwave mineraliser. Specific surface areas were determined from nitrogen adsorption at 77 K, using a Micromeritics 2000V2.03 apparatus. Prior to the measurement the samples were outgassed at 200°C. XRD analyses were performed on oriented samples prepared by spreading of the clay suspension on a glass slide followed by drying at room temperature. The XRD patterns were obtained with a DRON-3 diffractometer using Ni-filtered CuKα radiation. Brønsted and Lewis acidities were determined by IR spectroscopy of the chemisorbed pyridine. The samples were pressed into self-supporting wafers of 5–10 mg/cm^2 thickness and placed in a high-temperature IR cell connected to a vacuum line. After outgassing at 673 K under dynamic vacuum 1.33×10^{-3} Pa the wafer was exposed to pyridine vapour at ambient temperature. The concentration of Lewis and Brønsted acid sites was determined from the intensity of 1450 cm^{-1} and 1545 cm^{-1} IR absorption band, respectively. Strength of the acid sites was expressed as $E/E_0\times 100\%$, where E_0 corresponds to IR absorbance of the relevant pyridine band after chemisorption, E to IR absorbance of the pyridine remaining in the sample after desorption at elevated temperature (573 K). The IR spectra were recorded at room temperature on a UR-20 double-beam spectrophotometer (Zeiss, Jena).

Catalysis. Catalytic reaction of trichloroethylene (TCE) combustion was carried out in a fix bed flow reactor, in the temperature range 523–773 K, at concentration of TCE in air 2 g/m^3 and GHSV 10000 h^{-1}. The catalyst volume was 0.5 cm^3, which corresponded to *ca.* 0.6 g. Chlorine-containing products, except HCl, were analysed by an on-line GC (SRI 86 10A) with DCQF column. In order to determine HCl, a known volume of the reaction gas was passed through water and the amount of absorbed HCl was determined from the conductivity of the solution. CO and CO_2 were analysed by Chrom-5 GC with TCD and two columns: molecular sieve 5A for CO and HayeSep R for CO_2. Conversion and selectivities were determined with the accuracy of ±1%. Catalytic results were referred to the performance of a commercial $Pd-Pt/Al_2O_3$ CVOC catalyst manufactured by "Katalizator" Ltd.

RESULTS AND DISCUSSION

The chemical composition of the catalysts and their specific surface areas are presented in Table 1. The data show that as a result of pillaring the composite contains *ca*. 40 wt.% of TiO_2. This is in good agreement with the previous reports on montmorillonites pillared with Ti oligomers according to the method of Sterte [17–19]. The amount of introduced palladium corresponds exactly to the nominal value. Although from the point of view of chemical composition the samples prepared by different methods do not differ in any meaningful way, the specific surface area of the Pd-Ti-mt(773) sample, which was not calcined prior to Pd deposition, is significantly lower than that of Pd-Ti-PILC(773) catalyst, onto which Pd was introduced after calcination of the pillared support. This suggests that the presence of Pd facilitates sintering processes occurring during dehydration/dehydroxylation of the Ti-mt material.

Table 1. Chemical composition and specific surface areas (S^{BET}) of Pd-doped Ti-pillared montmorillonite catalysts.

Sample	SiO_2 [wt.%]	Al_2O_3 [wt.%]	TiO_2 [wt.%]	Fe_2O_3 [wt.%]	MgO [wt.%]	Pd [wt.%]	S^{BET} [m^2/g]
Pd-(Ti)-PILC	34.8	11.5	41.0	2.1	2.0	0.8	195
Pd-Ti-PILC	35.4	11.8	40.0	1.9	1.9	0.8	266

Fig. la shows the XRD pattern of a typical Ti-mt material. The major reflection corresponds to the d_{001} basal spacing of *ca.* 26 Å, followed by the second order peak at

