Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Hydrothermal Synthesis of a Layered-type W-Ti-O Mixed Metal Oxide and its Solid Acid Activity

Toru Murayama[1,2], Kiyotaka Nakajima[2,3], Jun Hirata[2], Kaori Omata[2, 5], Emiel J. M. Hensen[4], Wataru Ueda[2, 6]*

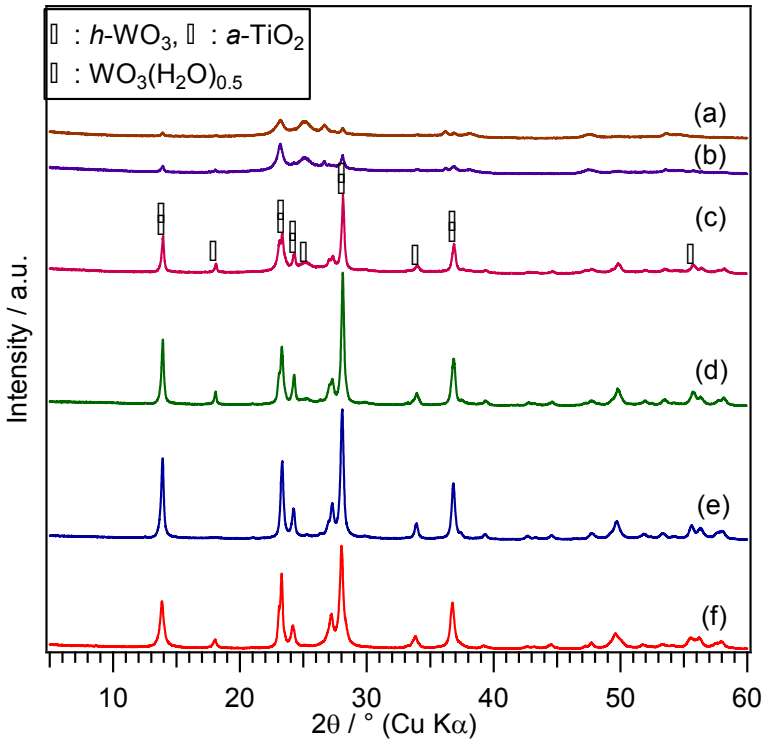


Figure S1. Effects of W / Ti ratio of the precursor on the XRD pattern of W-Ti-O samples. (W / Ti = (a) 3 / 2.84, (b) 3 / 2.13, (c) 3 / 1.42, (d) 3 / 0.711, (e) 3 / 0.5, (f) 3 / 0 (mmol / mmol) in 45 mL of precursor solution)

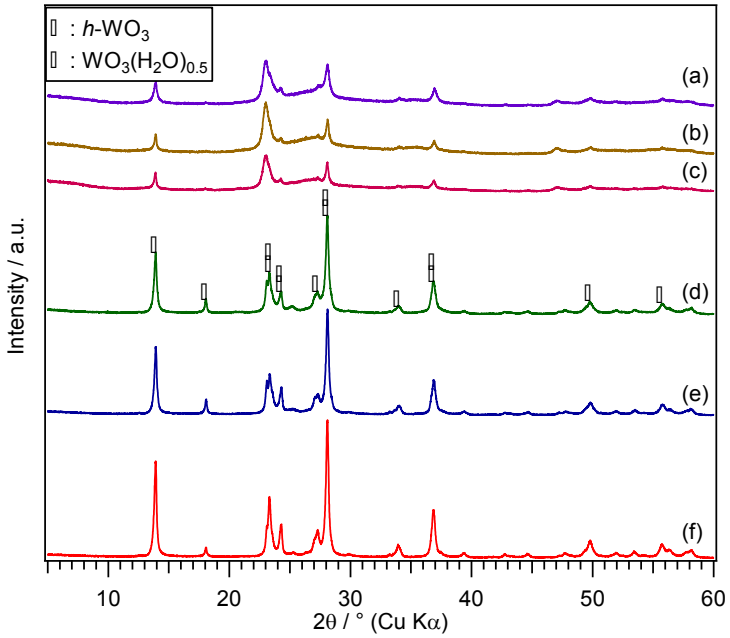


Figure S2. Effects of the amount of oxalic acid on the XRD pattern of W-Ti-O samples. (W / Ti = 3 / 0.711(mmol / mmol), amount of oxalic acid (a) 6 mmol, (b) 5 mmol, (c) 4 mmol, (d) 2 mmol, (e) 1 mmol, (f) 0 mmol in 45 mL of precursor solution)

