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Catalytic activity of lanthanoide(III) ions for dehydration of D-glucose to 5-(hydroxymethyl) furfural

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Abstract

Lanthanoide(III) ions are found to catalyze the dehydration of D-glucose to yield 5-(hydroxymethyl)furfural (HMF). The relationship between the activities and the atomic numbers of the ions follows a double arc-shaped pattern with the break point at Sm³⁺.

Keywords: Lanthanoide; Catalyst; Glucose; Furfural

As fossil fuels become scarcer, cellulose and hemicellulose, the most abundant products of photosynthesis, will become increasingly attractive in the near future as alternative sources of carbon for both chemicals and fuels. From this viewpoint, many studies have already been conducted [1]. However, when cellulose and hemicellulose (both complex macromolecules) are used as substrates for studies, it is difficult to obtain definitive results. Therefore, we have started studies on the catalytic conversion of D-glucose, a component of cellulose and hemicellulose, into useful chemicals.

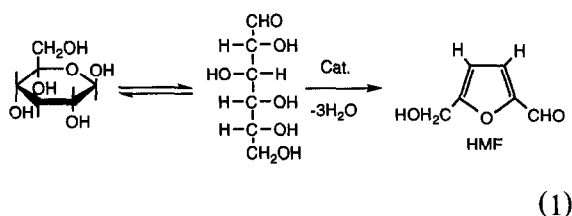
Recently, much attention has been paid to the utilization of lanthanoides as catalysts for organic syntheses because they are cheaper and less toxic than the typical transition metals.

There are many reports about the catalytic activities of lanthanoide ions or compounds for the conversion of tertiary amides to ketones [2], the reactions of amines with nitriles [3], hydroxymethylation [4] or the aldol reactions of silyl enol ethers [5], and so on [6]. However, there have been no reports about the catalytic activity for conversion of sugars (including cellulose) to chemicals. We report here that lanthanoide(III) ions were found to catalyze D-glucose dehydration to produce 5-(hydroxymethyl)furfural (HMF), which is a very expensive chemical. We will also describe the relationship between the catalytic activities and the atomic numbers of the ions.

In a typical experiment, a lanthanoide(III) ion (2.0×10^{-3} mol dm⁻³) as a catalyst and D-glucose (0.30 mol dm⁻³) as a substrate in a water solution (15 cm³) were placed in a glass tube. All lanthanoide(III) ions were purchased as

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chloride salts except for praseodymium(III) which was purchased as the acetate from Wako Pure Chemical Industries. The hydrogenation of D-glucose was carried out by heating a stainless bomb (100 cm³) containing the glass tube at 140°C under 10 atm of nitrogen pressure. After the reaction finished, the bomb was cooled to room temperature. In order to isolate the product, the reaction solution was extracted with benzene, and the benzene solution was evaporated to yield a pale-brown oil. The ¹H and ¹³C NMR spectra and the mass spectroscopy data of the product were identical with those of 5-(hydroxymethyl)furfural (HMF) (Eq. (1))¹. Quantitative analyses were performed using gas chromatography (Shimadzu GC-9A (FID); Chromosorb W-AW) without extracting the reaction solution with benzene. In almost all cases, the yields of HMF increased almost linearly with time up to ca. 60 min, at which saturation was then reached. For example, when YbCl₃ was used as the catalyst, the yield at the saturation point was 24.2 mmol dm⁻³. In the absence of the lanthanoide(III) ions, formation of a trace amount (less than 1 mmol dm⁻³) of HMF was observed. For comparison, activities of the typical transition metal ions, RuCl₃ and PdCl₂, were also tested. However, only trace amounts of HMF were observed in both cases.



In order to further examine the effects of lanthanoide(III) on the catalytic reaction, we

¹ 5-(Hydroxymethyl)furfural: ¹H NMR: δ(400 MHz, CDCl₃), 9.58 (s, 1H), 7.22 (d, 1H), 6.52 (d, 1H), 4.72 (s, 2H), 2.87 (s, 1H); ¹³C NMR: δ(400 MHz, CDCl₃), 177.7 (formyl), 160.7 (C(2)), 152.4 (C(5)), 122.9 (C(3)), 110.0 (C(4)), 57.6 (-CH₂-); MS: *m/e* 126 (M+).