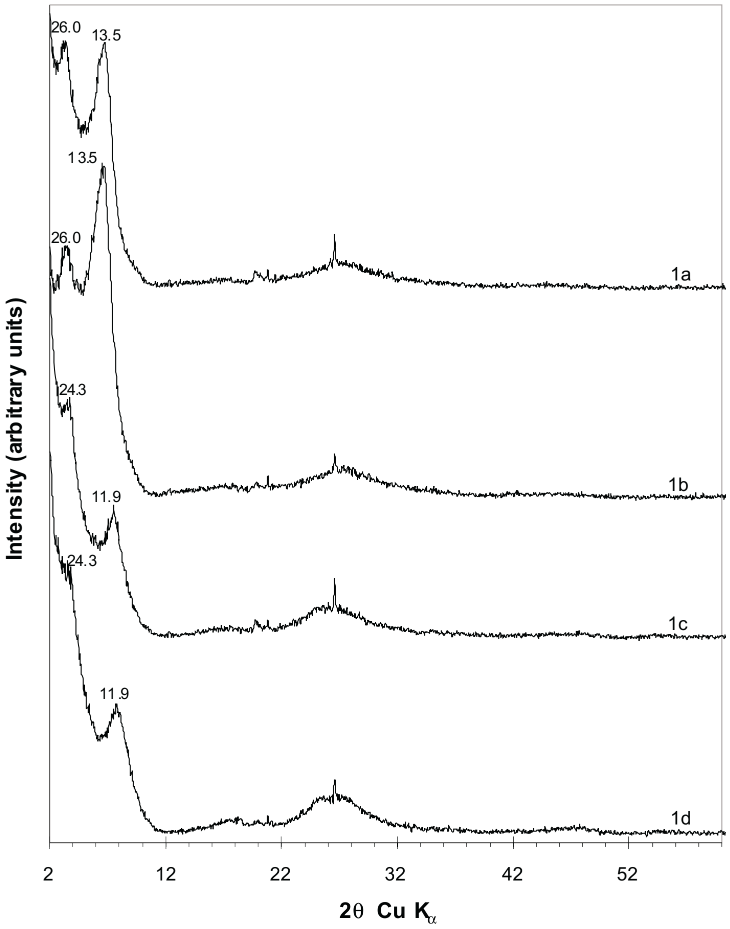


Figure 1. XRD patterns of pillared clay materials: a) Ti-mt (uncalcined Ti-pillared montmorillonite); b) Ti-mt impregnated with Pd; c) Ti-PILC (Ti-mt, after calcination); d) Pd-Ti-mt(773) (Ti-mt impregnated with Pd, after calcination).

13.5 Å. Impregnation of the uncalcined Ti-mt material with Pd salt solution leaves the d-spacings unchanged (Fig. 1b), but the d_{001} reflection becomes less pronounced. After calcination the differences between the samples persist. The XRD pattern of Ti-PILC sample (Fig. 1c) is better resolved than that of Pd-Ti-mt(773) material (Fig. 1d), although in both cases the d_{001} spacing appears at *ca*. 24.3 Å, with the second order peak at 11.9 Å.

Certain differences in the physico-chemical properties of Pd-Ti-mt(773) and Pd-Ti-PILC(773) are revealed also by the experiment with pyridine chemisorption. Table 2 compares the concentrations of Brønsted and Lewis acid sites at the surface of both materials and the strength of the centres. The data show that although in terms of the acid site concentration the samples possess similar properties, the strength of the centres formed in the material impregnated after calcination of the pillared support is higher. Indeed, after degassing at 573 K the Pd-Ti-PILC(773) catalyst retains 100% of pyridine bound to the acid sites, while the Pd-Ti-mt(773) sample subjected to similar treatment releases 25% of chemisorbed pyridine.

Table 2. Concentration of Brønsted and Lewis acid sites and acid site strength from pyridine chemisorption.

Sample	Brønsted		Lewis	
	Total [$\times 10^{19}$/g]	$E/E_0 \times 100\%$ (300°C)	Total [$\times 10^{19}$/g]	$E/E_0 \times 100\%$ (300°C)
Pd-(Ti)-PILC	1.2	75	1.6	75
Pd-Ti-PILC	1.3	100	1.5	100

The results of catalytic tests carried out on Pd-Ti-mt(773), Pd-Ti-PILC(773) and the reference commercial CVOC catalyst are presented in Figs 2–5. Fig. 2 shows the dependence of TCE conversion on the temperature of reaction. Both materials based on pillared clays are more active than the reference sample and lead to complete combustion of TCE at temperature by 100 K lower than the commercial catalyst. The higher activity of Pd-Ti-PILC(773) as compared to Pd-Ti-mt(773) may result from its higher specific surface area and higher strength of the surface acid sites. On all catalysts HCl is the main Cl-containing product, but undesired Cl_2 and small amounts of C_2Cl_4 (tetrachloroethylene) appear as well. The appearance of chlorine is associated with the stoichiometry of TCE, which is a hydrogen-lean compound and provides only one H atom per three Cl atoms. Thus, TCE molecule cannot be totally converted to HCl by using its own hydrogen only. The excess Cl appears as free chlorine. The formation of C_2Cl_4 has been observed previously in TCE oxidation by noble metal-based catalysts [20]. The evolution of HCl with the increasing reaction temperature is shown in Fig. 3. Comparison with the activity data in Fig. 2 demonstrates that at maximum TCE conversion achieved by a given sample it is the catalyst Pd-Ti-PILC(773) that yields the highest amount of the desired HCl product. Fig. 4 shows that the Cl_2 evolution gains on importance with increasing temperature of reaction.

