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MDPI

Assessment of the photo-catalytic efficiency of Pd-M (M=Cu, Ag) nanoparticles supported on TiO_2

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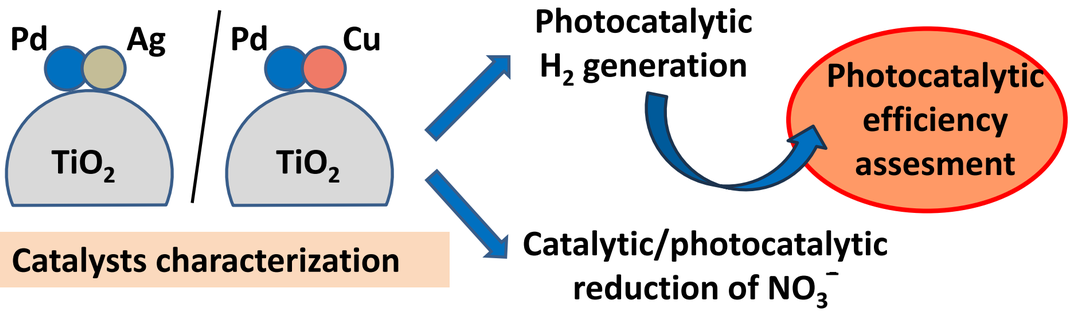
INTRODUCTION & AIM

Controlling the size, shape and dispersion of metal Nps[1, 2] is essential for an enhanced catalytic activity[3]

Modifying TiO_2 with Pd, as well as of Cu and Ag co-catalysts



Catalysts characterization

❖*Investigation of the physical and chemical properties of the Pd-M (M=Cu, Ag)/TiO_2 catalysts.*
❖*Study of the effect of modifying TiO_2 with Pd-Cu and Pd-Ag co-catalysts on the photocatalytic efficiency exhibited in the photocatalytic H_2 generation and nitrate reduction reaction.*

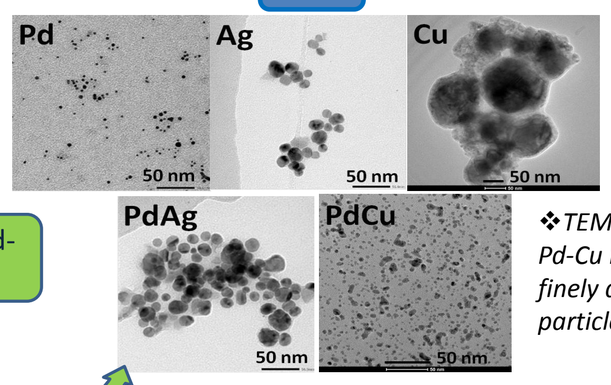
METHOD

TEM | Fractal analysis | XRD | CO chemisorption | XPS | TPR | UV-Vis

Synthesis

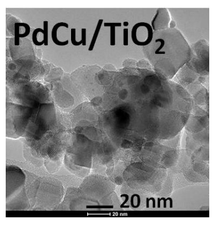
Metallic/ Bimetallic Nanoparticles

TEM



❖*TEM image of the Pd-Cu Nps contains finely dispersed particles (3-5 nm)*

The alkaline polyol method- a modified protocol[1]



PVP (MW = 8,000)

TiO_2 Supported Bimetallic Nanoparticles

Fractal Analysis

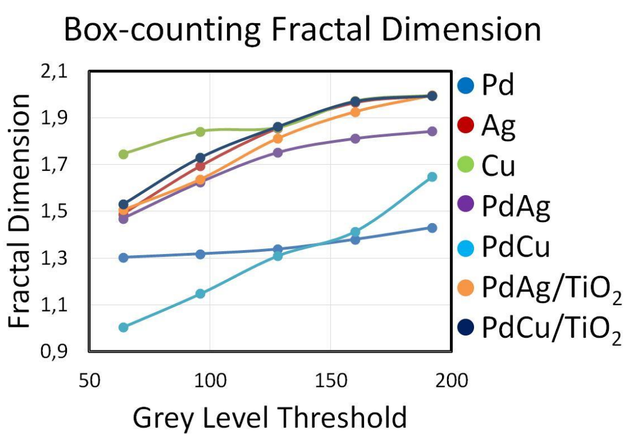
The Correlation Function Method

❖*Conversing the grey-level pixel as a height, the fractal dimensions was evaluated[4].*

