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Synthesis and characterization of Pd over novel TiO_2 mixtures: Insights on metal-support interactions

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Outline

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- Introduction
- Materials and methods
- Results and discussion
- Conclusions
- Acknowledgements

Introduction

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Pd supported catalysts → Widely used in oxidation reactions

Supports not only acting as carriers → Charge transfer between metal particles and support

Metal-support interactions →

- Reduction in metal amount needed
- Increase in adsorption capacity
- Sintering inhibition

Catalyst with high activity, reusability and low rate of deactivation

A rational design is crucial

Introduction

TiO_2

- Extensively used as support
- Different properties according to the polymorphs present
- Defective structures and unusual polymorphic mixtures have not been used for oxidation reactions until now

Goal

Study of Pd catalysts supported on novel mixtures of anatase, TiO_2 (II) and rutile obtained by high-energy ball milling in our previous work to evaluate the different metal-support interactions and their potential role in liquid-phase glycerol selective oxidation

Materials and methods

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Catalysts preparation

Wet impregnation of 3 different titania supports → Drying under vacuum at 70 °C overnight → Calcination under air at 500 °C for 4 h (10 °C/min)

↓

Pd/Tix Catalysts (0.25 wt% Pd)

where:

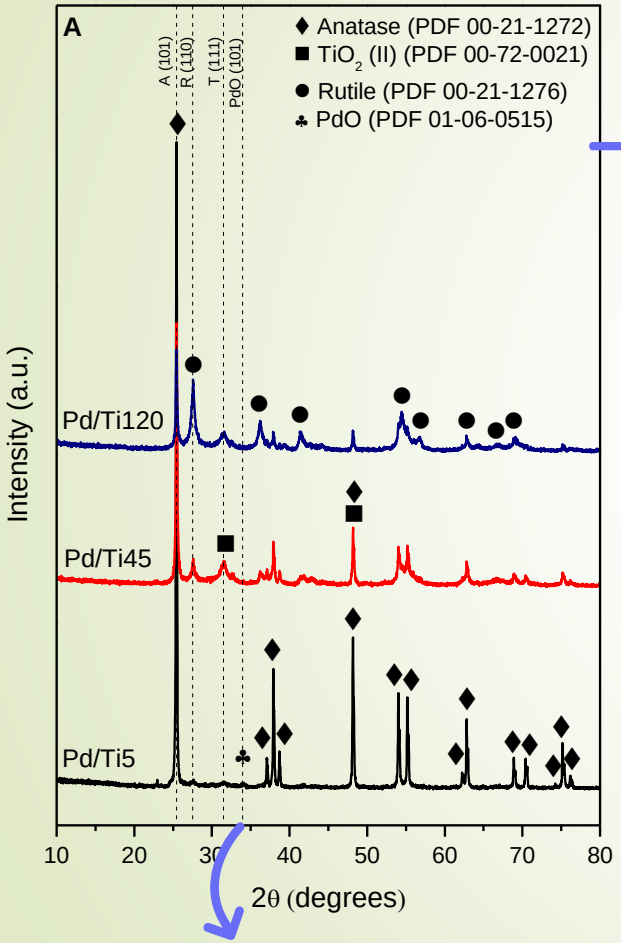
x = milling time (min) of supports

Characterization

XRD, STEM, EDS, BET method, ICP-OES, SEM, XPS, H_2-TPR and O_2-TPD

Results and discussion

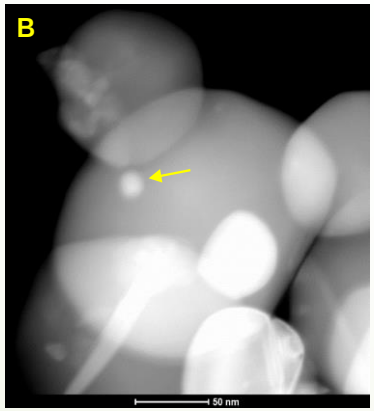
XRD and STEM-EDS analyses

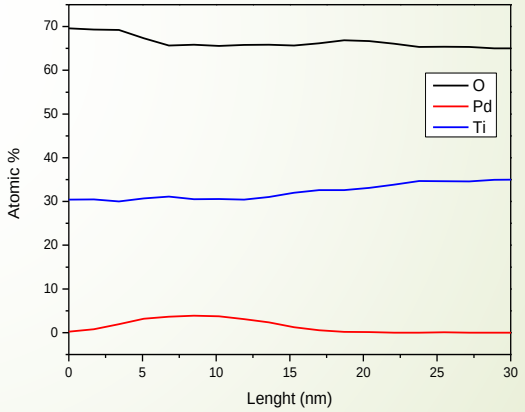


Unusual mixtures of anatase, TiO_2 (II) and rutile phases

Catalyst	Pd particles (nm)
Pd/Ti5	~20
Pd/Ti45	4-6
Pd/Ti120	5-10

Smaller sizes over more defective supports





Supported by STEM-EDS analysis

PdO signal only observed in Pd/Ti5 → Bigger size of Pd particles

Figure 1. XRD spectra of catalysts (A) and STEM image and EDS analysis of Pd/Ti5 sample (B)