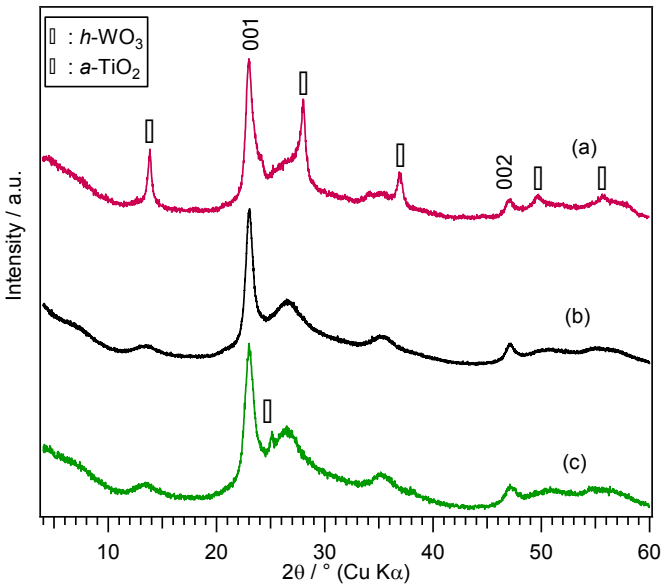


Figure S3. Effects of the ratio of W and Ti in the precursor solution on the XRD pattern of W-Ti-O samples. (W / Ti = (a) 5/1.10, (b) 5/ 1.27 and (c) 5/1.58 (mmol/mmol) with 5 mmol oxalic acid in 45 mL of precursor solution)

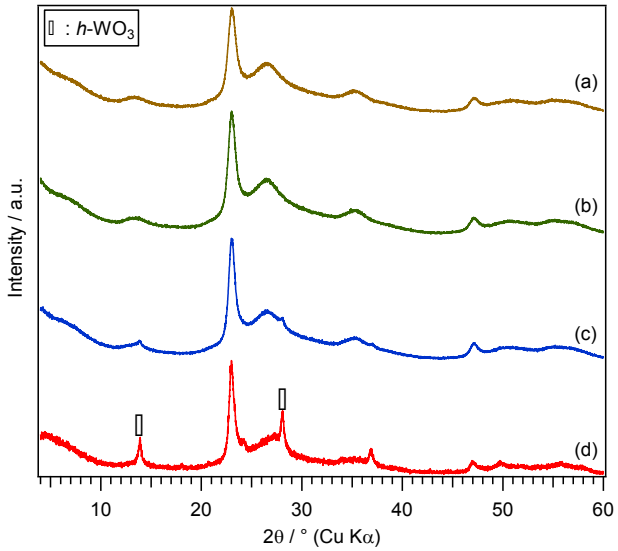


Figure S4. Effects of concentration of the precursor solution on the XRD pattern of W-Ti-O samples. (W / Ti = (a) 15 / 3.56, (b) 5 / 1.27, (c) 4 / 0.925, (d) 3 / 0.711(mmol / mmol) with 5 mmol oxalic acid in 45 mL of precursor solution)

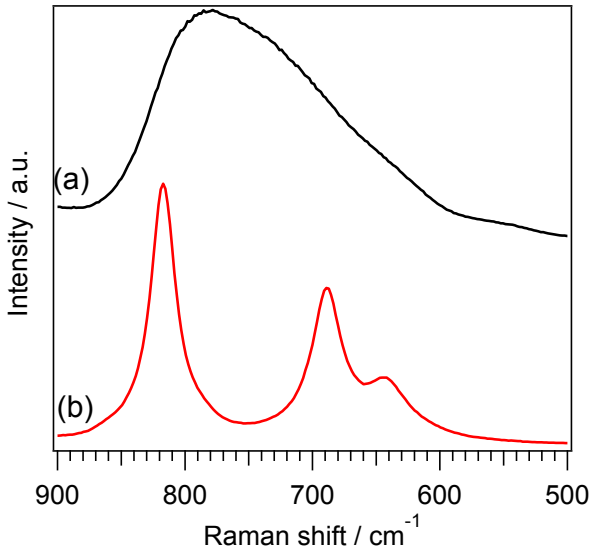


Figure S5. Raman spectra of a) layered-type W-Ti-O and b) hexagonal WO_3.

