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Simple TiO_2-based photocatalyst for HMF transformation under UV irradiation

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INTRODUCTION & AIM

HMF (5-hydroxymethylfurfural), a six-carbon heterocyclic organic compound containing both aldehyde and alcohol (hydroxymethyl) functional groups, is formed through the dehydration of hexose sugars (e.g. inulin, cellulose, glucose, fructose, and sucrose) under acidic conditions. In aqueous media, HMF undergoes hydrolysis, incorporating two water molecules and yielding formic acid and levulinic acid (LA).

The hydroxymethyl and carbonyl groups present in HMF can be oxidized to produce a variety of valuable furan-based chemicals.

In this work, we present a series of lanthanide-doped TiO_2 photocatalysts designed for the photo-oxidation of HMF under UV irradiation.

METHOD

Samples of TiO_2 containing different amounts of Er and Yb were prepared using the sol-gel method and then calcined at 500 and 750 C, respectively:

1% Er, 5% Er, 1% Yb, 5% Yb and TiO_2 co-doped with 1% Er-1% Yb, and 1% Er-5% Yb

The prepared samples were characterized by PXRD, Raman, DR-UV-Vis and DRIFT.

The catalytic activity of the prepared and characterized samples was tested in the **photocatalytic oxidation of 5-(Hydroxymethyl)-2-furaldehyde** (HMF), **without base addition.**

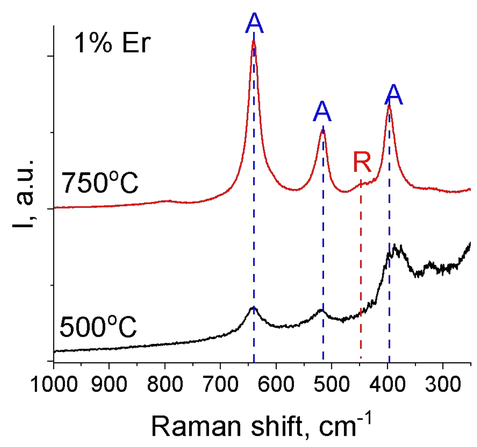
Photocatalytic HMF oxidation tests were carried out using a combination of two ultraviolet (UV) light lamps (365+254 nm), **3h.**

RESULTS & DISCUSSION

TiO_2 doping and co-doping leads to changes in anatase / rutile ratios as well as differences in estimated particle size:

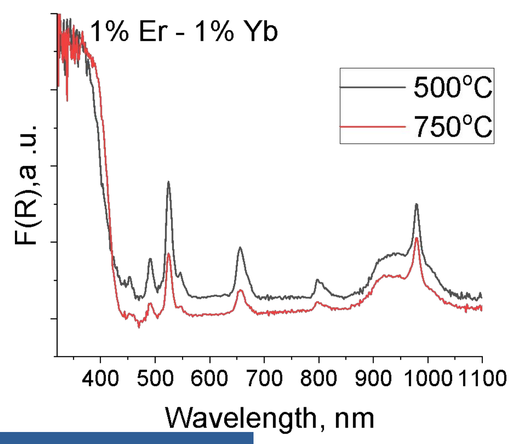
Sample	ANATASE	RUTILE	%A	%R
	Part. size (nm)	Part. size (nm)		
TiO_2 500	21	26	94.83	5.17
TiO_2 750	49	64	33.83	66.17
1%Er-TiO_2 500	10	-	100.00	0.00
1%Er-TiO_2 750	28	40	93.9	6.1
5%Er-TiO_2 500	4	26	91.48	8.52
5%Er-TiO_2 750	22	30	90.71	9.29
1%Yb-TiO_2 500	9	-	100.00	0
1%Yb-TiO_2 750	26	36	71.5	28.5
5%Yb- TiO_2 500	4	-	100.00	0.00
5%Yb- TiO_2 750	22	29	84.34	15.66
1%Yb-1%Er-TiO_2 500	7	-	100	0
1%Yb-1%Er-TiO_2 750	20	31	82.7	17.3
1%Er-5%Yb-TiO_2 500	9	-	100	0
1%Er-5%Yb-TiO_2 750	20	34	93.58	6.42

No Er_2O_3 or Yb_2O_3 were observed in the XRD or Raman.



The UV–Vis spectra display a series of **lines ascribed to the excitation of lanthanides** (f-f transitions).

Sample	Band-gap (eV)	
	500°C	750°C
TiO_2	2.97	2.93
1%Er- TiO_2	2.94	2.89
5%Er-TiO_2	3.00	2.95
1%Yb-TiO_2	2.89	2.88
5%Yb- TiO_2	2.95	2.93
1%Er-1%Yb-TiO_2	2.90	2.87
1%Er-5%Yb-TiO_2	2.98	2.95



The doped samples exhibited higher photocatalytic activity than pure TiO_2.

