

Title: Ru Loaded Biphasic TiO₂ Nanosheet-Tubes Enriched with Ti³⁺ Defects and Directionally Deficient Electrons as Highly Efficient Catalysts in Benzene Selective Hydrogenation

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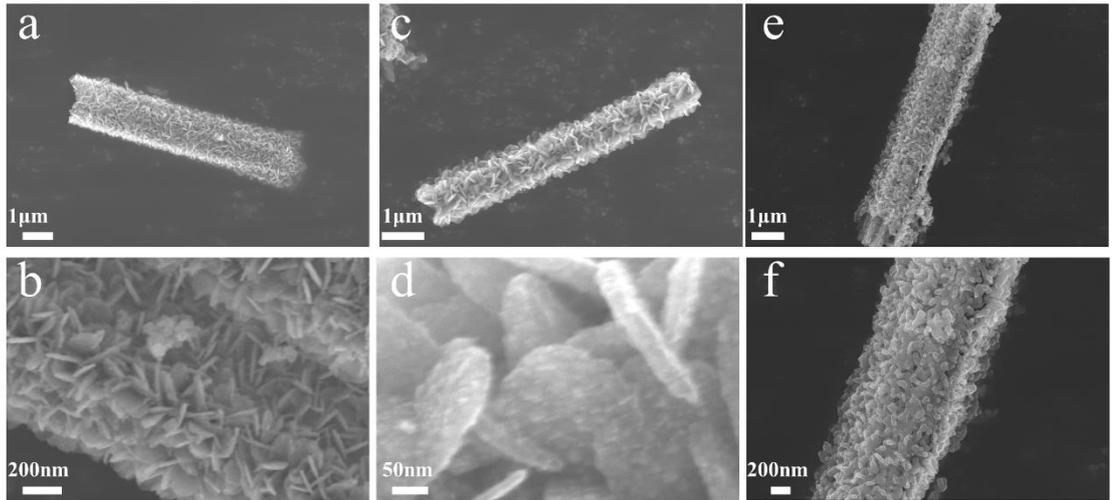


Fig S1. SEM images of of TNSTs-2(a,b), TNSTs-4(c,d), and TNSTs-6(e,f).

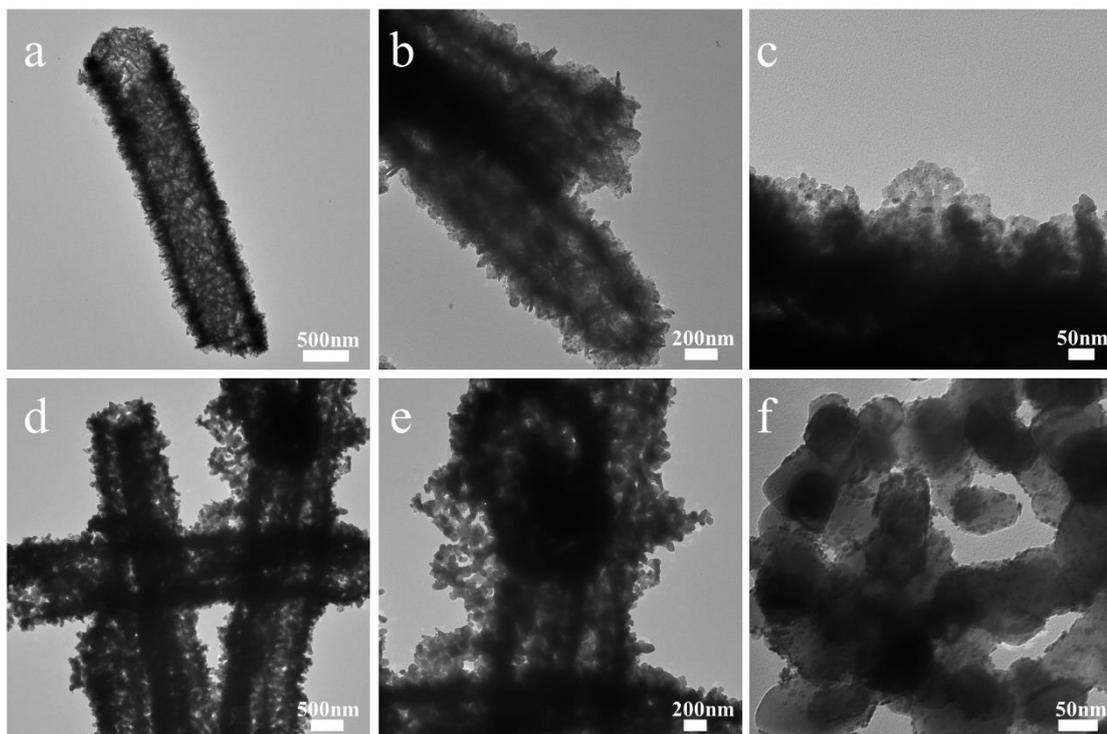


Fig S2. TEM images of Ru/TNSTs-2(a-c) and TNSTs-6(d-f).

