^{31}P SS-NMR and ATR-FTIR characterization of TiO_2 functionalized with phosphonic acids for solid phase extraction and purification applications

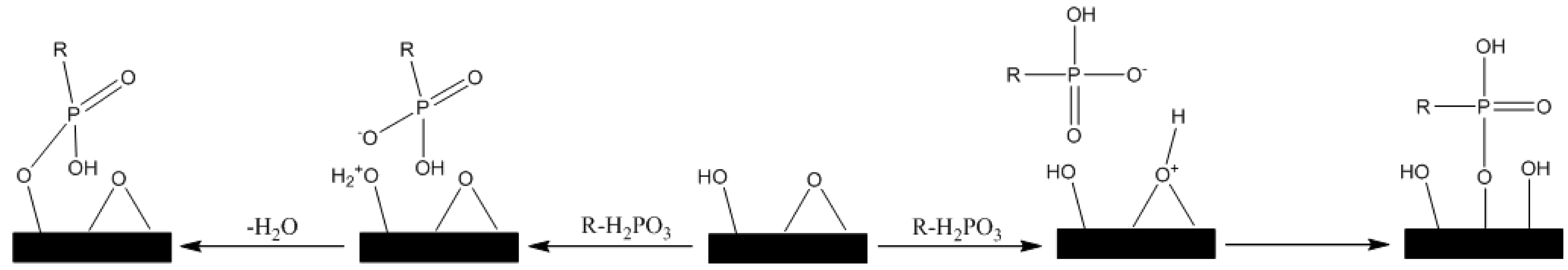
Marco Tassi, Gunter Reekmans, Martine Vanhamel, Peter Adriaensens, Robert Carleer

Hasselt University, TANC (Applied and analytical chemistry), Agoralaan-Building D, B-3590, Belgium

INTRODUCTION

Transition metal oxides, as titanium dioxide, are gaining interest because their intrinsic chemical and corrosive stability in a wide variety of solvents and pH-ranges. The modification of these materials is usually accomplished to incorporate chemical groups on the surface, introducing new functionalities that can be useful in several applications such as chromatography, absorbents, sensors and membranes. The reaction between titanium dioxide (TiO_2) and aromatic or alkyl phosphonic acids results in the formation of a hydrophobic layer on the transition metal oxide surface. Aromatic or alkyl phosphonic acids can be bonded to the surface by physical adsorption or chemically through covalent bonds. Generally there are two reaction mechanisms involved in the formation of Ti-O-P bonds that are characterized by ATR-FTIR and ^{31}P SS-NMR techniques.

Heterocondesation mechanism **Ti-O-Ti cleavage mechanism**



After the characterization these materials have been tested by solid phase extractions to evaluate the reactivity and stability of the hydrophobic layer formed.

EXPERIMENTAL

Hydrophilic fumed TiO_2 powder P25 (Aeroxide), with a specific surface area of 50 m^2/g and an average primary particle size of 21 nm has been modified using $PhPO_3H_2$ (PPA, 98%) or $C_8H_{19}O_3P$ (OPA, 97%). Functionalizations have been carried out at different reaction conditions using a solution 0.1M in water for PPA and a solution of 0.1 M in toluene/water for OPA. Physical mixtures of TiO_2/PPA and TiO_2/OPA have been prepared as references for the characterization of the reaction products.