Results and discussion

XRD, textural and morphological analyses

Table 1. Weight fraction (%) of titania polymorphs, average crystallite size and textural properties of the catalysts

Catalyst	Anatase wt%	TiO_2 (II) wt%	Rutile wt%	Avg crystallite size (nm)	S_{BET} ($m^2 g^{-1}$)	Pore diameter (nm)	Total Pore Volume ($cm^3 g^{-1}$)
Pd/Ti5	99.2	0.3	0.5	54	10	21	0.05
Pd/Ti45	48.4	43.3	8.3	44	15	26	0.1
Pd/Ti120	23	49.4	27.6	42	17	9	0.04

Crystallite size, particle size and S_{BET} values in accordance with the milling time of the supports

Higher enough to avoid internal diffusion limitations

Low porosities may indicate an almost entirely external surface area

Preferential location of Pd species on the external surface is favored

120-220 nm 100-200 nm 80-180 nm

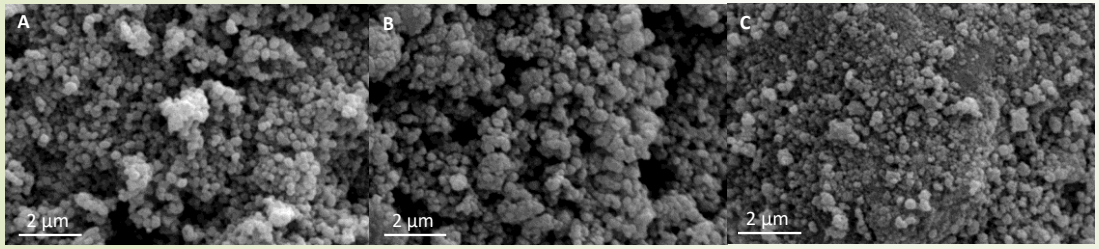


Figure 2. SEM micrographs (10 kx) of the catalysts: Pd/Ti5 (A), Pd/Ti45 (B) and Pd/Ti120 (C)

Results and discussion

ICP-OES and XPS analyses

Catalyst	Pd loading (wt%, ICP-OES)
Pd/Ti5	0.20
Pd/Ti45	0.29
Pd/Ti120	0.36

→ Differences respect to the theoretical value (0.25 wt%) were attributed to experimental errors

Oxygen vacancies contents in the same order as in the supports

Table 2. XPS analysis of catalysts

Catalyst	Binding Energy (eV)						XPS, at%		
	Ti $2p_{3/2}$	Ti $2p_{1/2}$	O 1s (O_{lat})	O 1s (O_{ads})	Pd $3d_{5/2}$ (Pd^0)	Pd $3d_{5/2}$ ($Pd^{\delta+}$)	$Pd^0/Pd^{\delta+}$	$O_{ads}/(O_{lat}+O_{ads})$	Pd/Ti
Pd/Ti5	458.81	464.47	529.75	531.24	334.68	336.62	64.45	13.76	0.39
Pd/Ti45	458.4	464.05	529.65	531.29	334.28	336.42	50.20	9.48	0.51
Pd/Ti120	458.35	464	529.59	531.15	334.62	336.32	30.55	10.93	0.64