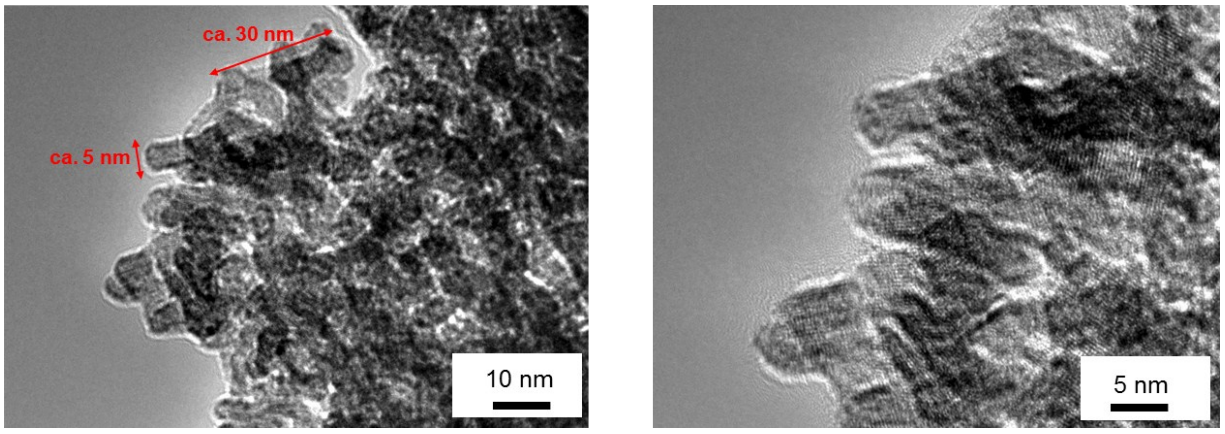


Figure S6. TEM images of the layered-type W-Ti-O catalyst. (Ratio of the precursor was W/ Ti= 5/ 1.27 (mmol/mmol) with oxalic acid (5 mmol).)

