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Supporting Information

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Sulfated Mesoporous Ta Oxides in the Shape Selective Synthesis of Linear Alkyl Benzene

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The selective synthesis of alkylbenzene is an area of great interest in detergency industry. Because of rapid deactivation and low selectivity, the application of microporous solid acid catalysts in the alkylations involving bulky substrates was limited. In this work, mesoporous Ta oxides were treated with 1.0 M sulfuric acid and evaluated for their catalytic activity and selectivity to 2-phenyl isomers in the alkylation of benzene with bulky olefins.

The acid strength of the solid acids was determined by the color change of the indicators adsored on the surface of solid acid powders. Acid form of the indicators indicates that the acid strength of the solid acid is equal to or higher than that of the indicators. To show the color changes, the indicators were adsorbed on the surface of solid acids by mixing 0.2 g dried solid acids with 2.0 mL solution of indicators in benzene (0.5 wt.%). The p*Ka* of the indicators, the corresponding wt.% of H_2SO_4 solution and color changes were sumarized in Table S3.

The acid amounts of the solid acids were measured by the amine titration method using methyl yellow as indicator. Before titration, H-Y and H-ZSM5 zeolites were activated at 500 ^oC for 3 h in air, whereas sulfated mesoporous Ta and Nb oxides were dried at 120 ^oC for 12 h. The dried samples (0.2 g) were mixed with 3.0 mL indicator solution (0.2 mg methyl yellow per 100 mL benzene) to form the red acidic state of the indicator. Then, 0.1 M *n*-butylamine solution in benzene was added dropwise until the end point at which the red color disappeared. The acid amounts were calculated from the amounts of *n*-butylamine used for the neutralization of the acid sites on solid acids.

XRD and nitrogen adsorption/desorption results demonstrated that the mesostructure was retained during acid treatment. The sulfated mesoporous Ta oxide showed comparable activity to H-Y zeolite, one of the best solid acid catalysts ever reported for liquid-phase alkylation of benzene with olefins, but higher selectivity towards the desired isomer (2-phenyldodecane) under mild reaction

conditions. The high activity and selectivity was rationalized by the eased diffusion of bulky reactants in the mesoporous frames.

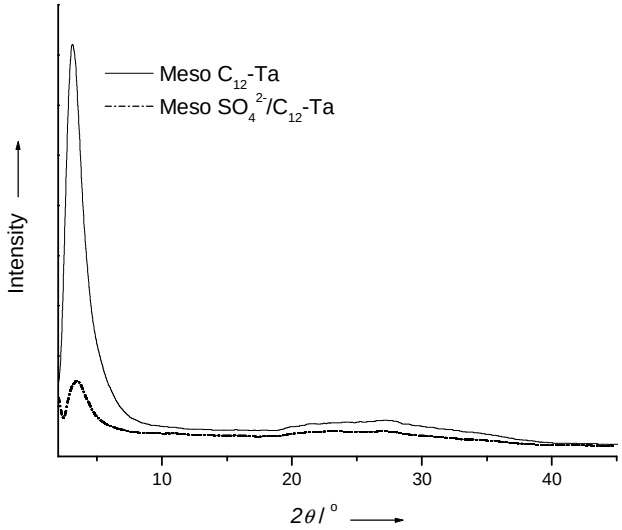

Figure S1. X-ray diffraction patterns of (a) mesoporous C_{12}-Ta oxide and (b) sulfated mesoporous C_{12}-Ta oxide.

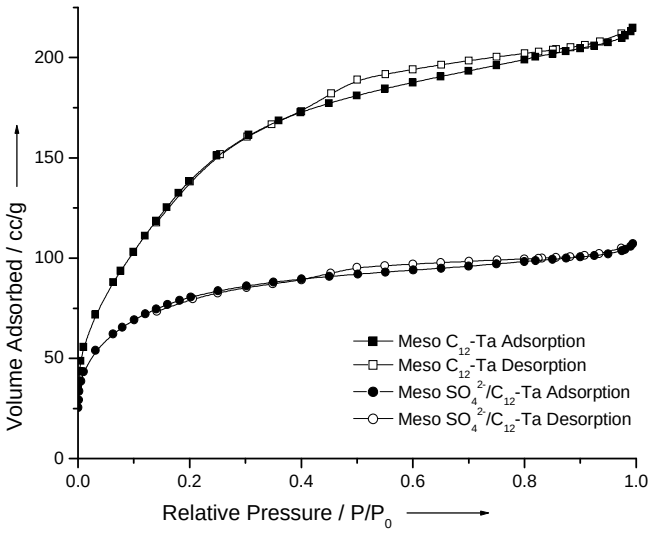

Figure S2. N_2 adsorption/desorption isotherms of (a) mesoporous C_{12}-Ta oxide and (b) sulfated mesoporous C_{12}-Ta oxide.