Catalyst	S (%)				C (%)
	HMFCA	LA	GA	Others	
TiO_2 500	-	86.66	-	13.34	15.9
TiO_2 750		79.24	15.23	5.53	13.2
1%Er- TiO_2 500	-	91.50	8.50	-	28.56
1%Er- TiO_2 750	**31.85**	62.74	5.41	-	22.87
5%Er- TiO_2 500	-	91.91	8.09		82.23
5%Er- TiO_2 750	-	81.80	18.20	-	74.7
1%Yb-TiO_2 500	-	95.28	4.72	-	32.5
1%Yb-TiO_2 750	-	90.25	9.75	-	19.7
5%Yb-TiO_2 500	-	92.25	7.75	-	65.8
5%Yb-TiO_2 750	-	82.87	17.13	-	46.18
1%Er-1%Yb-TiO_2 500	**40.00**	60.00	-	-	68.1
1%Er-1%Yb-TiO_2 750	-	100.00	-	-	65.14
1%Er-5%Yb-TiO_2 500	-	93.74	6.26	-	66.88
1%Er-5%Yb-TiO_2 750	-	93.63	6.37	-	57.33

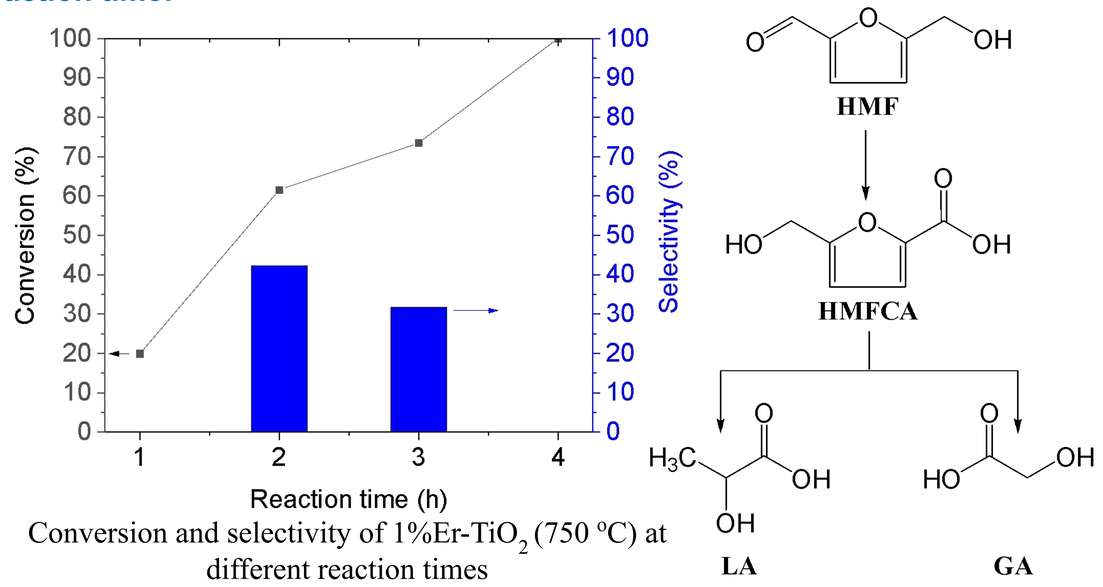
Nature of the dopant: Conversion Er^{3+} > Yb^{3+}.

Amount of dopant: Conversion 5% Er^{3+} or Yb^{3+} > 1% Er^{3+} or Yb^{3+}

Calcination temperature: 500 °C > 750 °C.

Catalyst amount: 2 X 1%Er-1%Yb-TiO2 500 and 1%Er-TiO2 750 - 3 h: the conversion was 100% with only LA as product in the liquid phase, as result of advanced oxidation.

Reaction time:



Conversion and selectivity of 1%Er-TiO_2 (750 °C) at different reaction times

CONCLUSIONS

- Er and Yb modified TiO_2 were synthesised by sol-gel method and the calcined at 500, 750 °C, respectively
- The phase composition of these samples varies from that of the undoped materials.
- The synthesized catalysts exhibited activity under UV irradiation and showed higher performance than undoped TiO_2; however, most of them primarily converted HMF into levulinic acid (LA).
- The activity increased with the amount of dopant, and decreased with the increase of the calcination temperature.
- The only catalysts that produced HMFCA were 1% Er–TiO_2 calcined at 750 °C and 1% Er–1% Yb–TiO_2 calcined at 500 °C.
- Increasing the catalyst loading resulted predominantly in more advanced oxidation products.

FUTURE WORK/ ACKNOWLEDGMENT

Future prospects: **improvement of selectivity to HMFCA.**

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