

Oxidation of dichloromethane over Pt and Au impregnated on extracted and calcined $\text{TiO}_2\text{-ZrO}_2$ supports

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1 Introduction

Chlorinated volatile organic compounds (CVOCs) emitted into air from various industrial processes (e.g. production of pharmaceuticals) represent a serious environmental problem because of their toxic properties. Besides that the CVOCs abatement from flue gases is more difficult in comparison with non-chlorinated VOCs, higher temperatures (above 450°C) are generally required for the total CVOCs oxidation in industrial oxidation units. For both reasons – increasingly stringent regulations of CVOCs emissions [1] and improvement of energy efficiency of the abatement process – the development of highly active catalysts for the CVOCs abatement is still under keen research. Oxide catalysts containing noble metals like Pt, Pd and Au are currently preferred in oxidation of low molecular weight CVOCs owing to their stability and high activity [2-4]. Metal oxides (vanadia- and chromia-based catalysts) are cheaper and more active but less stable [4, 5]. The different activity and selectivity of catalysts mostly depends on divergences in their textural (BET specific surface area, micro- and meso-size distribution, total pore volume) and structural properties (present crystalline and/or amorphous oxide phases, various crystallite sizes) or in the other properties like dispersion of noble metal particles on the mesopore surface or in micropores, metal particle sizes, amount of active acid sites on the support surface, reducibility of metal species etc. With the development of new preparation methods of porous metal oxides using ionic or nonionic surfactants like structure-directing agents for forming of ordered highly-mesoporous structures [6, 7] significant improvements in catalytic performance has been expected [8]. Due to the interconnected monomodal and/or multimodal pores, high mesoporous surface areas and pore volumes gaseous species should be more efficiently transported and consecutively oxidized inside the porous framework of the metal oxide.

Thus, in this study, a new highly micro-mesoporous $\text{TiO}_2\text{-ZrO}_2$ support (molar ratio of 50/50) has been synthesized by a sol-gel method controlled in reverse micellar environment of nonionic surfactant Triton X-114 in cyclohexane in combination with subcritical fluid extractions (using water and subsequently methanol like pressurized solvents, SubWE/PFE) [9]. The prepared highly-porous extracted titania-zirconia support has been stabilized and impregnated with 1.5 wt-% of platinum or gold under vacuum at temperature of 50°C for 25 min. These catalysts have been studied in dichloromethane (DCM) oxidation at the laboratory scale with the aid of light-off tests. In addition, the calcined micro-mesoporous $\text{TiO}_2\text{-ZrO}_2$ equivalent has been synthesized, impregnated with Pt and Au and tested by the same way. The performance of all the laboratory prepared catalysts (1.5%Pt/ $\text{TiO}_2\text{-ZrO}_2$ extracted, 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ extracted, 1.5%Pt/ $\text{TiO}_2\text{-ZrO}_2$ calcined, 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ calcined) were compared with a commercial catalyst suitable for CVOCs oxidation - 0.3 wt-% PtPd/ $\alpha\text{-Al}_2\text{O}_3$ (EnviCat HHC-5557, Süd-Chemie).

DCM oxidation was carried out in a quartz fixed-bed tubular reactor at atmospheric pressure in the temperature range of 100–450°C with the heating rate of 10°C min⁻¹. The gas phase analysis was performed

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by Gasmeter DX-4000N FTIR gas analyzer. The inlet concentration of DCM in air (total air flow $60 \text{ dm}^3\text{h}^{-1}$) was adjusted to 500 ppm, the addition of H_2O for increasing the selectivity towards HCl formation was 1.5 vol-%. All catalysts were investigated in initial light-off tests at WHSV of $150 \text{ dm}^3\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$. The T_{50} and T_{90} temperatures, at which 50% and 90% conversions of DCM were obtained, were chosen as the criterion of catalytic activity.

2 Objectives of the research

In this study the definite correlation between textural and structural properties and catalytic performances of platinum- and gold-impregnated $\text{TiO}_2\text{-ZrO}_2$ catalysts in DCM total oxidation has been found. Textural properties, micro/mesoporosity, dispersion of noble metal particles, structural properties and morphology of four laboratory prepared (1.5%Pt/ $\text{TiO}_2\text{-ZrO}_2$ extracted, 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ extracted, 1.5%Pt/ $\text{TiO}_2\text{-ZrO}_2$ calcined, 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ calcined) and one commercial (0.3%PtPd/ $\alpha\text{-Al}_2\text{O}_3$) catalysts were characterized by nitrogen physisorption at 77K (before and after catalytic tests), chemisorption, XRD, SEM, TPR and TPD techniques. Besides the initial light-off tests carried out over all the catalysts at high WHSV of $150 \text{ dm}^3\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$ also the effect of various WHSV on the catalytic activity and selectivity of platinum and gold-impregnated and calcined $\text{TiO}_2\text{-ZrO}_2$ catalysts was investigated. The durability of all tested catalysts was also studied.