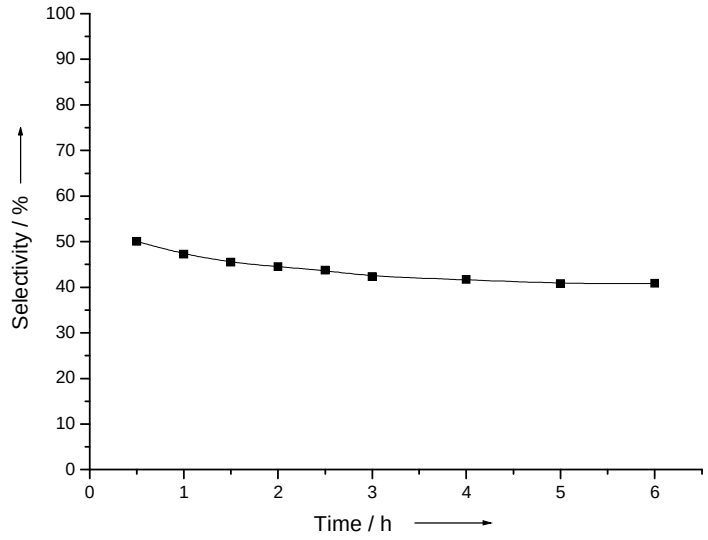

Figure S3. Selectivity to 2-phenyltetradecane over sulfated mesoporous C_{12}-Ta oxide. Reaction conditions: 80 ^{o}C, catalyst loading = 4.0 wt.%.

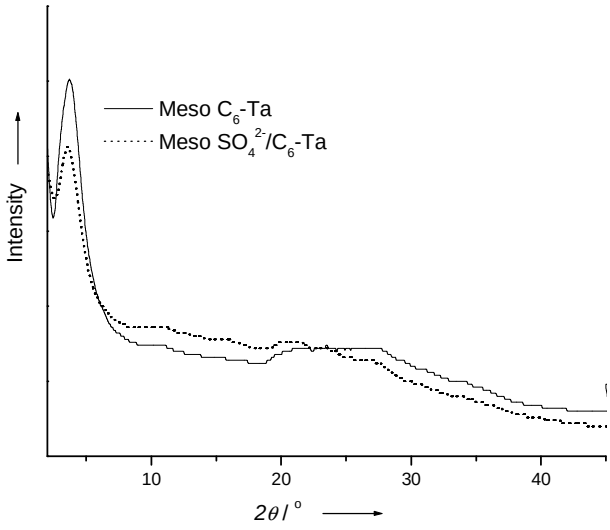

Figure S4. X-ray diffraction patterns of (a) mesoporous C_6-Ta oxide and (b) sulfated mesoporous C_6-Ta oxide.

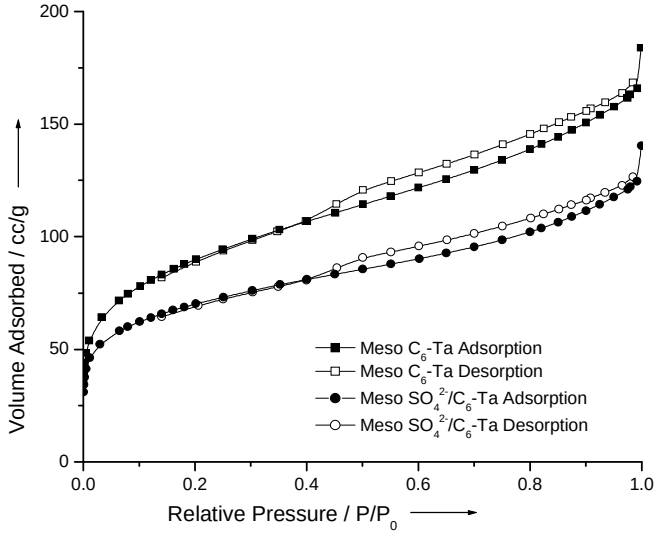

Figure S5. N_2 adsorption/desorption isotherms of (a) mesoporous C_6-Ta oxide and (b) sulfated mesoporous C_6-Ta oxide.