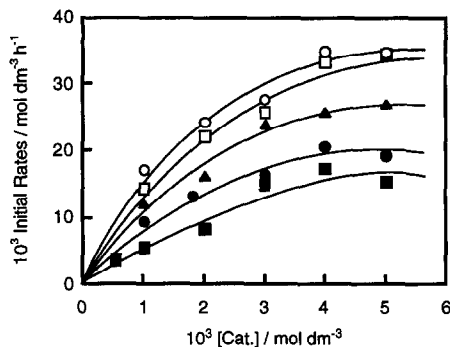


Fig. 1. Dependencies of the initial rates of D-glucose dehydration on the lanthanoide(III) ion concentration: LaCl₃ (■), NdCl₃ (●), EuCl₃ (▲), DyCl₃ (□), and YbCl₃ (○). Experimental conditions are described in the text.

determined the initial rates obtained from the time dependent formation of HMF at various concentrations of the catalysts (Fig. 1). In almost all cases, the catalytic activities attained maximum saturation at a catalyst concentration around 5.0×10^{-3} mol dm⁻³. Therefore, we estimated the degree of efficiency of the catalytic activities of the ions using the initial rates (2.0×10^{-3} mol dm⁻³) at the concentration of the lanthanoide(III) ions (Fig. 2). The relationship between the activities and the atomic numbers of the lanthanoide(III) ions is not linear and follows a double arc-shaped pattern with the first arc between La³⁺ and Sm³⁺ with its apex at Nd³⁺ and the second and higher arc between

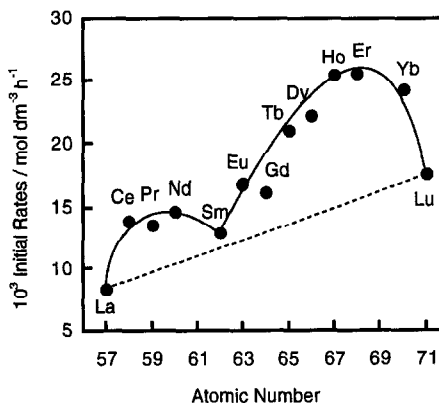


Fig. 2. Relationship between the atomic numbers of the lanthanoide(III) ions and the initial rates of HMF generation at a catalyst concentration of 2.0×10^{-3} mol dm⁻³.

Sm^{3+} and Lu^{3+} with Er^{3+} as its peak. Interestingly, this pattern is very similar to that showing the relationship between the magnetic moment and their atomic numbers [7].

Pentose and hexose are generally known to be dehydrated when using an acid catalyst such as sulfuric acid to yield furfural and 5-(hydroxymethyl)furfural (HMF), respectively [1]. However, in the case of hexose, HMF quickly decomposes into levulinic acid which is much cheaper than HMF in the presence of sulfuric acid [1]. We postulate that the lanthanoid(III) ions catalyze the dehydration of D-glucose to HMF and no further decomposition takes place at least under the present reaction conditions. Furthermore, we postulate that the lanthanoid(III) ions coordinate with D-glucose and act as Lewis acid catalysts for the present reaction because the lanthanoid(III) ions are known to have a high affinity for oxygen atoms. In order to examine the interaction between the lanthanoid(III) ions and D-glucose, we measured the NMR spectra for the mixture of lanthanoid(III) ions and D-glucose in D_2O ; however, no spectral changes were found. This suggests that D-glucose does not substitute for water molecules which coordinate to the lanthanoid(III) ions at room temperature. From this, we surmise that the relationship between the catalytic activities and their atomic numbers may relate to the degree of facile coordination of D-glucose by the lanthanoid(III) ions.

In summary, we found that the lanthanoid(III) ions catalyze the dehydration of D-glucose to produce 5-(hydroxymethyl)furfural (HMF), which is only slightly decomposed un-

der the same reaction conditions. The correlation between catalytic activities and the atomic numbers of the lanthanoid(III) ions was found to follow a double arc-shaped pattern with the break point at Sm^{3+} . This finding is helpful for designing more active catalysts. Further investigation from the viewpoint of the interaction between the lanthanoid(III) ions and D-glucose is currently in progress.

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