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Acceptorless dehydrogenative lactonization of diols by Pt-loaded SnO_2 catalysts†

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We report herein a new heterogeneous catalytic system for dehydrogenative lactonization of various diols under solvent-free and acceptor-free conditions using 1 mol% of Pt-loaded SnO_2, providing the first successful example of acceptorless lactonization of 1,6-hexanediol to ε-caprolactone by a heterogeneous catalyst.

Lactones are important compounds in organic synthesis and industrial production of solvents, flavors, and pharmaceutical compounds. Dehydrogenative[1–8] and oxidative[9–20] lactonizations of diols are potentially useful methods for the synthesis of lactones. A number of homogeneous and heterogeneous catalytic systems have been reported to be effective for the oxidative lactonization of diols by oxidants, such as carbonyl compounds,[9–14] oxygen[15–19] and hydrogen peroxide.[20] In view of atom-efficiency, a more preferable methodology is lactonization of diols in the absence of an oxidant (acceptor) *via* an acceptorless dehydrogenative coupling strategy.[21] Homogeneous Ru[1,2,4] and Ir[3,5] catalysts were reported to be effective for this reaction, but these systems suffer from difficulties in catalyst/product separation and catalyst reuse except for a Ir-catalyzed system recently reported by Fujita *et al.*[5] Although heterogeneous Cu catalysts are effective for the gas phase dehydrogenative lactonization of 1,4-butanediol,[6,7] these systems suffer from limited scope. An exceptional example of the heterogeneous catalytic system for acceptorless lactonization of various diols is reported by Kaneda *et al.*[8] using 7.1 mol% of Cu-loaded hydrotalcite. During our continuing studies in heterogeneous Pt catalysts for acceptorless dehydrogenation of alcohols,[22] dehydrogenative coupling of *o*-aminobenzamide with alcohols[23] and acceptorless self-coupling of primary alcohols to esters,[24] we found a new heterogeneous catalyst for the acceptorless lactonization; the solvent-free and acceptor-free lactonization of various diols was effectively catalyzed by 1 mol% of Pt-loaded SnO_2 (Pt/SnO_2).

As listed in Table 1, we tested lactonization of 1,2-benzenedimethanol **1a** under solvent-free conditions in N_2 at 180 °C for 36 h as a model reaction using the catalysts containing 1 mol% (0.01 mmol) of transition metals (Pt, Ir, Re, Pd, Rh, Ru, Ag, Ni, Cu, Co). Among various transition metal-loaded SnO_2 (entries 1–10), Pt/SnO_2 (entry 1) showed the highest yield (90%) of the corresponding lactone, phthalide **2a**. GCMS and TLC analyses of the reaction mixture showed no indication of byproducts such as products of intermolecular reactions such as oligomers. The lactonization of **1a** did not occur in the presence of 39 mg of SnO_2 itself (entry 11). Comparison of various Pt catalysts on different support materials (SnO_2, Al_2O_3, Nb_2O_5, C, SiO_2, TiO_2, ZrO_2, MgO, HBEA zeolite) shows that SnO_2 is the best support material (entries 1, 12–19).

After the reaction with Pt/SnO_2 for 5 h, we carried out quantification of the H_2 evolved in the gas phase. The yields of gas phase H_2 (35%) and the lactone **2a** (35%) were identical to each other (eqn (1)), indicating that H_2 was evolved quantitatively during the dehydrogenative lactonization. The reaction under N_2 flow did not result in higher yield than the yield under the standard closed system.