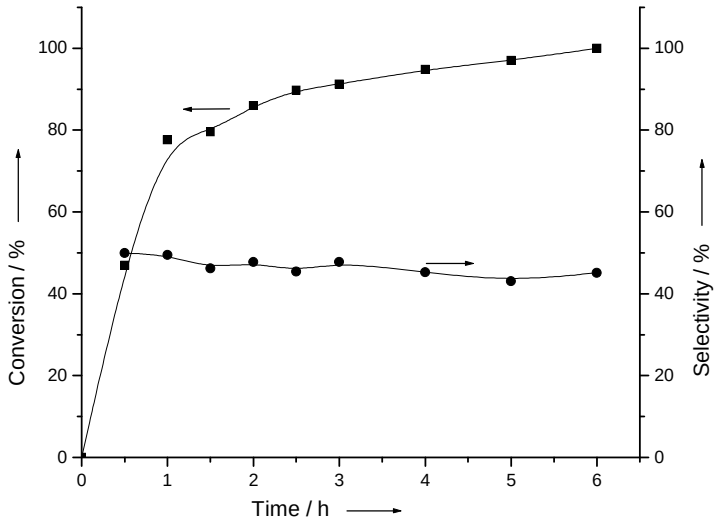

Figure S6. 1-Dodecene conversion and 2-phenyldodecane selectivity over sulfated mesoporous C_6-Ta oxide. Reaction conditions: 80 ^{o}C, catalyst loading = 4.0 wt.%.

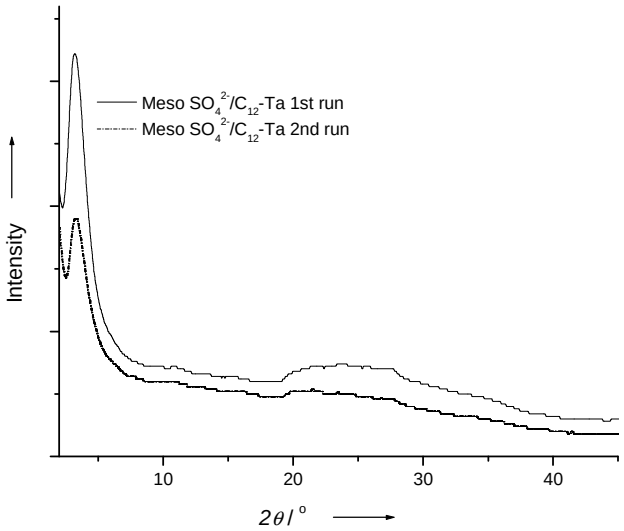

Figure S7. X-ray diffraction patterns of sulfated mesoporous C_{12}-Ta oxide after (a) 1st run and (b) 2nd run.

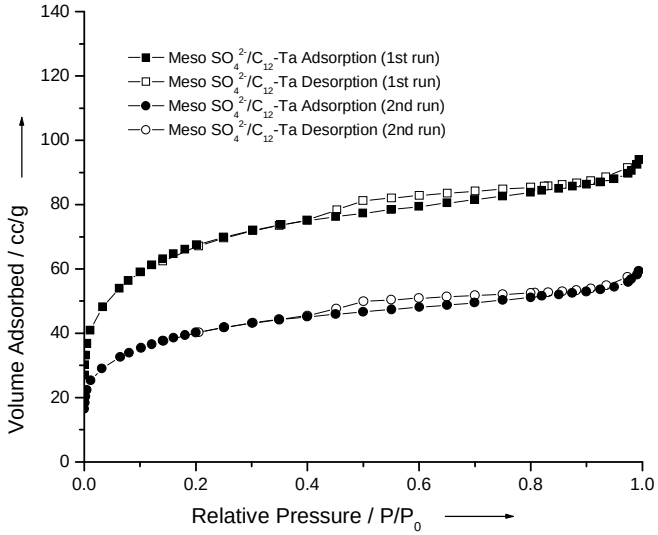

Figure S8. N_2 adsorption/desorption isotherms of sulfated mesoporous C_{12}-Ta oxide after (a) 1st run and (b) 2nd run.