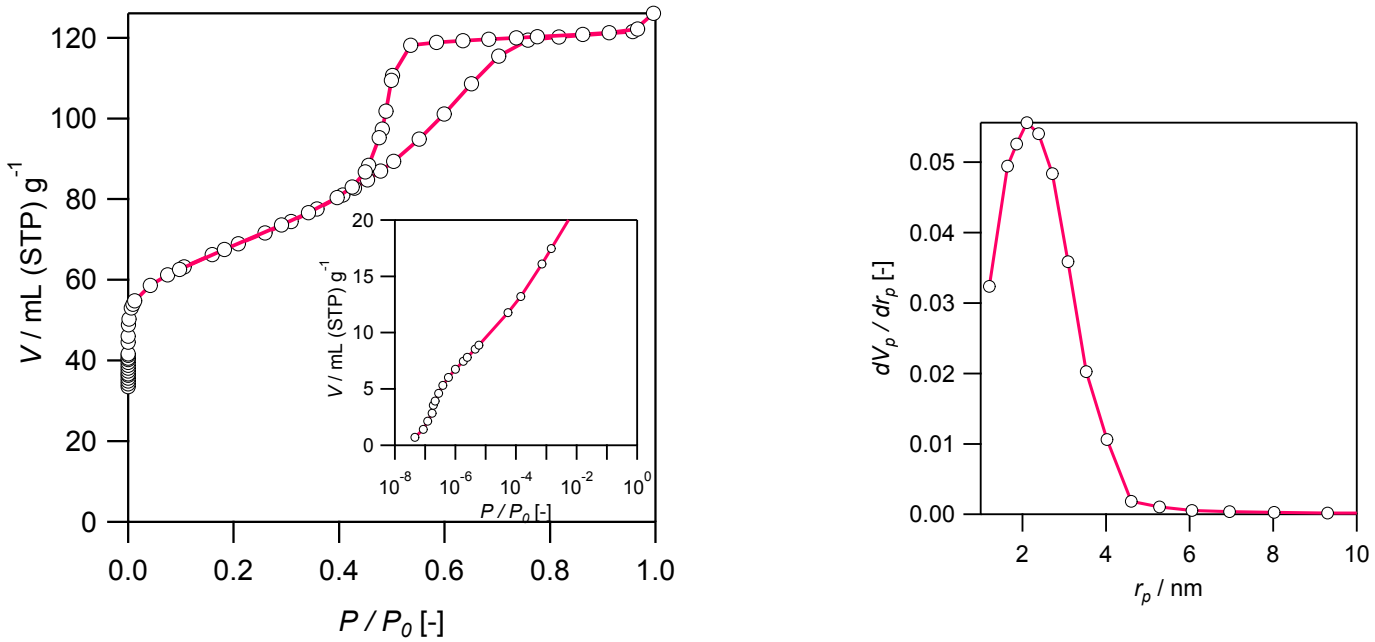


Figure S7. Nitrogen isotherm-adsorption of layered-type W-Ti-O and BJH plot. (Ratio of the precursor was W/ Ti= 5/ 1.27 (mmol/mmol) with oxalic acid (5 mmol) in 45 mL of precursor solution.)

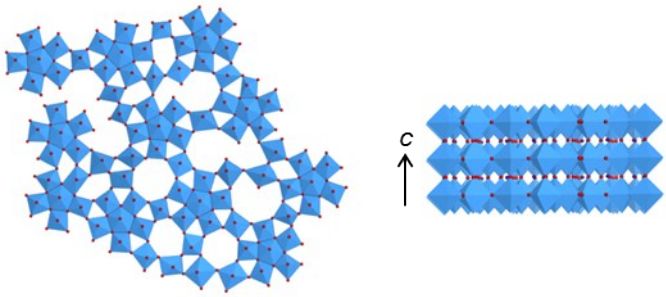


Figure S8. Structure model of the layered-type W-Ti-O sample.

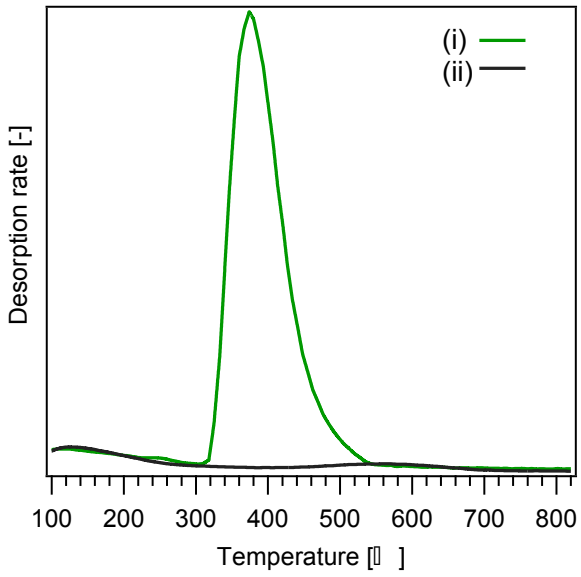


Figure S9. TPD spectra (m/ z = 16) of the layered-type W-Ti-O catalyst in He flow ((i) uncalcined sample and (ii) calcined at 400°C).

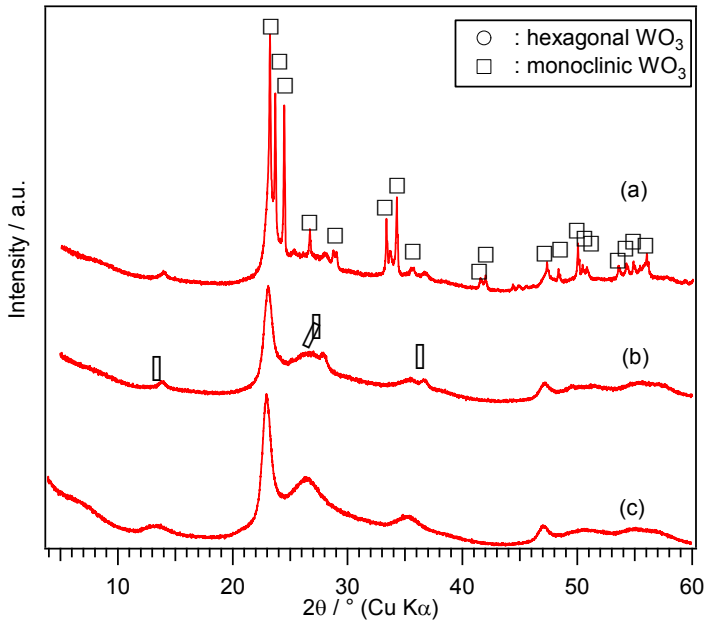


Figure S10. Effects of calcination temperature on the XRD pattern of W-Ti-O samples. ((a) 400°C, (b) 500°C, (c) 600°C)