TiO_2/PPA

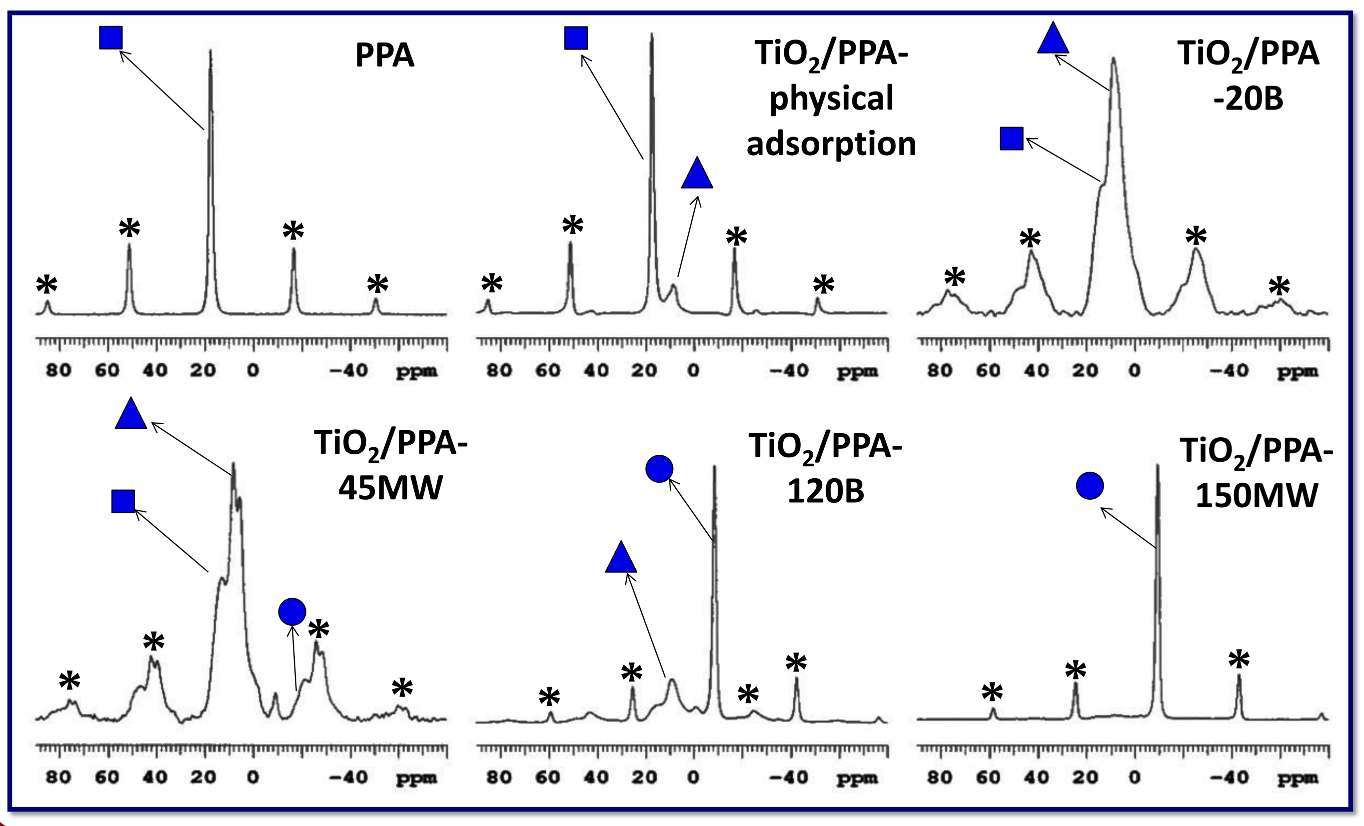
SAMPLE	CONDITIONS
TiO_2/PPA-150MW	150°C Microwave reactor
TiO_2/PPA-120B	120°C batch reactor
TiO_2/PPA-45MW	45°C Microwave reactor
TiO_2/PPA-20B	20°C batch reactor

