Catalytic oxidation of trichloroethylene in humid air over titania-zirconia supported palladium catalysts

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Introduction

Due to their widespread applications in industry, chlorinated volatile organic compounds (CVOC) play an important role in air and water pollution. Therefore the abatement of CVOC is highly relevant in order to meet the stringent environmental regulations. Today the most commonly process for elimination of CVOC is thermal incineration. In comparison with thermal incineration catalytic oxidation is favoured when the CVOC concentration is low in the gaseous effluent [1]. This implies high activity and selectivity toward the more desirable products (CO_2, H_2O and HCl), minimising formation of potentially toxic by-products for catalyst design.

Noble-metal based (Pt and Pd) show the highest activity for the oxidation of VOC, however it was found that the support nature plays an important role in improvement the efficiency of the catalyst. Recently a family of binary oxides compositions, including titania-zirconia (TiZr) with a hierarchical bimodal meso-macroporous structure was prepared through the surfactant templating technique combining with the used of mixed alkoxide oxides solution. The binary metal oxide materials obtained have a homogeneous distribution of the components and the attractive structural properties of a large pore volume and high specific surface area [2]. A series of hierarchical bimodal macro-mesoporous titania-zirconia (x/y) oxides, labeled Ti_xZr_y, has been synthesized using the procedure of ref. [2] by a simple method in the presence of a CTMaBr surfactant and calcined at 600°C (Ti_xZr_y). The main scope of this work is to investigate the influence of the binary oxide composition on the catalytic performances of 0.5w% Pd/Ti_xZr_y in TCE abatement (1000ppm) with 1% H_2O. TCE has been chosen here as it is a toxic solvent widely used in dry cleaning and degreasing processes.

Materials and Methods

The titania-zirconia samples having uniform macropores of 300-600 nm in diameter with wormhole–like mesoporous walls and high surface area were calcined at 600°C (Ti_xZr_y) and impregnated with 0.5wt% of palladium by wet impregnation and finally calcined at 400°C (Pd/ Ti_xZr_y). X-ray diffraction (XRD) measurements were conducted in a diffractometer SIEMENS using Cu K_α radiation. The specific surface areas were measured with a sorptometer quantasorb Jr. using the single point BET surface area determination. NH_3-TPD: Sample was heated to 400°C for 1 h under Ar flow (10°C/min) then cooled to 100°C and saturated with pulses of NH_3. The excess NH_3 was removed with a N_2 flow. NH_3 desorption was carried out by increasing the temperature at 10°C/min until 400°C.
TCE oxidation was carried out in a fixed bed reactor and studied between 25 to 450°C. A reduction was performed at 200°C in pure H_2 for 10h (1°C/min). After a sweep in N_2, the catalyst was submitted to 1000 ppmv of TCE diluted in air with 1% H_2O (F/w = 260 NmL/min/g). HCl and Cl_2 were trapped at the exit of the reactor in a bubble chamber containing an aqueous solution of KI.

Results and discussion

The specific surface areas and the crystalline phases clearly identified by XRD for all catalysts studied are summarized in Table 1. This surface increases to have a maximum for the Zr/Ti ratio of 1 before to decrease with the increase of zirconium content (Zr/Ti ratio). The diffraction intensities of the anatase phase in the TZs decrease with the increase of the zirconia content. For Pd/Ti_8Zr_2 in addition to the anatase phase, the mixed oxide $TiZrO_4$ was also identified. A further increase of the zirconia content inhibits crystallization, as no crystalline phase could be detected by XRD in the Pd/TiZrs with zirconia content of 50 and 70 mol% indicating here a homogeneous mixing of the Ti and Zr components. As the zirconia content increases further were detected the tetragonal phase of ZrO_2 with an amorphous phase (Pd/Ti_2Zr_8). The XRD of Pd/Zr shows the mixed phases of tetragonal and monoclinic.

Easiness of TCE destruction was found to follow the sequence based on the T_{50} values (Temperature at which 50% of TCE was converted into products in °C): Pd/Ti_5Zr_5 (250) > Pd/Ti_3Zr_7 (282) > Pd/Ti_7Zr_3 (295) ~ Pd/Ti_2Zr_8 (298) > Pd/Zr (323) > Pd/Ti_8Zr_2 (335). For both catalysts the selectivity in CO_2 and HCl is very high, the perchloroethylene (PCE) production issued from the chlorination of TCE as well as the Cl_2 one being at a very low level. It has been shown that the activity correlated with the S_{BET} of the samples and with the acidity of the support.

Table 1: Crystalline phases, Specific surface areas, NH_3 consumption and T_{50} of the catalysts

Formula	XRD - identified phases	S_{BET} (m^2/g)	S_{BET} * (m^2/g)	NH_3 consumption µmol/g**	T_{50} (°C)
Pd/Zr	$Z_T + Z_M$	96	88	228	323
Pd/Ti_2Zr_8	Z_T + amorp.	198	158	-	298
Pd/Ti_3Zr_7	amorp.	320	262	453	282
Pd/Ti_5Zr_5	amorp.	364	313	493	250
Pd/Ti_7Zr_3	A + amorp.	237	200	325	295
Pd/Ti_8Zr_2	A + $TiZrO_4$	134	130	298	335

Z_T: tetragonal zirconia ; Z_M: monoclinic zirconia ; A: anatase ; amorp.: amorphous ; *: for the used catalysts ; **: performed on the support alone.

Significance

This work deals with the study of the potentiality of novel meso-macroporous supports for the total oxidation of TCE in humid conditions.

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