SUPPLEMENTARY INFORMATION

Synthesis of Niobium-doped Titanate Nanotubes as Solid Acid Catalysts

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Table S1 Nb contents of Nb-TiO_2 and Nb-TiNTs measured by ICP and XPS.

Catalyst	Nb/Ti ratio (%)	
	ICP	XPS
Nb(1%)-TiO_2	0.8	1.6
Nb(1%)-TiNT	0.9	1.7
Nb(5%)-TiO_2	4.7	9.2
Nb(5%)-TiNT	4.9	10
Nb(10%)-TiO_2	11	20
Nb(10%)-TiNT	10	25

Table S2 Surface area and pore volume of various titanate materials.

Catalyst	Surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
TiNT	350	0.63
Nb(1%)-TiNT	388	0.87
Nb(3%)-TiNT	423	0.40
Nb(5%)-TiNT	431	0.60
Nb(7%)-TiNT	457	0.58
Nb(10%)-TiNT	438	0.50

Table S3 The catalytic performance of Nb-based catalysts for the alkylation of aromatics with benzyl alcohol.

Catalyst	Substrate	Reaction temperature (K)	Time (h)	Yield (%)	Ref.
Nb(5%)-TiNT	toluene	373	6	100	This work
$Nb_2O_5 \cdot nH_2O$	anisole	Reflux temperature[a]	9	37.6	S1
$Nb_2O_5 \cdot nH_2O$	toluene	Reflux temperature[b]	9	3.3	S1
H_3PO_4 treated $Nb_2O_5 \cdot nH_2O$	anisole	Reflux temperature[a]	9	85.2	S1
H_3PO_4 treated $Nb_2O_5 \cdot nH_2O$	toluene	Reflux temperature[b]	9	31.8	S1
Mesoporous Nb-oxide	anisole	Reflux temperature[a]	9	80	S2
Sulfated Mesoporous Nb-oxide	anisole	Reflux temperature[a]	0.5	100	S2
Nb_2O_5/Al_2O_3	anisole	413	3	50	S3
Layered niobium oxide	anisole	373	2	36.4	S4
$HTiNbO_5$ nanosheets	anisole	373	2	0	S5
HNb_3O_8 nanosheets	anisole	373	2	1.8	S5

[a]The temperature would be higher than 423 K because the boiling temperature of anisole and benzyl alcohol is 426.8 K and 478 K, respectively.

[b]The temperature would be higher than 383 K because the boiling temperature of toluene is 383.6 K.

Table S4 Acid amount of Nb-TiNT.

Catalyst	Acid amount (mmol g^{-1})	
	Brønsted	Lewis
TiNT	0.21	0.27
Nb(1%)-TiNT	0.21	0.21
Nb(5%)-TiNT	0.22	0.23
Nb(10%)-TiNT	0.22	0.27

Table S5 Relative ratios for various acid sites observed in Fig. 9.

Catalyst	Relative ratio (%)			
	56 ppm	61ppm	65 ppm	70 ppm
TiNT	21.2	35.2	27.7	15.8
Nb(1%)-TiNT	18.9	33.8	28.4	18.9
Nb(3%)-TiNT	11.4	38.1	31.1	19.4
Nb(5%)-TiNT	16.8	31.4	31.4	20.5
Nb(7%)-TiNT	16.1	32.8	29.5	21.6
Nb(10%)-TiNT	18.0	31.5	30.3	20.2