TiO_2/OPA

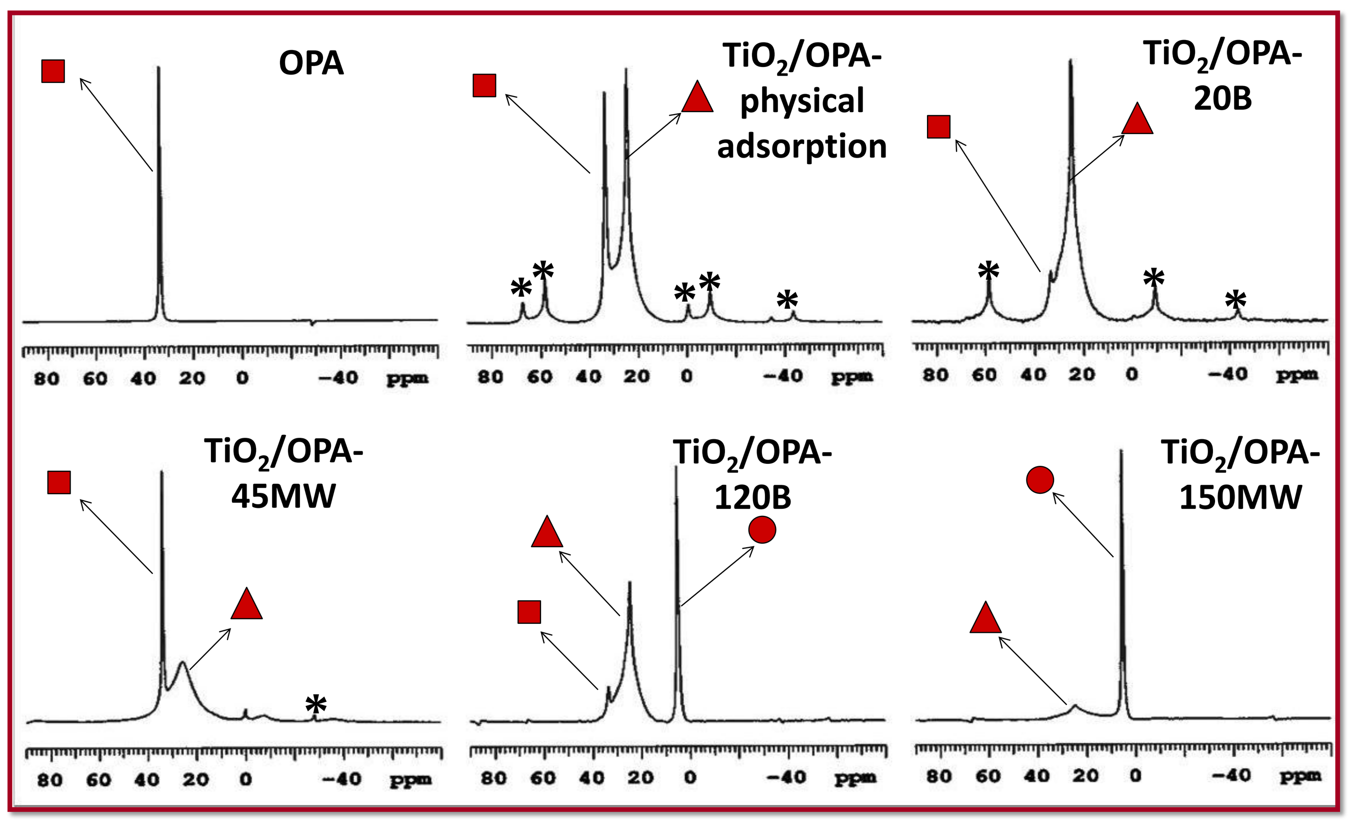
SAMPLE	CONDITIONS
TiO_2/OPA-150MW	150°C Microwave reactor, two phases
TiO_2/OPA-120B	120°C batch reactor, two phases
TiO_2/OPA-45MW	45°C Microwave reactor, two phases
TiO_2/OPA-20B	20°C batch reactor, two phases