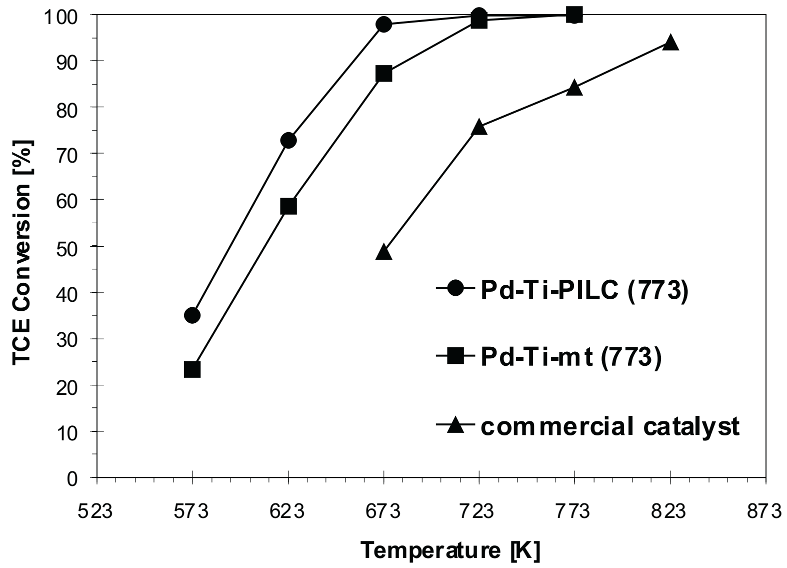


Figure 2. TCE conversion *vs*. temperature of reaction.

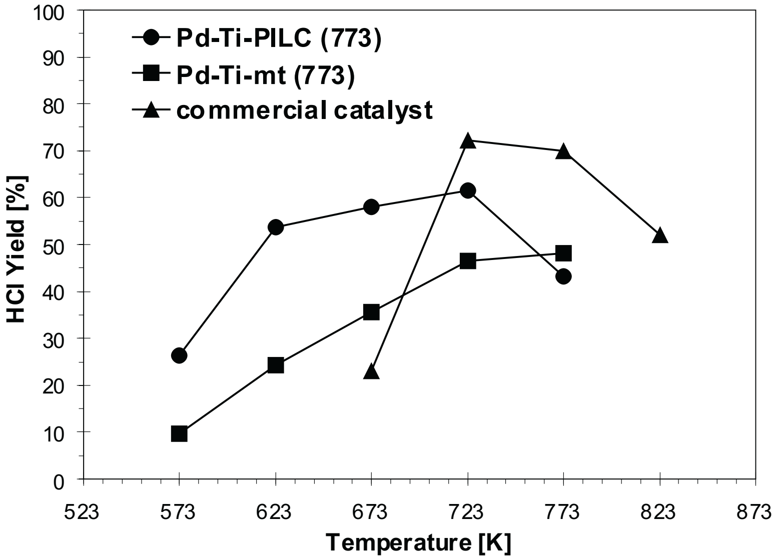


Figure 3. Yield of HCl *vs*. temperature of reaction.

This effect is due to the increasing contribution of the Deacon reaction, in which the primary HCl species undergo consecutive oxidation.

Comparison of the two clay catalysts shows that Pd-Ti-mt(773) sample yields significantly less HCl that the Pd-Ti-PILC(773) catalyst. This sample has been selected to investigate the influence of addition to the reaction feed of a hydrogen-rich compo-

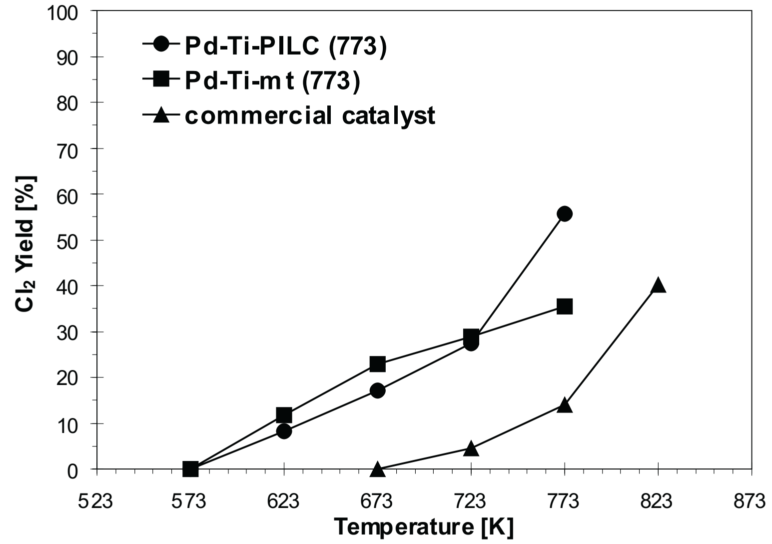
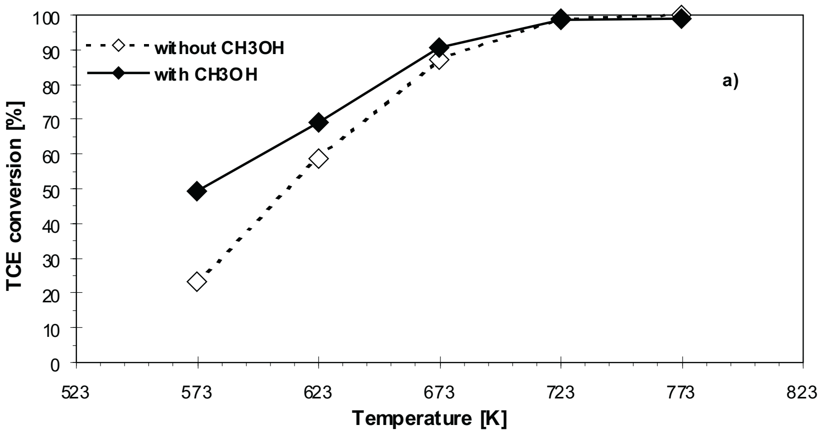