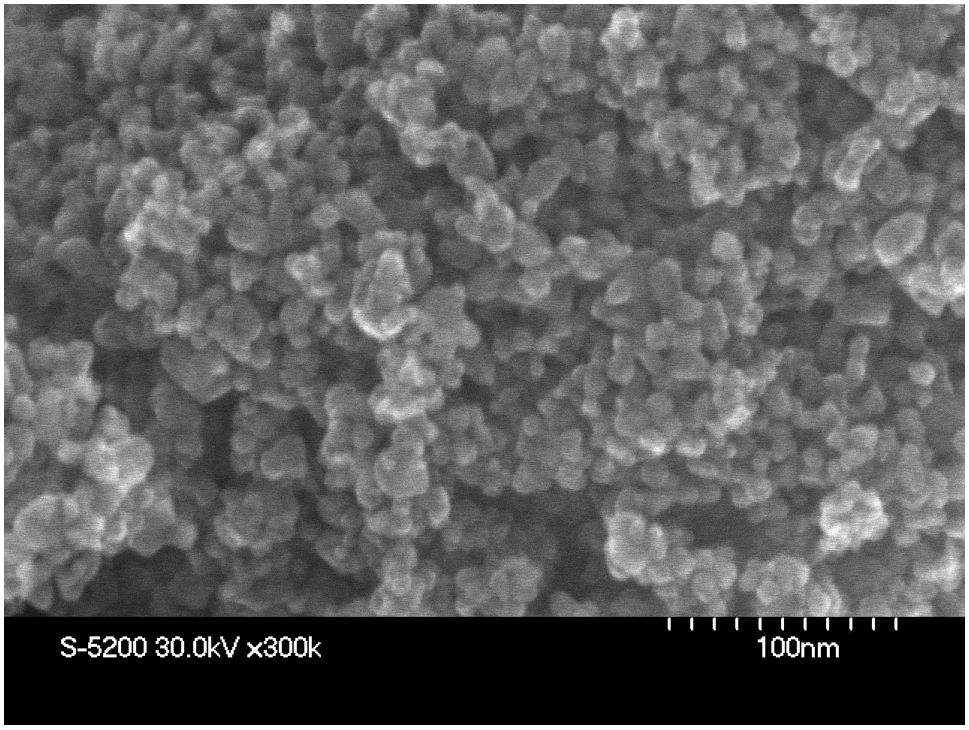

Figure S1 SEM image of Nb(5%)-TiO_2.

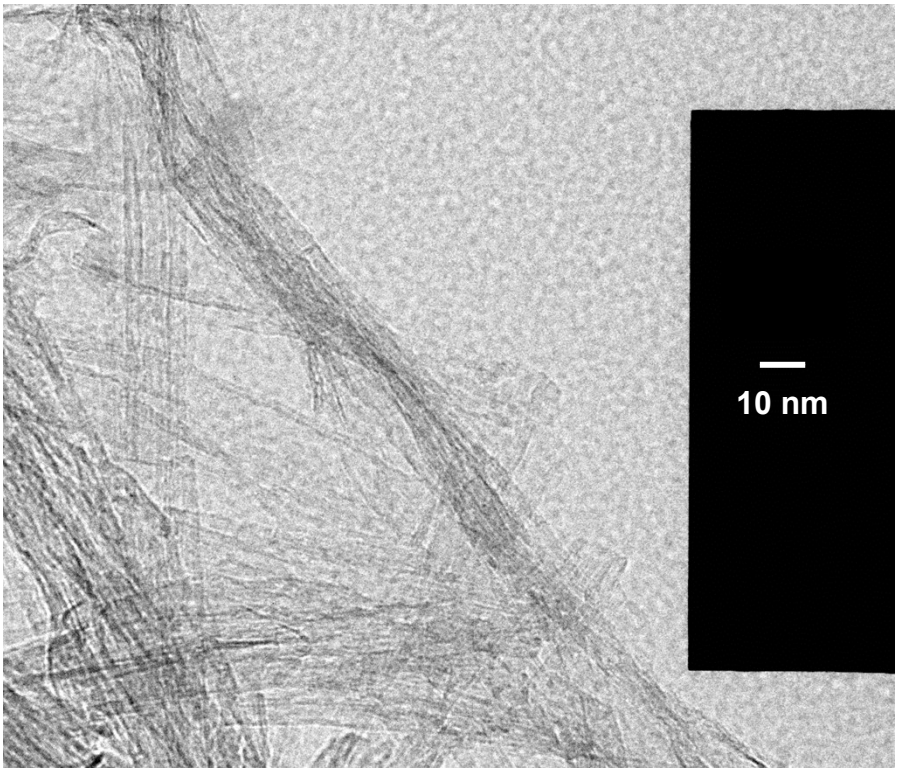

Figure S2 TEM image of Nb(5%)-TiNT.