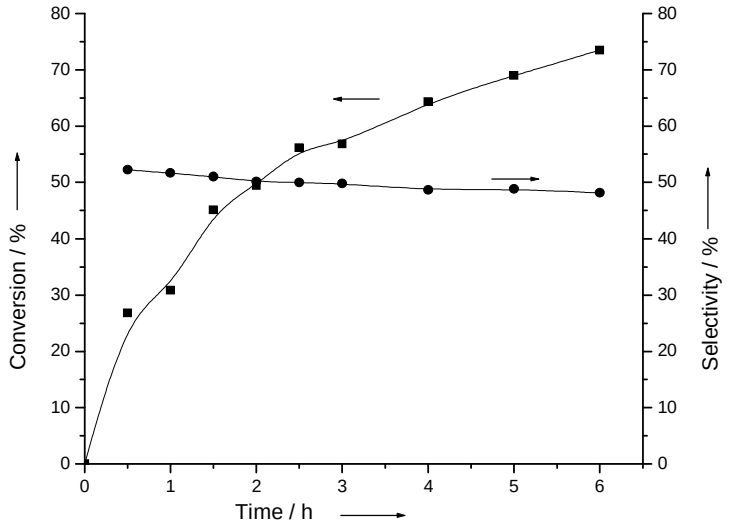

Figure S9. 1-Dodecene conversion and 2-phenyldodecane selectivity over sulfated mesoporous C_{12}-Ta oxide in 2nd run. Reaction conditions: 80 ^{o}C, catalyst loading = 4.0 wt.%.

Table S1. The internal structures and surface properties of mesoporous Ta and Nb oxide before and after sulfuric acid treatment.

	BET surface area [m^2/g]	**Pore volume [cm^3/g]**	**BJH pore size [Å]**
Meso C_6-Ta	253.26	0.1905	17.5
Meso SO_4^{2-}/C_6-Ta	206.40	0.1314	17.0
Meso C_{12}-Ta	582.70	0.3651	18.8
Meso SO_4^{2-}/C_{12}-Ta	292.19	0.0989	18.2
Meso C_{18}-Ta	234.74	0.0538	22.7
Meso SO_4^{2-}/C_{18}-Ta	188.79	0.0347	22.5
Meso C_{12}-Nb	612.02	0.3199	20.6
Meso SO_4^{2-}/C_{12}-Nb	413.97	0.2423	20.5

Table S2. Properties of the recovered sulfated mesoporous C_{12}-Ta oxide.

	BET surface area [m^2/g]	**Pore volume [cm^3/g]**
1st run	241.5	0.0872
2nd run	143.7	0.0583

Table S3. Acid strength of solid acids determined with Hammett indicators.

Indicator	**p*Ka***	**[H_2SO_4] [%]**	**Meso C_{12}-Ta**	**Meso SO_4^{2-} / C_{12}-Ta**	**Meso C_{12}-Nb**	**Meso SO_4^{2-} / C_{12}-Nb**	**H-Y zeolite**	**H-ZSM5**
Methyl red	+5.0	-	+	+	+	+	+	+
Methyl yellow	+3.3	3×10^{-4}	+	+	+	+	+	+
Crystal Violet	+0.8	0.1	+	+	+	+	+	+
Dicinnamalacetone	-3.0	48	+	+	+	+	+	+
2,4-Dinitroaniline	-4.4	-	+	+	+	+	+	+
Benzalacetophenone	-5.6	71	+	+	+	+	+	-
2-Bromo-4,6-dinitroaniline	-6.6	-	+	+	+	+	+	-
9,10-Anthraquinone	-8.2	90	-	+	-	+	-	-
3-Nitrotoluene	-11.99	>100	-	-	-	-	-	-
1-chloro-4-Nitrobenzene	-12.70	>100	-	-	-	-	-	-
2,4-Dinitrofluorobenzene	-14.52	>100	-	-	-	-	-	-

"+" color changed, "-" color unchanged.