The Variable Length Scale Method

Sample	Method	Fractal Dimension	Self-similarity Limits (nm)	Linear correlation coefficient
PdAgNp/ TiO_2	Correlation Method	2.745 ± 0.002	0.8 – 3.5	0.997
	Correlation Method	2.645 ± 0.017 2.823 ± 0.005 2.700 ± 0.001	0.4 – 1 1 – 1.6 1.6 - 20	0.984 0.989 0.999
	Variable Length Scale Method	2.714 ± 0.005	2-34	0.991
PdCuNp/ TiO_2	Correlation Method	2.819 ± 0.002 2.706 ± 0.001	1.2 – 3 3 - 12	0.992 0.999
	Variable Length Scale Method	2.846 ± 0.005 2.703 ± 0.007	2 – 9 9 - 28	0.993 0.990

Box – Counting Method



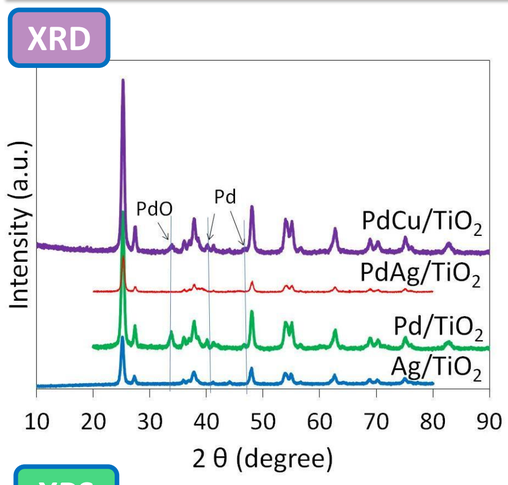
❖*Analyzing the black and white images obtained by considering different grey-level thresholds, the box-counting fractal dimensions indicate higher fractal dimensions for PdAg/TiO_2 and PdCu/TiO_2.*

NP size (CO chemisorption, TEM)

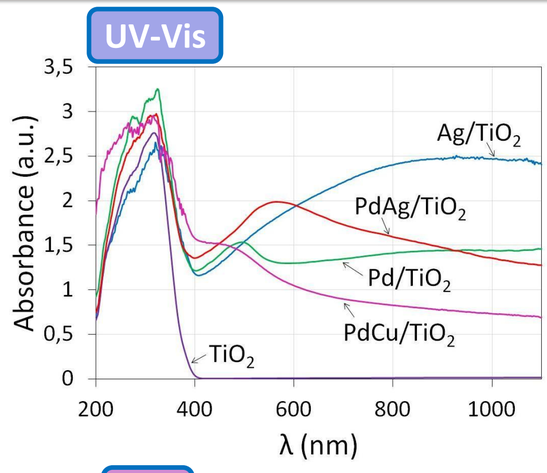
Sample	D_{TEM} (nm) (Unsupported)	$D_{CO\ chem}$ (nm) (TiO_2 Supported)
Pd Np	2.47~10.00	1.40
Ag Np	1.48~30.00	-
PdAg Np	1.48~25.00	2.09
PdCu Np	4.00~5.00	3.60

RESULTS & DISCUSSION

XRD



UV-Vis

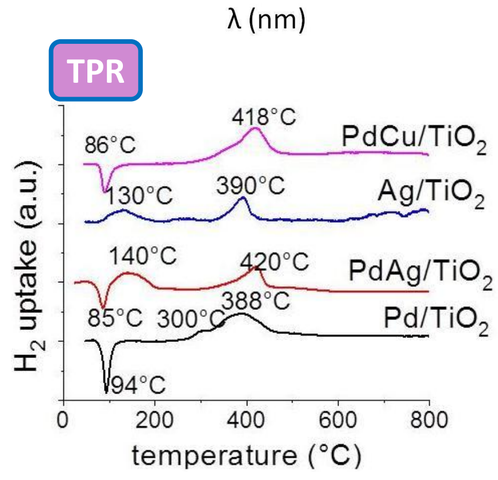


XPS

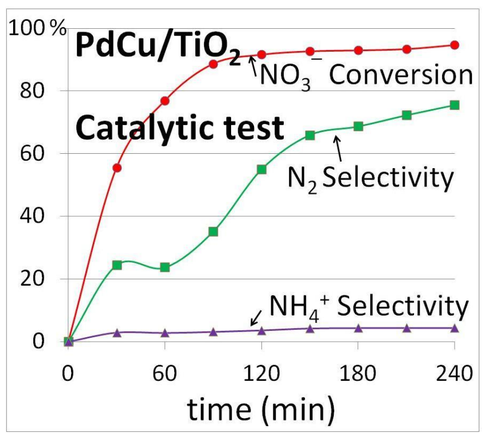
Sample	Binding Energy (eV)		
	Pd 3d	Ag 3d	Cu2p
PdAg Np	A=334.17 B=339.51	A=367.32 B=373.37	
PdCu Np	A=334.90 B=340.12	-	A=932.50
PdCu /TiO_2	A=335.51 B=340.59	-	A=933.02

