Alkylation-Acylation of Aromatics with γ-Butyrolactone Catalyzed by Heteropolyacids Supported on Silica

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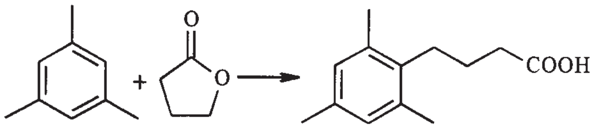
Silica-supported $H_4SiW_{12}O_{40}$ catalyzed efficiently alkylation/acylation of 1,3,5-trimethylbenzene or *p*-xylene with γ-butyrolactone to 4-(2,4,6-trimethylphenyl) butyric acid or to dimethyl-α-tetralone (5,8-dimethyl-3,4-dihydro-2H-naphtalen-1-one), while other typical solid acids such as zeolites and SiO_2-Al_2O_3 were much less active.

Derivatives of α-tetralone (3,4-dihydro-2H-naphtalen-1-one) are important raw materials for medical supplies. Practically, α-tetralone has been synthesized from benzene and succinic anhydride via multi-steps.[1,2] While one-step synthesis of α-tetralone from benzene using γ-butyrolactone was proposed, until the present day, only a system using an excess amount of $AlCl_3$ has been reported.[3,4]

Here we wish to report the catalytic synthesis of dimethyl-α-tetralone from γ-butyrolactone by using the supported heteropolyacids. The catalytic activities for 1,3,5-trimethylbenzene with γ-butyrolactone (Eq. (1)) were first examined over various solids. Then the reaction of *p*-xylene with γ-butyrolactone (Eq. (2)) was performed with the selected solid acid catalysts.



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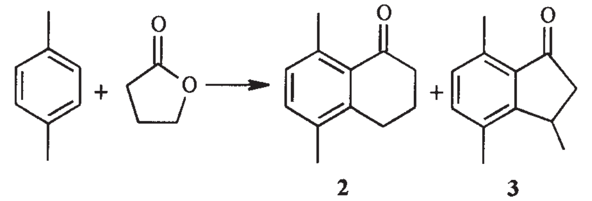

(2)

2 **3**

The reactions of 1,3,5-trimethylbenzene and *p*-xylene with γ-butyrolactone were performed in a stainless autoclave (volume, 100 or 40 cm^3) using a mixture of 1,3,5-trimethylbenzene (40 cm^3, 288 mmol) and γ-butyrolactone (2.6 cm^3, 34 mmol) and a mixture of *p*-xylene (81 mmol) and γ-butyrolactone (0.74 mmol), respectively. The following solid acids were used; $H_3PW_{12}O_{40}$ (6 m^2g^{-1}) and $H_4SiW_{12}O_{40}$ (5 m^2g^{-1}, Nippon Inorganic Color and Chemical) and their silica (Aerosil 300, 274 m^2g^{-1})-supported catalysts (abbreviated as $HSiW/SiO_2$ and HPW/SiO_2, respectively) calcined at 523 K in air. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared as described previously.[5,6] H-β zeolite (Si/Al = 12.5, Sud Chem.), H-ZSM-5 (Tosoh, HSZ-860HOA, Si/Al = 37), H-Y (JRC-Z-HY 4.8, Si/Al = 2.4), H-mordenite (JRC-Z-HM-20, Si/Al = 10), and SiO_2-Al_2O_3 (JRC-SAL 2, 546 m^2g^{-1}) were also used after the calcination at 773 K in air. The products were analyzed with a GC (Shimadzu 14B) with a capillary column (5%PHME silane), ^{1}H NMR spectrometer, GC-MS, and IR spectrometer.

Table 1 summarizes the catalytic data for the reaction of 1,3,5-trimethylbenzene with γ-butyrolactone over various solid acids. The main product was identified to 4-(2,4,6-trimethylphenyl) butyric acid (**1** in Eq. (1)) with the GC, IR spectrometer, ^{1}H NMR spectrometer, and GC-MS, showing that the alkylation took place. A possible product by the acylation, 4-hydroxy-1-(2,4,6-trimethylphenyl)-butan-1-one and derivatives were little formed under these reaction conditions. Table 1 demonstrates that the heteropolyacids and their SiO_2-supported catalysts exhibited high conversions of γ-butyrolactone and the yields of **1**. On the contrary, zeolites (H-β, H-Y, H-ZSM-5, and H-mordenite), and SiO_2-Al_2O_3 gave poor activities for the formation of **1**. While H-β gave a high conversion of γ-butyrolactone, the product was only the oligomers. The superiority of these heteropoly compounds in the yield suggests that their strong acidities[6–8] are responsible for the acceleration of the reaction.

Table 1. Catalytic data for reaction between 1,3,5-trimethylbenzene and γ-butyrolactone

Catalyst	Conv. /%	Yield /%	TON[a]	S[b] /%	M.B.[c] /%
10 wt%$HSiW/SiO_2$	44.9	30.7	49.1	97.1	87
10 wt%HPW/SiO_2	41.6	25.1	56.2	100.0	84
$H_4SiW_{12}O_{40}$	85.1	33.5	5.4	97.6	49
$H_3PW_{12}O_{40}$	91.0	46.6	10.4	96.3	56
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	60.9	23.5	34.9	88.9	66
H-Y	11.7	2.6	0.2	67.9	91
H-ZSM-5	4.1	1.7	1.2	40.4	91
H-β	47.2	0.0	0.0	0.0	53
H-mordenite	5.9	0.0	0.0	0.0	94
SiO_2-Al_2O_3	17.7	0.0	0.0	0.0	82

[a]Turnover number defined by the ratio of the amount of product to the total amount of acid sites. [b]Selectivity was defined as the percent of **1** among all the products detected by GC. [c]Mass balance on the basis of γ-butyrolactone. Reaction conditions: 1,3,5-trimethylbenzene 288 mmol, γ-butyrolactone 34 mmol, catalyst weight: 1.5 g, 453 K and 6 h.