^{31}P SS-NMR EXPERIMENTS

TiO_2/PPA ^{31}P SS-NMR experiments

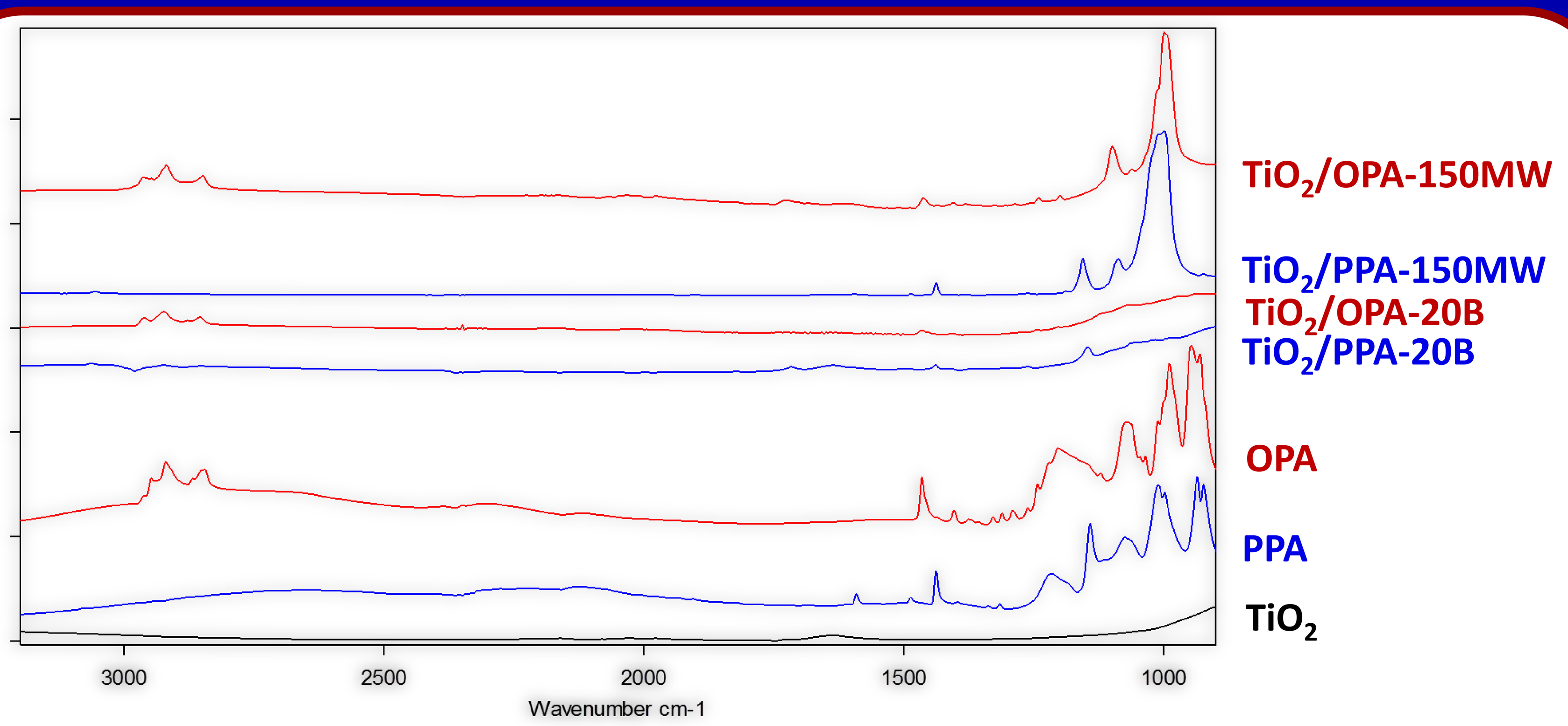


TiO_2/OPA ^{31}P SS-NMR experiments



SYMBOL	ASSIGMENT	σ (ppm)
■ (blue)	FREE PPA	17
▲ (blue)	WEAK INTERACTIONS	9
● (blue)	P-O-Ti STABLE COVALENT BOND	-8
■ (red)	FREE PPA	33
▲ (red)	WEAK INTERACTIONS	24
● (red)	P-O-Ti STABLE COVALENT BOND	5
*	SPINNING SIDE BANDS	-

ATR-FTIR ANALYSIS



- ATR-FTIR analysis of TiO_2/PPA-150MW shows a broad peak at 1023 cm^{-1} assigned to P-O-Ti covalent bonds
- ATR-FTIR analysis of TiO_2/PPA-150MW shows a peak at 1000 cm^{-1} assigned to P-O-Ti covalent bonds

SOLID PHASE EXTRACTION (SPE)

The hydrophobicity of the obtained materials has been evaluated in a solid phase extraction process with the aim to separate two organic solvents with a different polarity (MeOH/Tol for TiO_2/PPA and MeOH/Heptane for TiO_2/OPA).

SAMPLE	MIXTURE	% TOLUENE SEPARATED
TiO_2/PPA-150MW	MeOH/Tol 4:1	40
TiO_2/PPA-120B	MeOH/Tol 4:1	3
TiO_2/PPA-45MW	MeOH/Tol 4:1	10
TiO_2/PPA-20B	MeOH/Tol 4:1	5
SAMPLE	**MIXTURE**	**% HEPTANE SEPARATED**
TiO_2/OPA-150MW	MeOH/Heptane 4:1	32
TiO_2/OPA-120B	MeOH/Heptane 4:1	25
TiO_2/OPA-45MW	MeOH/Heptane 4:1	11
TiO_2/OPA-20B	MeOH/Heptane 4:1	10

CONCLUSION

- P-O-Ti bond of TiO_2/PPA is characterized by a signal at -8 ppm in ^{31}P SS-NMR and an absorption at 1023 cm^{-1} in ATR-FTIR.
- TiO_2/PPA -150°C MW is characterized by a high amount of P-O-Ti bonds.
- TiO_2/PPA -150°C MW shows the best performance in SPE.

- P-O-Ti bond of TiO_2/OPA is characterized by a signal at 5 ppm in ^{31}P SS-NMR and an absorption at 1000 cm^{-1} in ATR-FTIR.
- TiO_2/OPA -150°C MW is characterized by a high amount of P-O-Ti bonds.
- TiO_2/PPA -150°C MW shows the best performance in SPE.

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