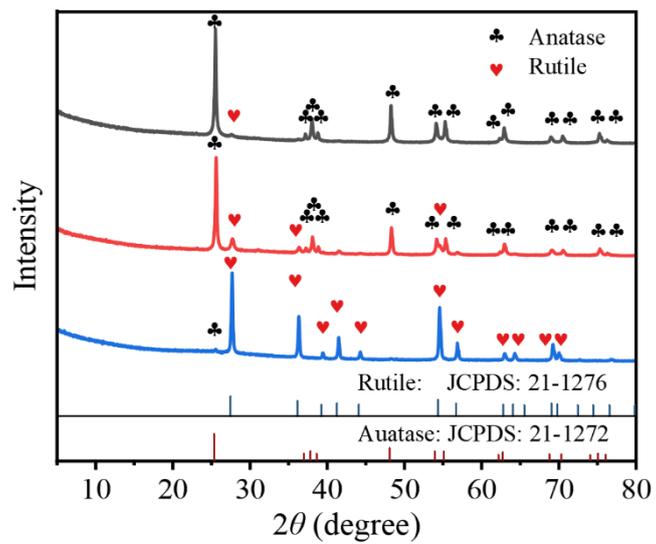


Fig S3. XRD patterns of TNSTs-2(a), TNSTs-4(b), and TNSTs-6(c).

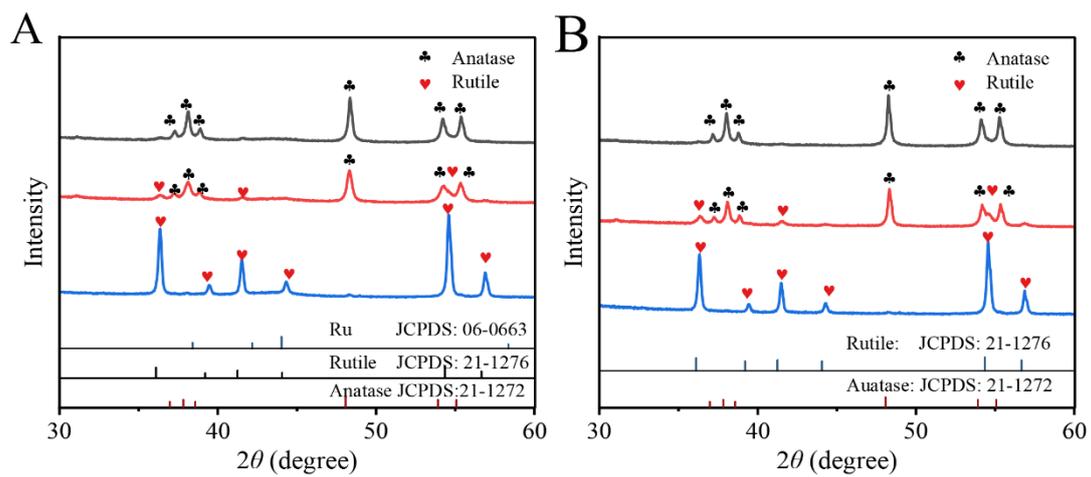


Fig S4. XRD patterns (A) of Ru/TNSTs-2(a), Ru/TNSTs-4(b), and Ru/TNSTs-6(c).



Fig S5. SEM images of TNSTs-4 after reaction

Table S1. Structure parameters of various samples.

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	V_{p}^{b} (cm ³ /g)	D_{p}^{c} (nm)
Ru/TNSTs-2	35	0.14	19.3
Ru/TNSTs-4	39	0.17	31.1
Ru/TNSTs-6	20	0.09	18.1

^a BET surface area determined from N₂ isotherm.

^b Total pore volume.

^c Average pore diameter determined by BJH model.

Table S2. The binding energy of Ru 3d_{5/2} of the catalyst.

Catalysts	Binding Energy (eV)	
	Ru ⁰ 3d _{5/2}	Ru ^{δ+} 3d _{5/2}
Ru/TNSTs-2	280.31	281.94
Ru/TNSTs-4	280.37	282.10
Ru/TNSTs-6	280.50	282.10

Table S3. Results of benzene selective hydrogenation over TiO₂ supported Ru catalysts reported in recent literature.