Table 1 further shows that the supported heteropolyacids exhibited high selectivities and mass-balances ($\geqq$84%). When the loading amount of $H_4SiW_{12}O_{40}$ was varied, the yield gave a maximum (about 51%) at 40 wt% of the loading, while the mass balance decreased as the loading amount of $H_4SiW_{12}O_{40}$ increased.

Figure 1 shows the results of repeated runs over 10 wt%$HSiW/SiO_2$. Between the runs, the solid catalyst was

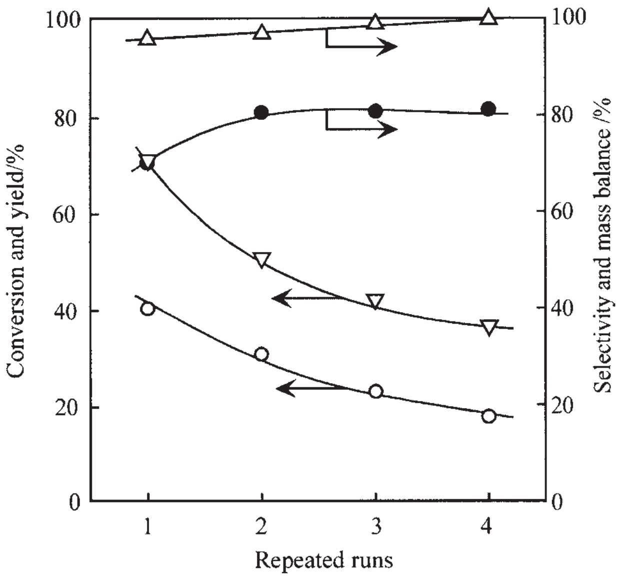

Figure 1. Changes of conversion, yield, selectivity and mass balance by repeating the reaction of 1,3,5-trimethylbenzene with γ-butyrolactone over 10 wt%$H_4SiW_{12}O_{40}/SiO_2$. (▽): Conversion of γ-butyrolactone, (○): Yield, (●) Mass balance, (△): Selectivity of 4-(2,4,6-trimethylphenyl) butyric acid. Reaction conditions: 1,3,5-trimethylbenzene 288 mmol, γ-butyrolactone 34 mmol, catalyst 3.0 g, 453 K, 6 h.

separated from the reaction suspension, and washed with *n*-hexane at room temperature. It should be noted that the conversion tended to reach a near constant value, indicating that this solid was reusable for this reaction.

Table 2 presents the results of the synthesis of 5,8-dimethyl-α-tetralone from γ-butyrolactone and *p*-xylene. Both 10 wt% and 25 wt%$HSiW/SiO_2$ gave higher yields than those over the other solid acids. Especially, the yield over 25 wt%$HSiW/SiO_2$ reached about 70%. It is presumed that the alkylation/acylation took place subsequently and selectively over the supported heteropoly acids. In conclusion, SiO_2-supported heteropolyacids were excellent for one-step synthesis of dimethyl-α-tetralone from *p*-xylene and γ-butyrolactone.

There are some reports as for analogous reactions catalyzed by heteropoly compounds. Izumi et al. showed that an acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, was active for acylation with benzoic anhydride.[9] Corma et al.[10,11] studied acylation/alkylation of anisole with α,β-unsaturated acids like crotonic acid. They claimed that $H_3PW_{12}O_{40}/SiO_2$ was more active and selective towards acylation reactions than zeolites such as HY and Hβ, when the activity was compared in the unit of acid amount. Kozhevnikov et al.[12] reported Friedel-Crafts acylation of anisole with acetic anhydride over heteropolyacids like $H_3PW_{12}O_{40}$. However, the direct synthesis of tetralone-derivatives from γ-butyrolactone has not been reported yet. Thus this is the first example for the catalytic synthesis of α-tetralone derivatives.

Table 2. Synthesis of dimethyl-α-tetralone from *p*-xylene and γ-butyrolactone over various solid acid catalysts

Catalyst	Conv. /%	Yield /%	TON[a]	S[b] /%	M.B.[c] /%
10 wt%$HSiW/SiO_2$	67.5	47.7	15.7	86.4	84
25 wt%$HSiW/SiO_2$	75.2	68.7	9.1	78.7	99
$H_4SiW_{12}O_{40}$	16.6	2.9	0.1	61.8	88
H-Y	33.8	5.3	0.1	42.0	73
H-ZSM-5	27.4	2.4	0.4	100.0	75
H-β	55.6	16.2	0.4	86.4	63

[a]Turnover number defined by the ratio of the amount of product to the total amount of acid sites. [b]Selectivity was calculated as percent of **2** among all the products detected by GC. [c]Mass balance on the basis of γ-butyrolactone. Reaction conditions: *p*-xylene 81 mmol, γ-butyrolactone 0.74 mmol, catalyst weight: 0.16 g, 483 K and 2 h.

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