3 Results

3.1 Light-off tests

During the first phase of laboratory experiments light-off tests over all the catalysts at WHSV of $150 \text{ dm}^3\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$ were carried out to compare the effect of the nature of support (calcined vs. extracted) and the noble metal used (Pt vs. Au) on DCM conversion and HCl and CO_2 selectivity. It is evident (see Figure 1 and Table 1) that the catalytic activity of the catalysts decreases in the following order: 1.5%Pt/ $\text{TiO}_2\text{-ZrO}_2$ extracted > 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ extracted > 1.5%Pt/ $\text{TiO}_2\text{-ZrO}_2$ calcined > 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ calcined > 0.3%PtPd/ $\alpha\text{-Al}_2\text{O}_3$. Moreover the HCl selectivity in humid conditions (1.5 vol-% of water) decreases in the same order. In both cases (Pt- and Au-impregnated catalysts), the originally extracted titania-zirconia support shows the higher catalytic activity and HCl selectivity than the calcined support. At the other hand it is necessary to mention that the DCM total oxidation to CO_2 and HCl over Au-impregnated catalysts does not occur and CO, CH_2O and CH_3Cl were detected as undesired reaction by-products. In addition, more CH_2O (~36 ppm) and CH_3Cl (~11 ppm) was generated over the 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ calcined than over the 1.5%Au/ $\text{TiO}_2\text{-ZrO}_2$ extracted catalyst (CH_2O ~6 ppm, CH_3Cl ~5 ppm).

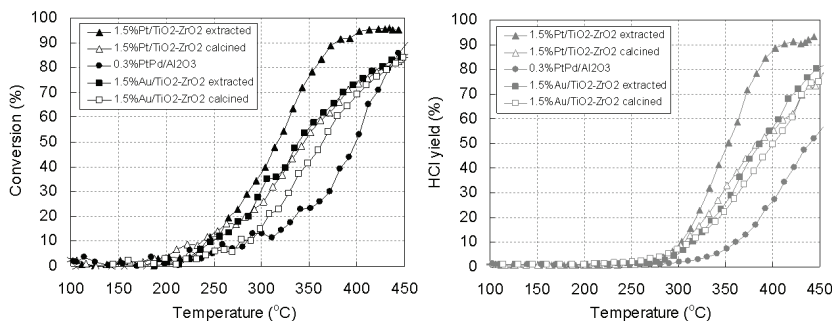


Figure 1 DCM oxidation light-off curves and HCl formation over 1.5 wt-% Pt and 1.5 wt-% Au impregnated on the calcined $\text{TiO}_2\text{-ZrO}_2$ support and the extracted $\text{TiO}_2\text{-ZrO}_2$ support and over the commercial catalyst 0.3 wt-% PtPd/ Al_2O_3 at WHSV $150 \text{ 000 cm}^3/\text{g}_{\text{cat}} \text{ h}$.

Table 1 T_{50} and T_{90} of tested catalysts at WHSV 150 000 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$.

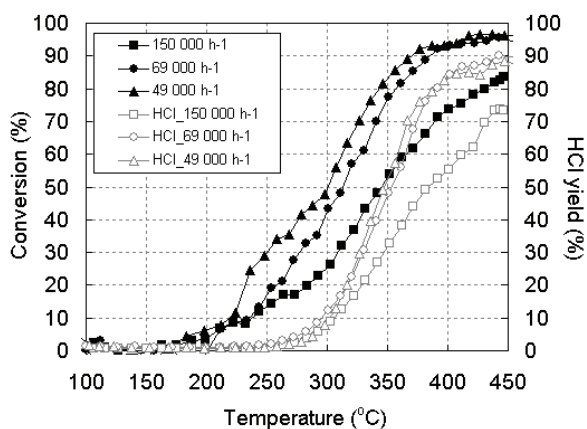
Sample	$T_{50} [^{\circ}\text{C}]$	$T_{90} [^{\circ}\text{C}]$
1.5%Pt/TiO ₂ -ZrO ₂ extracted	316.2	377.1
1.5%Pt/TiO ₂ -ZrO ₂ calcined	344.5	-
0.3%PtPd/ α -Al ₂ O ₃	399.1	-
1.5%Au/TiO ₂ -ZrO ₂ extracted	339.1	-
1.5%Au/TiO ₂ -ZrO ₂ calcined	365.5	-

3.2 The influence of various operation conditions

Some tests were performed in order to study the effect of various weight hourly space velocities (WHSV) on the catalyst's performance (see Table 2 and Figure 2). It was confirmed that with decreasing WHSV the catalyst's performance is higher, even for the calcined titania-zirconia support; 1.5%Pt/TiO₂-ZrO₂ calcined at WHSV 69 000 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ possesses nearly the same activity and selectivity as 1.5%Pt/TiO₂-ZrO₂ extracted at WHSV 150 000 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$. This trend can be explained with the longer contact time, when the gas molecules have more time to adsorb and react on surface of the dispersed noble metal particles.

Table 2 T_{50} and T_{90} of some tested catalysts at various WHSV.

Sample	WHSV		
	$[\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}]$	$T_{50} [^{\circ}\text{C}]$	$T_{90} [^{\circ}\text{C}]$
1.5%Pt/TiO ₂ -ZrO ₂ calcined	150 000	344.5	-
	69 000	312.9	385.9
1.5%Au/TiO ₂ -ZrO ₂ calcined	150 000	365.5	-
	69 000	339.1	447.6

**Figure 2** DCM oxidation light-off curves and HCl formation over the calcined 1.5 wt-% Pt/TiO₂-ZrO₂ at various WHSV; 49 000, 69 000 and 150 000 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$.

4 Relevance of the research

Considering the strict emission limits required by EU [1], the total oxidation CVOCs represents an important topic in the environmental R&D area. The development of new catalysts for total oxidation of CVOCs is still under keen investigation.

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