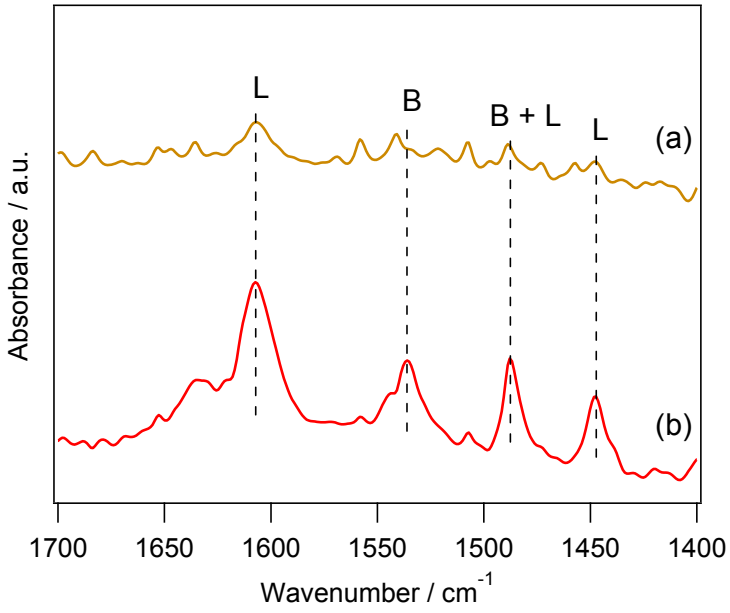


Figure S11. Pyridine-adsorbed FT-IR spectra desorbed at 350°C on (a) hexagonal W-Ti-O and (b) layered-type W-Ti-O catalyst.

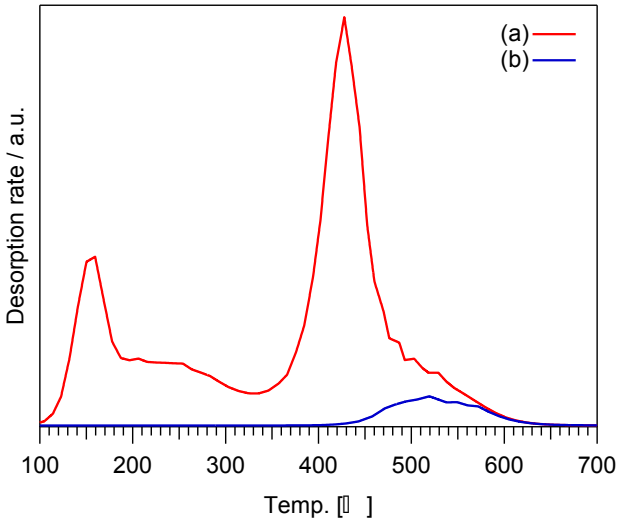


Figure S12. TPD spectra (m/z = 92) of (a) the layered-type W-Ti-O catalyst used for alkylation of toluene and benzyl alcohol at 100°C for 3 h and (b) after calcination at 400°C of the W-Ti-O catalyst used.