Table 2 shows the effect of reaction conditions on the catalytic activity of Pt/SnO_2 for the standard lactonization of **1a**. The reaction under the solvent-free conditions gave higher yield (90%) than the yields (62–80%) in the presence of 1 mL solvents (*o*-xylene, diglyme, mesitylene, *n*-dodecane). In the solvent-free condition, the reaction under 1 atm N_2 gave higher yield than that under 1 atm O_2 (51%). Under O_2, the metallic Pt surface can be partly covered with oxygen atoms, which inhibit the activation of the diol and lower the yield. In the solvent-free condition under N_2, the reaction at lower temperature (150 °C) resulted in low yield of **2a** (55%). Consequently, the standard conditions was found to be the solvent-free conditions under 1 atm N_2 at 180 °C for 36 h, which gave full conversion of **1a** and 90% yield of **2a**. After completion of the reaction, 2-propanol (10 mL) was added

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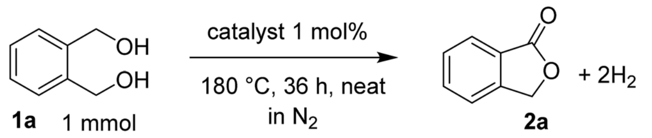
Table 1 Lactonization of 1,2-benzenedimethanol (**1a**) by various catalysts



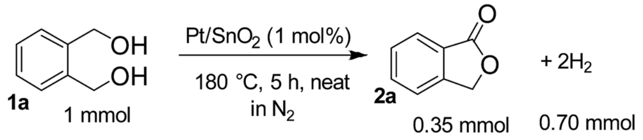
Entry	Catalyst	Conv. (%)	Yield (%)
1	Pt/SnO_2	100	90
2	Ir/SnO_2	15	9
3	Ni/SnO_2	15	7
4	Pd/SnO_2	10	6
5	Co/SnO_2	10	4
6	Rh/SnO_2	5	3
7	Cu/SnO_2	5	1
8	Ru/SnO_2	4	1
9	Re/SnO_2	3	1
10	Ag/SnO_2	2	0
11[a]	SnO_2	0	0
12	Pt/Al_2O_3	9	3
13	Pt/Nb_2O_5	7	2
14	Pt/C	6	1
15	Pt/SiO_2	2	0
16	Pt/TiO_2	2	0
17	Pt/ZrO_2	2	0
18	Pt/MgO	5	0
19	Pt/HBEA	2	0

[a] Catalyst amount was 39 mg.

Table 2 Lactonization of **1a** by Pt/SnO_2[a]

Solvent	Gas	Conv. (%)	Yield (%)
No solvent	N_2	100	90
o-Xylene	N_2	80	72
Diglyme	N_2	92	80
Mesitylene	N_2	85	76
n-Dodecane	N_2	70	62
No solvent	O_2	67	51
No solvent (150 °C)	N_2	69	55

[a] Conditions: 1 mol% Pt/SnO_2 (0.01 mmol Pt), 1 mmol **1a**, 0 or 1 mL solvent, 180 °C, 36 h. Yield was determined by GC.



(1)

to the reaction mixture and catalyst was separated by centrifugation. The catalyst was then washed by acetone three times, followed by centrifugation and drying in oven (under air) at 90 °C for 3 h, followed by H_2-reduction at 150 °C for 0.5 h. The recovered catalyst was reused three times, but the yield of **2a** gradually decreased with increase in the cycle (Fig. 1). ICP-AES analysis of the solution after the first cycle showed that the content of Pt in the solution (1.6 ppm, 0.02% of Pt in the catalyst used) and that of Sn (3.0 ppm, 0.002% of Sn in the catalyst used) were quite low.

To study the substrate scope of the present catalytic system, the reactions of various diols were conducted (Table 3). Benzylic diols (entries 1–4), linear (entries 5–7) and non-linear (entries 8–11) aliphatic diols were converted to the corresponding lactones in moderate to high yields of 66–90%. GC charts of the reaction mixture for entries 8–10 showed four to five small peaks due to byproducts with high boiling points, but the amount of the byproducts were too small for their identification. From a viewpoint of biorefinery, the lactonization of 1,6-hexanediol (1,6-HD) into ε-caprolactone is of particular importance, because 1,6-HD can be produced by multistep hydrogenation of lignocellulosic biomass such as 5-hydroxymethyl-2-furfural (HMF)[12,13] and furfural[25] and ε-caprolactone can be converted to ε-caprolactam as an important bulk chemical.[12,13] Heeres and co-workers[12,13] reported the first example of the oxidative lactonization of 1,6-HD to ε-caprolactone using methyl isobutyl ketone (MIBK) as oxidant and a Ru complex as homogeneous catalyst, but the system suffers from drawbacks such as a need of excess amount of MIBK and difficulty in catalyst/product separation. Obviously, acceptorless lactonization of 1,6-HD to caprolactone by a heterogeneous catalyst is preferred from an industrial viewpoint. Our result (entry 7) gave the first example of acceptorless lactonization of 1,6-HD by a heterogeneous catalyst, giving ε-caprolactone in high yield (86%). After the reactions, followed by adding 2-propanol (10 mL) to the mixture, Pt/SnO_2 was removed from the mixture and the lactones were isolated by column chromatography, resulting in high isolated yield (81%) of ε-caprolactone.