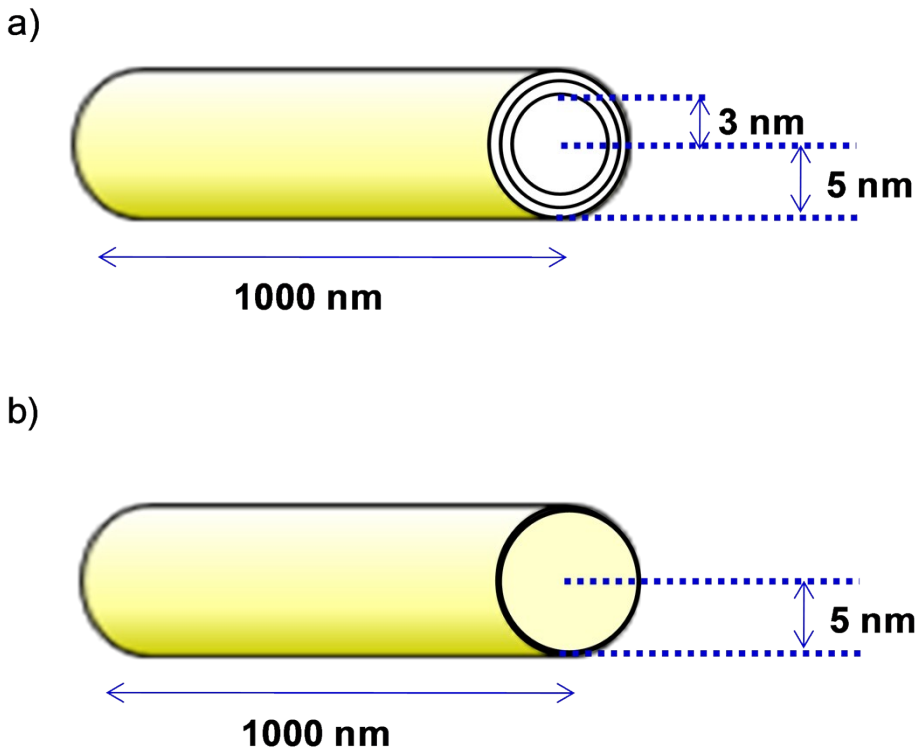

Figure S3 Schematic showing an ideal a) nanotube and b) nanorod model.

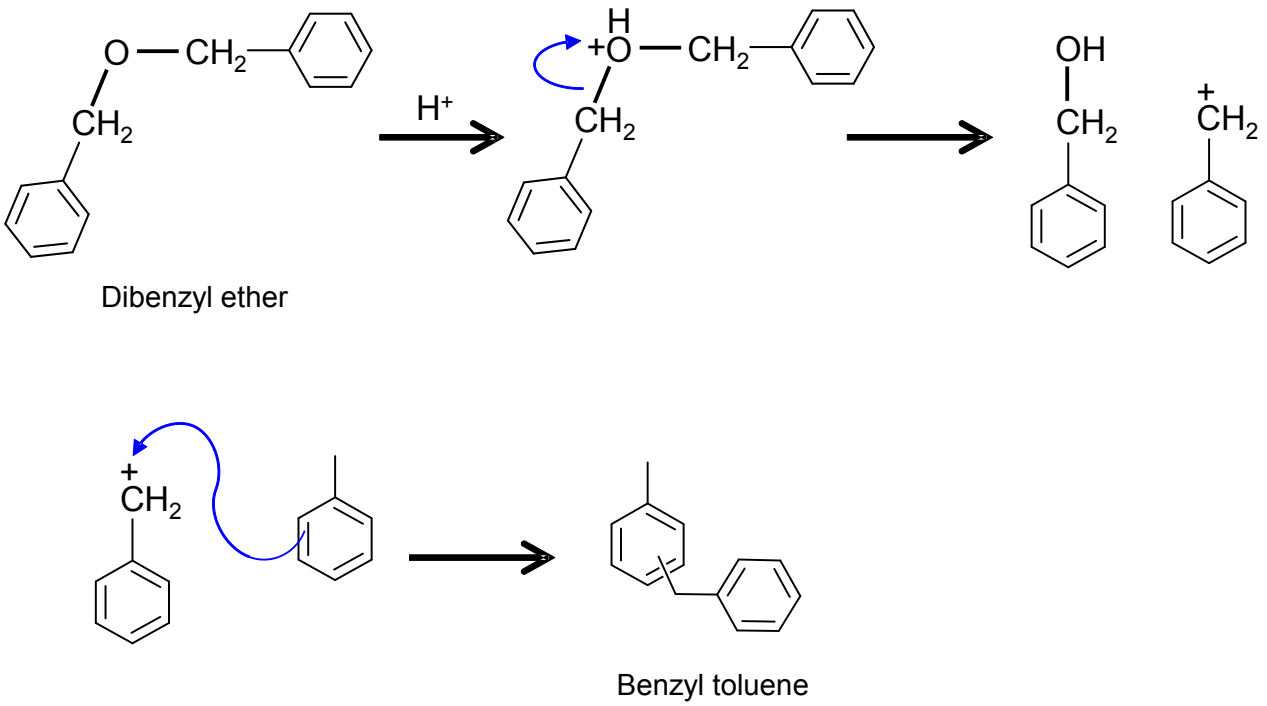

Figure S4 Possible reaction mechanism of the formation of benzyl toluene by the reaction of toluene with dibenzyl ether in the presence of protonic acid catalyst.

References

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