❖Pd^{2+}/ Pd^0
❖Cu^{1+} /Cu^0

TPR

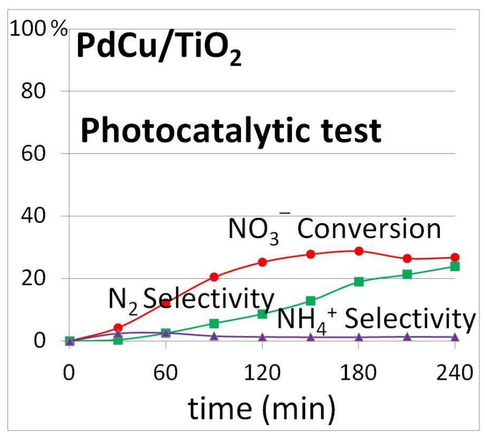


NO_3^- Reduction Reaction



❖*1 wt% PdCu/TiO_2 Pd:Cu=1:0.25 molar ratio.*

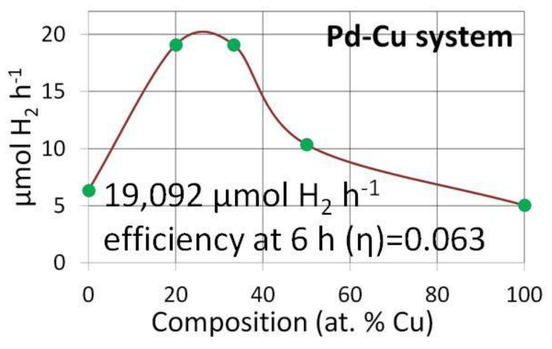
❖*150 mL NO_3^- solution,100ppm; 0.1g cat.; H_2*

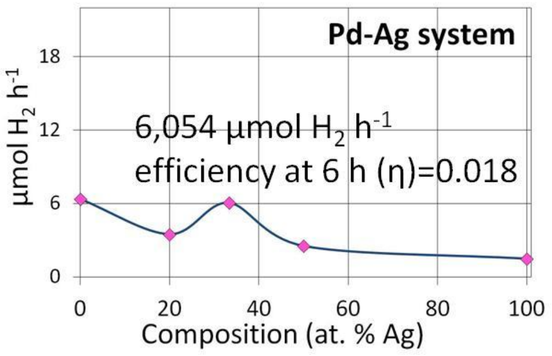


❖*70 mL NO_3^- solution,100ppm; 0.035g cat.; D(Ar)=30 cm^3/min; T(reactor)=18 °C*

Photocatalytic H_2 generation

Light source-high pressure lamp, 150 W, inner UV irradiation





❖*70 mL H_2O; 0.035g cat.1 wt% Pd-Cu,Ag/TiO_2; Pd:Cu,Ag=1:0.25 molar ratio; D(Ar)=30 cm^3/min*

CONCLUSION

❖*The PdCu Nps supported on TiO_2 (1% metal loading) showed excellent activity for the catalytic reduction of NO_3^- ions in the liquid phase (~95% nitrate conversion); a lower NO_3^- conversion (~30%) was obtained under UV photocatalytic test.*
❖*Bimetallic PdCu Nps dispersed on TiO_2 with various molar ratios showed better activity for photocatalytic water splitting compared to PdAg/TiO_2 samples.*
❖*The formation of Pd hydride in the bulk metal results in the dissociation rate of H_2 on the Pd surface that exhibits high activity and selectivity for numerous catalytic processes, such as the catalytic reduction of nitrate and nitrite ions in water.*
❖*All samples exhibit fractal behavior; the equivalent surface of PdAg /TiO_2 and PdCu/TiO_2 exhibit the highest fractal dimensions (2.823 and 2.846, respectively).*

REFERENCES

1. Papa, F., Miyazaki, A., Scurtu, M., Ianculescu, A. C., & Balint, I.J. Nanoparticle Res. 16 (2014): 1-12.
2. Vasile, A., Scurtu, M., Munteanu, C., Teodorescu, M., Anastasescu, M., & Balint, I. Process Saf. Environ. Prot. 108 (2017): 144-152.
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4. Vasile, A., Dobrescu, G., Bratan, V., Teodorescu, M., Munteanu, C., Atkinson, I., ... & Balint, I.Catalysts 14.9 (2024): 619.