Recently, we studied the dehydrogenative esterification of primary alcohols to esters by Pt/SnO_2.[24] On the basis of the results of model reactions and the IR result that the benzaldehyde adsorbed on SnO_2 gave the C=O stretching band at lower wavenumber than those on γ-Al_2O_3 and SiO_2, we proposed a possible pathway *via* dehydrogenation alcohol to adsorbed aldehyde species (on Sn^{4+} Lewis acid site) which undergo nucleophilic attack of another alcohol to give hemiacetal followed by its dehydrogenation to the ester. Considering that the similarity between this intermolecular esterification and the

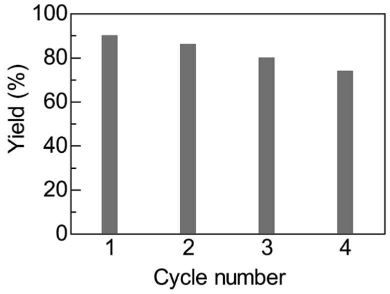
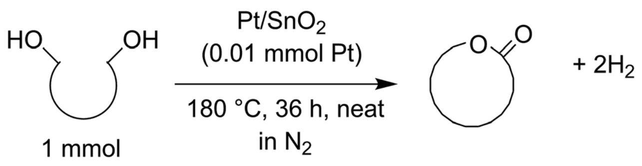
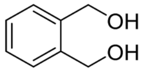
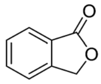
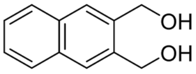
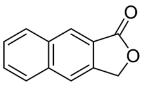
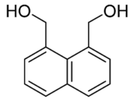
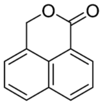
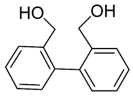
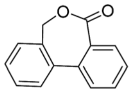
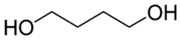
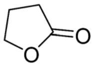
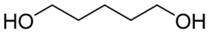
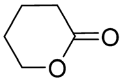
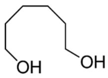
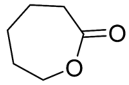
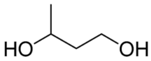
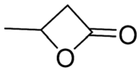
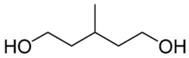
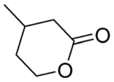
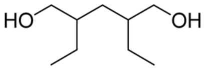
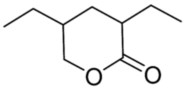
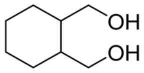
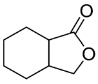


Fig. 1 Reuse of Pt/SnO_2 for lactonization of **1a**. Conditions are shown in Table 1.

Table 3 Dehydrogenative lactonization of various diols catalyzed by Pt/SnO_2



Entry	Diol	Product	Conv. (%)	Yield[a] (%)
1			100	90 (87)
2			93	85 (81)
3			74	66
4			96	83 (78)
5			100	80 (76)
6			100	85 (82)
7			93	86 (81)
8			97	75
9			96	75
10			98	70
11			91	83

[a] GC yields. Isolated yields are in parentheses.

lactonization (intermolecular esterification), it is suggested that Sn^{4+} Lewis acid site is responsible for the high activity of Pt/SnO_2 for the present lactonization system.