Figure 4. Yield of Cl_2 *vs.* temperature of reaction.

und, the method described in the literature as capable of enhancing the HCl yield in the catalytic oxidation of hydrogen-lean chlorinated VOCs [20]. Methanol has been chosen as the hydrogen-rich additive (C_2HCl_3:CH_3OH = 1:1). Indeed, as shown in Figs. 5a and 5b, a spectacular improvement of the catalytic performance of pillared Pd-(Ti)-PILC catalyst may be achieved in this way. Two effects are seen upon methanol addition: almost complete suppression of chlorine formation and a simultaneous promotion of the HCl evolution. Noteworthy, addition of methanol vapour improves also the catalyst activity in the low temperature range. Another beneficial effect brought about by the methanol addition is an improvement of the Cl balance, which is otherwise rather poor and points to the partial retention of the element by the catalysts. This is demonstrated by the data in Table 3, which compare the Cl balance achieved at 673 K for the reaction carried out with and without methanol additive and show the improvement in the latter case by over 30%.

Table 3. Influence of the CH_3OH presence in the feed on the Cl balance in the reaction of TCE combustion over Pd-(Ti)-PILC catalyst at 400℃.

Sample	Selectivity [%]			
	HCl	Cl_2	C_2Cl_4	ΣCl
Pd-(Ti)-PILC without CH_3OH	41	26	2	69
Pd-(Ti)-PILC with CH_3OH	95	2	4	101



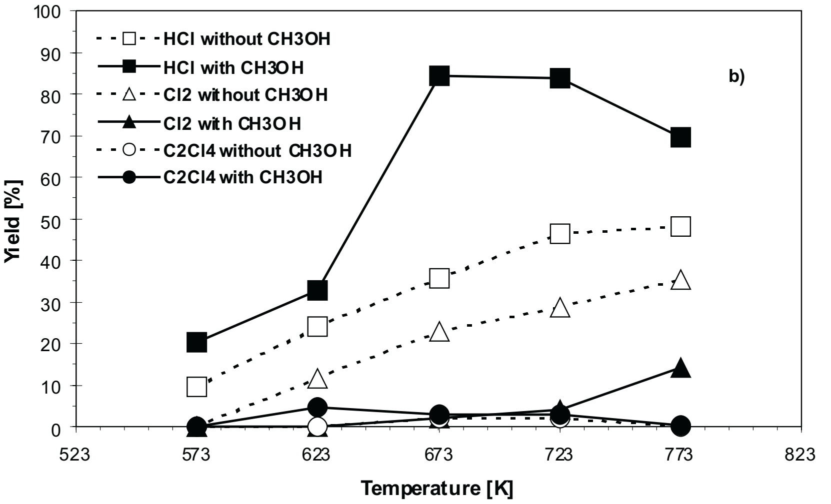


Figure 5. Influence of the methanol vapour addition on the catalytic performance of Pd-(Ti)-PILC (without methanol – dashed line, with methanol – solid line): a) TCE conversion, b) yield to different products.

CONCLUSIONS

The composites of the Pd/TiO_2/montmorillonite type are promising catalysts for destruction of CVOC. Their catalytic activity is higher than that of a commercial Pt-Pd CVOC catalyst. The best HCl yield at maximum conversion is achieved for one of the clay samples. The catalytic performance of the clay catalyst may be significantly improved by addition of methanol vapour to the reaction feed. The latter eliminates chlorine evolution, enhances HCl yield, and improves the chlorine balance. Methanol addition has also a beneficial effect on the catalyst activity in the low temperature range.

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