Catalyst	Reaction additive	t^a (min)	Conv. ^a (%)	S_{CHE}^a (%)	Y_{CHE}^a (%)	S_0^c (%)	Ref.
Ru/TMTFs-573	ZnSO ₄ ·7H ₂ O	7	n.p. ^b	n.p.	17	47	[1]
Ru/TMTFs-673	ZnSO ₄ ·7H ₂ O	8	n.p.	n.p.	28	63	[1]
Ru/TMTFs-773	ZnSO ₄ ·7H ₂ O	12	n.p.	n.p.	42	78	[1]
Ru/TMTFs-873	ZnSO ₄ ·7H ₂ O	12	n.p.	n.p.	32	65	[1]
Ru/BTNSTSSs-1	ZnSO ₄ ·7H ₂ O	10	71.2	39.4	28.1	53.7	[2]
Ru/BTNSTSSs-2	ZnSO ₄ ·7H ₂ O	10	77.4	48.5	37.6	73.5	[2]
Ru/BTNSTSSs-12	ZnSO ₄ ·7H ₂ O	45	87.5	49.2	43.0	90.3	[2]
Ru/BTNSTSSs-48	ZnSO ₄ ·7H ₂ O	25	64.0	56.8	36.4	77.3	[2]
Ru/TiO ₂ -101	ZnSO ₄ ·7H ₂ O	80	56	54	30	82	[3]
Ru/TiO ₂ -001	ZnSO ₄ ·7H ₂ O	45	60	56	34	79	[3]
Ru/TiO ₂ -010	ZnSO ₄ ·7H ₂ O	45	86	52	45	79	[3]
Ru/TS (6:1)	ZnSO ₄ ·7H ₂ O	15	61.6	44.5	28.7	76.4	[4]
Ru/TS (7:1)	ZnSO ₄ ·7H ₂ O	12	52.4	72.9	38.2	87.3	[4]
Ru/TS (8:1)	ZnSO ₄ ·7H ₂ O	15	62.4	53.5	33.3	84.1	[4]
Ru/TS (9 : 1)	ZnSO ₄ ·7H ₂ O	15	58.4	51.3	29.9	76.6	[4]
Ru/TiO ₂	ZnSO ₄ ·7H ₂ O	15	60.5	43.5	26.3	69.8	[4]
Ru/anatase	ZnSO ₄ ·7H ₂ O	25	50	66	33	n.p.	[5]
Ru/rutile	ZnSO ₄ ·7H ₂ O	45	50	46	23	n.p.	[5]
Ru/anatase-750	ZnSO ₄ ·7H ₂ O	60	50	61	31	n.p.	[5]
Ru/TiO ₂ nanospheres	ZnSO ₄ ·7H ₂ O	18	84	61	51	83	[6]
Ru/TiO ₂ submicrospheres	ZnSO ₄ ·7H ₂ O	23	87	60	52	90	[7]
Ru/TiO ₂ -1.5%HF	ZnSO ₄ ·7H ₂ O	25	67	61	41	95	[8]
Ru/brookite-nanoflower	ZnSO ₄ ·7H ₂ O	45	53	50	27	73	[9]
Ru/brookite-nanorod	ZnSO ₄ ·7H ₂ O	45	68	58	39	78	[9]
Ru/brookite-nanosheet	ZnSO ₄ ·7H ₂ O	50	85	53	45	86	[9]

Ru@MTSS-P	ZnSO ₄ ·7H ₂ O	5	65	7	52	n.p.	[10]
Ru@MTSS-0	ZnSO ₄ ·7H ₂ O	14	82	54	44	n.p.	[10]
Ru@MTSS-0.8%	ZnSO ₄ ·7H ₂ O	19	84	58	49	n.p.	[10]
Ru@MTSS-1.6%	ZnSO ₄ ·7H ₂ O	23	87	60	52	n.p.	[10]
Ru@MTSS-3.2%	ZnSO ₄ ·7H ₂ O	17	80	63	50	n.p.	[10]
Ru@MTSS-6.3%	ZnSO ₄ ·7H ₂ O	14	81	49	40	n.p.	[10]
Ru@MTSS-9.1%	ZnSO ₄ ·7H ₂ O	14	79	49	39	n.p.	[10]
Ru/anatase-nanorod	ZnSO ₄ ·7H ₂ O	40	84	64	54	93	[11]
Ru-Fe/TiO ₂	ZnSO ₄ ·7H ₂ O	77	63	30	19	51	[12]
Ru-Ni/TiO ₂	ZnSO ₄ ·7H ₂ O	82	75	35	26	53	[12]
Ru-Cu/TiO ₂	ZnSO ₄ ·7H ₂ O	120	74	48	36	75	[12]
Ru-Co/TiO ₂	ZnSO ₄ ·7H ₂ O	69	62	66	41	85	[12]
Ru/TiO ₂	ZnSO ₄ ·7H ₂ O	60	85	51	43	n.p.	[13]
Ru@TiO ₂	ZnSO ₄ ·7H ₂ O	15	85	62	53	n.p.	[14]
(Ru/TiO ₂)@p-TiO ₂	none	210	98	77	75	n.p.	[15]
Ru/TiO ₂	NaOH + ZnO	150	72	58	42	n.p.	[16]
Ru/P25	ZnSO ₄ ·7H ₂ O	20	88	69	61	90	[17]
Ru/TNSTs-2	ZnSO ₄ ·7H ₂ O	60	80	57	46	85	This work ^d
Ru/TNSTs-4	ZnSO ₄ ·7H ₂ O	100	79	64	51	95	This work
Ru/TNSTs-6	ZnSO ₄ ·7H ₂ O	80	64	53	34	83	This work

^a Values recorded at the maximum yield of cyclohexene.

^b n.p.: not provided.

^c The initial selectivity of cyclohexene obtained by extending the fitted linear relationship of selectivity against t to $t = 0$

^d Reaction conditions: 0.50g of catalyst, 30 mL of benzene, 60 ml of H₂O, 12.0 g of ZnSO₄·7H₂O, reaction temperature of 413 K, overall pressure of 5.0 MPa, and stirring rate of 1000 rpm.

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