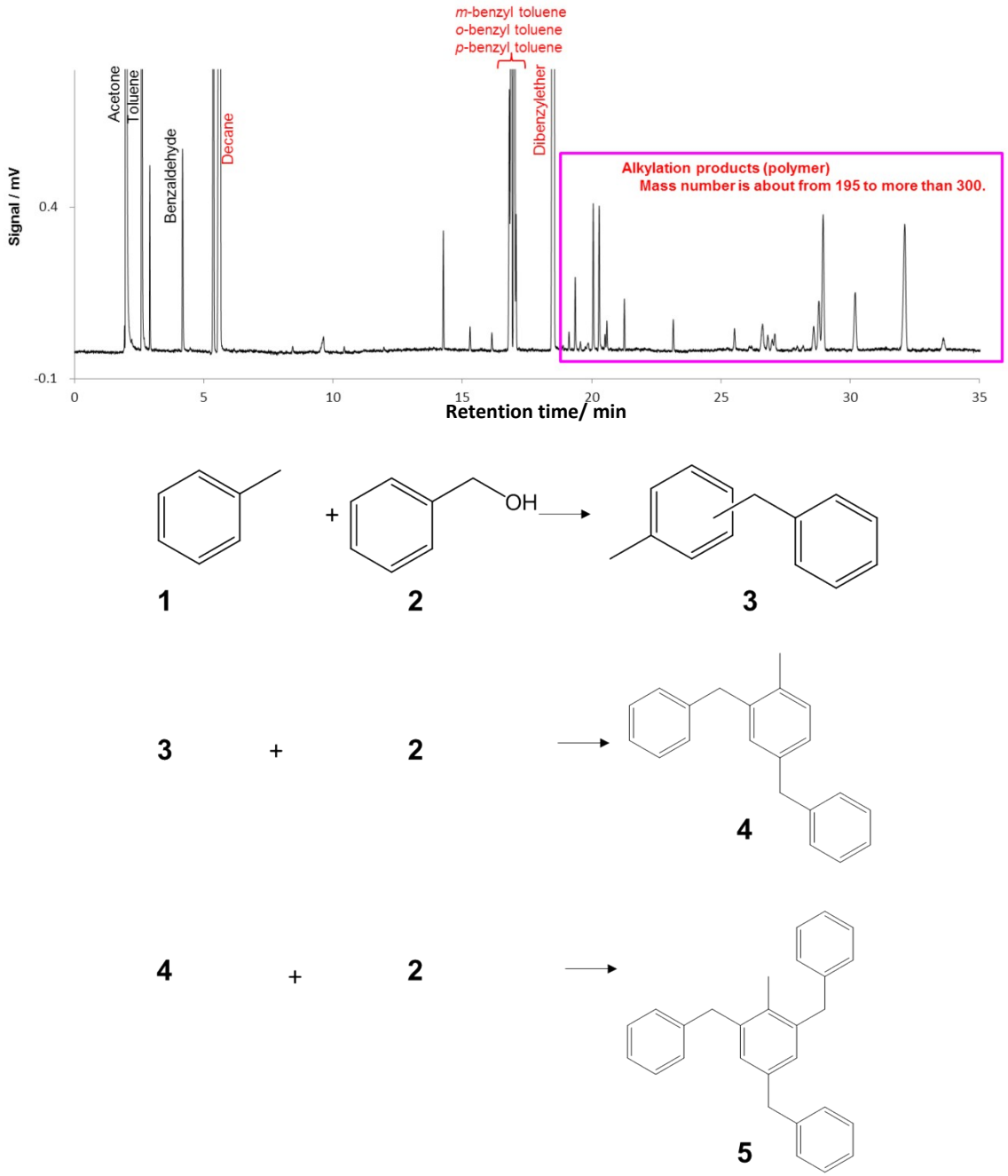
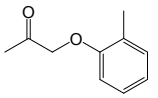


Figure S13. Chromatogram of alkylation products over the layered-type W-Ti-O catalyst. (**1** toluene, **2** benzyl alcohol, **3** benzyltoluene, **4** dibenzyltoluene, **5** tribenzyltoluene)

Table S1. Catalytic activity over the layered-type W-Ti-O sample in the presence of water[a].

Reaction	catalyst	Reaction rate Per weight	Per acid amount	Per surface area
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ (catalyst 0.8 g, 60°C)		mmol g^{-1} min^{-1}	mmol $mmol_{-acid}^{-1}$ min^{-1}	mmol m^{-2} min^{-1}
	Layered-type W-Ti-O	18.7	41.5	0.17
	ZSM-5	19.8	57.4	0.06
	WO_3/TiO_2	2.1	-	-
	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [b]	30.1	200.1	1.9
	SO_4^{2-}/ZrO_2 [b]	25.5	25.5	1.6
	Nb_2O_5 [b]	4.0	12.9	0.24
 + $H_2O \rightarrow$  + CH_3COOH (catalyst 0.2 g, 60°C)		mmol g^{-1} min^{-1}	mmol $mmol_{-acid}^{-1}$ min^{-1}	mmol m^{-2} min^{-1}
	Layered-type W-Ti-O	8.3	18.4	7.8×10^{-2}
	ZSM-5	0.3	0.87	0.1×10^{-2}
	WO_3/TiO_2	3.3	-	-
	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [b]	10.7	71.3	0.42
	SO_4^{2-}/ZrO_2 [b]	0.4	2	0.02
	Nb_2O_5 [b]	0.5	1.7	0.02

[a] Details of reaction conditions are shown in the experimental section, [b] results from the reference [31] in the text.