In conclusion, we developed a new heterogeneous catalyst, Pt/SnO_2, for the acceptorless dehydrogenative lactonization of diols under solvent-free conditions. The method was effective for the synthesis of various lactones. We gave the first example of the catalytic acceptorless lactonization of 1,6-HD to ε-caprolactone as an intermediate of ε-caprolactam, the monomer for nylon-6. Considering recent advances in the catalytic synthesis of 1,6-HD from biomass-derived furfurals[12,13,25] this method can provide a key process in sustainable production of nylon-6 from renewable resources.

Experimental

Commercially available organic compounds (from Tokyo Chemical Industry or Kanto Chemical) were used without further purification. The GC (Shimadzu GC-2014) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra

ALLOY capillary column UA$^+$-1 (Frontier Laboratories Ltd.) using N_2 and He as the carrier gas.

SnO_2 was prepared by calcination of H_2SnO_3 (Kojundo Chemical Laboratory Co., Ltd.) at 500 °C for 3 h. Nb_2O_5 was prepared by calcination of niobic acid (CBMM) at 500 °C for 3 h. γ-Al_2O_3 was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. ZrO_2 was prepared by calcination (500 °C for 3 h) of $ZrO_2 \cdot nH_2O$ prepared by hydrolysis of zirconium oxynitrate 2-hydrate in water by aqueous NH_4OH solution, followed by filtration of precipitate, washing with water three times, and drying at 100 °C for 12 h. SiO_2 (Q-10, 300 $m^2\ g^{-1}$) was supplied from Fuji Silysia Chemical Ltd. HBEA zeolite (JRC-Z-HB25, $SiO_2/Al_2O_3 = 25 \pm 5$), MgO (JRC-MGO-3), TiO_2 (JRC-TIO-4) were supplied from Catalysis Society of Japan. Active carbon (296 $m^2\ g^{-1}$) was purchased from Kishida Chemical.

Precursor of Pt/SnO_2 was prepared by impregnation method; a mixture of SnO_2 and an aqueous HNO_3 solution of $Pt(NH_3)_2(NO_3)_2$ (Furuya Metal Co, Ltd.) was evaporated at 50 °C, followed by drying at 90 °C for 12 h. Before each catalytic experiment, the Pt/SnO_2 catalyst (containing 5 wt% of Pt) was prepared by *in situ* pre-reduction of the precursor in a pyrex tube under a flow of H_2 (20 $cm^3\ min^{-1}$) at 150 °C for 0.5 h. Other supported Pt catalysts (containing 5 wt% of Pt) were prepared by the same method. SnO_2-supported metal catalysts, M/SnO_2 (M = Pt, Ir, Re, Pd, Rh, Ru, Ag, Ni, Cu, Co) with metal loading of 5 wt% were prepared by the impregnation method in the similar manner as Pt/SnO_2 using aqueous solution of metal nitrates (for Ni, Cu, Co, Ag), $RuCl_3$, $IrCl_3 \cdot nH_2O$ or NH_4ReO_4 or aqueous HNO_3 solution of $Pd(NH_3)_2(NO_3)_2$ (Kojima Chemicals Co, Ltd.).

Pt/SnO_2 was used as a standard catalyst. After the pre-reduction at 150 °C, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air as follows. *n*-Dodecane (0.2 mmol) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube, 18 cm^3) through a septum inlet, followed by adding diols (1 mmol) under ambient conditions and by filling with 1 atm N_2. Then, the mixture was stirred and heated at 180 °C for 36 h. Conversion and yields of products were determined by GC using *n*-dodecane as an internal standard. The products were identified by GC-MS equipped with the same column as GC analyses as well as ^1H NMR and ^{13}C NMR analyses of the isolated products. The analysis of the gas phase product (H_2) was carried out by the mass spectrometer (BELMASS). For the catalytic tests in entries 1, 4, 5 and 7 of Table 2, we determined isolated yields of lactones as follows. After the reaction, the catalyst was removed by filtration and the reaction mixture was concentrated under vacuum evaporator to remove the volatile compounds. Then, the lactones were isolated by column chromatography using silica gel 60 (spherical, 63–210 μm, Kanto Chemical Co. Ltd.) with hexane/ethylacetate (98–80/2–20) as the eluting solvent, followed by analyses by ^1H NMR, ^{13}C NMR and GCMS.

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