Signals associated to Ti^{4+} only

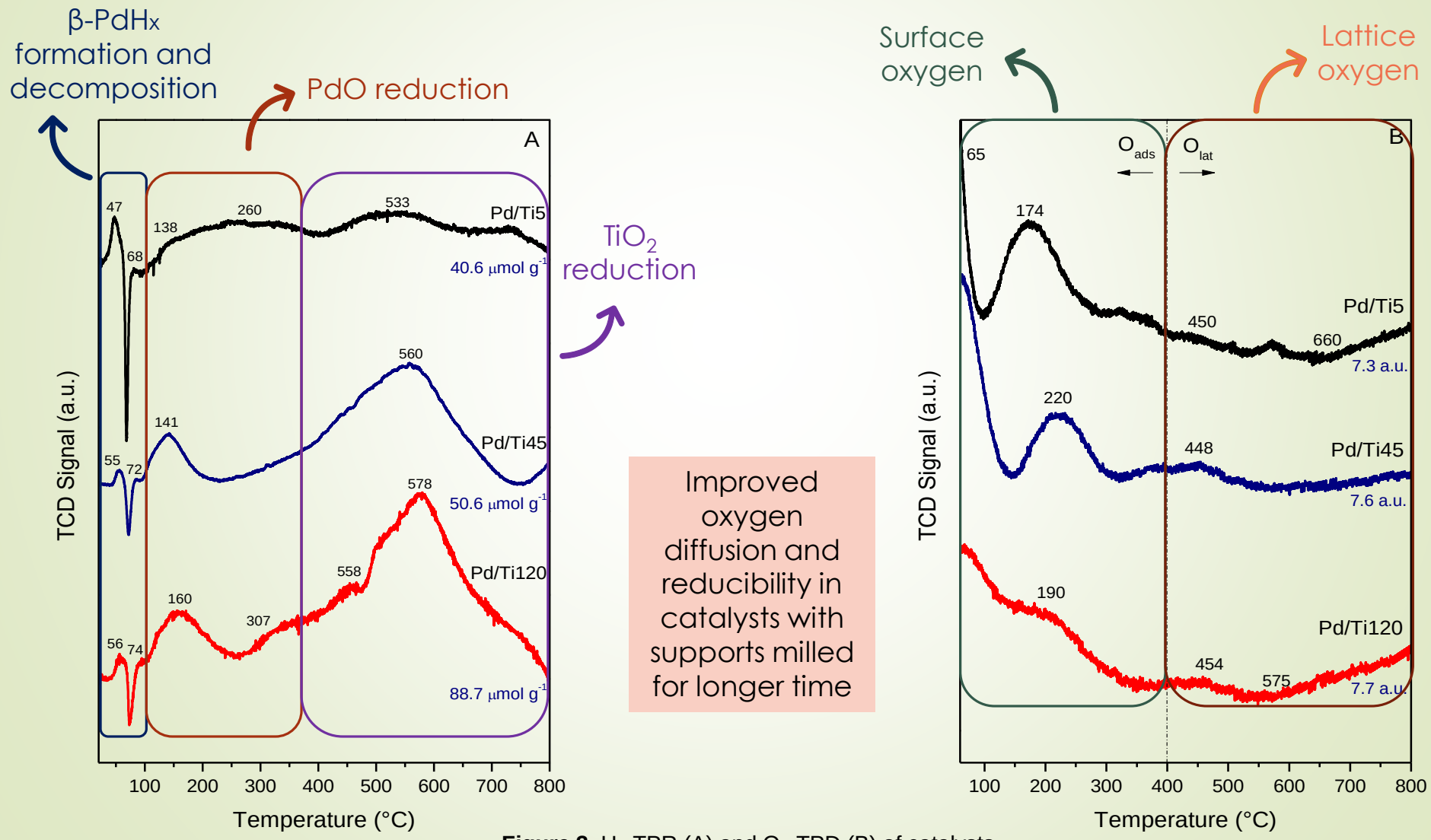
Increase in cationic species ($Pd^{\delta+}$ with $\delta \geq 2$) and/or Pd/PdO_x interfaces with the decrease in anatase phase

Supports with greater amount of defects could enhance the charge transfer from Pd to support

Good distribution of Pd species on the external surface of supports

Results and discussion

H_2-TPR and O_2-TPD analyses



Improved oxygen diffusion and reducibility in catalysts with supports milled for longer time

Figure 3. H_2-TPR (A) and O_2-TPD (B) of catalysts

Conclusions

- ✓ Pd-based catalysts reported in this work showed distinctive properties associated to the unusual mixtures of titania phases present in the supports.

- ✓ Metal nanoparticles were well dispersed on the outer surface of TiO_2, as confirmed by XPS and STEM-EDS analyses.

- ✓ Pd/Ti5 tended to form more anionic Pd species in the form of $TiPd_xO$ structures, whilst Pd/Ti45 and mainly Pd/Ti120 formed more cationic PdO_x species, as observed by XPS measurements.

- ✓ Achieved metal-support interactions could improve redox properties, inducing low-temperature reducibility and an increase in the mobility of reactive oxygen species, as evidenced by H_2-TPR and O_2-TPD analyses.

- ✓ Present catalysts are being tested in liquid-phase glycerol selective oxidation in order to study the influence of metal-support interactions on the catalytic performance.

Acknoledgements

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