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## ***N,N*-Dimethylformamide-stabilized ruthenium nanoparticle catalyst for $\beta$ -alkylated dimer alcohol formation via Guerbet reaction of primary alcohols†**

Tatsuki Nagata,<sup>a</sup> Kanji Okada,<sup>a</sup> Ryota Kondo,<sup>a</sup> Takashi Toyao,<sup>b</sup> Ken-ichi Shimizu,<sup>b</sup> Takeyuki Suzuki<sup>c</sup> and Yasushi Obora<sup>a</sup>                                        <img alt="OR

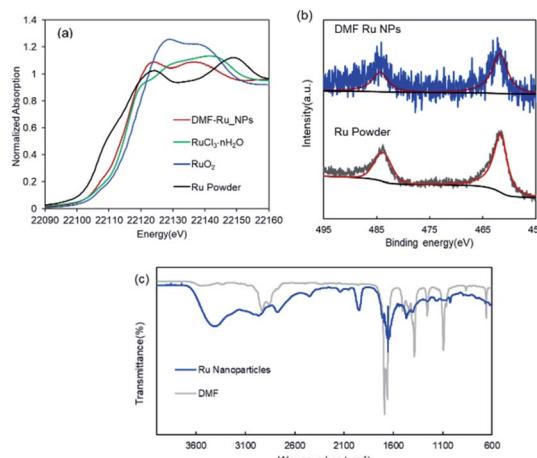


Fig. 2 (a) Ru K-edge XANES spectra of DMF-stabilized Ru NPs (red), RuO<sub>2</sub>, and Ru powder; (b) Ru 3p XPS spectra of DMF-stabilized Ru NPs (blue) and Ru powder (gray); and (c) FT-IR spectra of DMF-stabilized Ru NPs (blue) and DMF (gray).

The electronic state of the Ru species in the DMF-stabilized Ru NPs was clarified. The X-ray absorption near-edge structure (XANES) spectrum was compared with those of metallic Ru powder and RuO<sub>2</sub> (Fig. 2a). The absorption edge position of the DMF-stabilized Ru NPs lay between those for metallic Ru and RuO<sub>2</sub>, which indicates that reduced Ru species were formed by reduction of the precursor (Ru<sup>III</sup>). Fig. 2b shows the X-ray photoelectron spectroscopy (XPS) results for the DMF-stabilized Ru NPs. Ru signals ascribed to Ru 3p<sub>3/2</sub>, 3p<sub>1/2</sub>, and 3d<sub>5/2</sub> are present at 461.5, 444.2, and 280.8 eV, respectively; in the Ru powder spectrum, the signals appear at 461.2 and 279.9 eV, respectively in addition C 1s signals were detected at 284.2, 284.9, 286.0 (Fig. 2b and S1†).<sup>15</sup> Formation of the DMF-stabilized Ru NPs by reduction of the Ru precursor is consistent with the XANES analysis. Fourier-transform infrared (FT-

IR) spectra were recorded. Fig. 2c shows the Ru NP spectrum after DMF removal. The absorption peaks for the C=O (1652 cm<sup>-1</sup>) and C-N (1390 cm<sup>-1</sup>) vibrational modes of DMF in the spectrum of the DMF-stabilized Ru NPs differ from those in the spectrum of the DMF solvent. The IR absorption attributed to metal carbonyl in the absence of DMF appears at approximately 1950 cm<sup>-1</sup>. This suggests that CO generated from DMF interacts with metal species.<sup>16</sup>

In this process, DMF acts as a reducing agent at above 100 °C in metal nanoparticle synthesis and the DMF molecules strongly coordinate to the metal center and stabilize the Ru NPs.<sup>13</sup>

Thermogravimetric (TG) analysis was used to investigate the thermal stability of the Ru NPs (Fig. S2†). The TG curves in the range 50–400 °C suggest that the DMF-stabilized Ru NPs were stabilized by various molecules on the surface. The 5% weight loss temperature of the Ru NPs was 190 °C, whereas the decomposition temperature of Ru<sub>3</sub>(CO)<sub>12</sub> was reported in the 160–220 °C range.<sup>17</sup> The decomposition products were identified by thermogravimetry-electron ionization high-resolution time-of-flight mass (TG-EI-HR-TOF MS) analysis of the Ru NPs; H<sub>2</sub>O, DMF, CO, CO<sub>2</sub>, and dimethylamine were detected (Fig. S3–S5†). These compounds were derived from the Ru NPs. DMF decomposes to give dimethylamine, CO<sub>2</sub> and CO.<sup>18</sup> Four ions (DMF, dimethylamine, CO<sub>2</sub>, and CO) were used to analyze the thermal behavior of the Ru NPs. The extracted ion chromatograms of these ions are shown in Fig. S5.† Dimethylamine, which was released around 100–550 °C, is a product of DMF thermal decomposition. DMF was also released at 100–280 °C. Dimethylamine and DMF served as a part of stabilizer. On heating the Ru NPs, a portion of the stabilizers DMF and dimethylamine were expected to be liberated from the Ru metal, generating Ru NPs with partially open sites that could act as active catalysts. Considerable attention must be given to the temperature at which CO is detected because it can also be formed *via* CO<sub>2</sub> fragmentation. CO was detected, not

Table 1 Alkylation of 1-dodecanol with various Ru catalysts<sup>a</sup>

Entry	Ru catalyst	1-dodecanol 1a	Catalyst (0.05 mol%) Base (10 mol%), 150 °C, neat, 24 h	 2a			
					Base	Conv. (%)	Yield <sup>b</sup> (%) (selectivity, %)
1	Ru NPs		KO'Bu		95		93 (98) [83]
2	Ru NPs		KOH		85		83 (98)
3	Ru NPs		Cs <sub>2</sub> CO <sub>3</sub>		12		2 (17)
4	Ru NPs		K <sub>2</sub> CO <sub>3</sub>		15		3 (20)
5	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub>		KO'Bu		35		30 (86)
6	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>		KO'Bu		60		55 (92)
7	Ru <sub>3</sub> CO <sub>12</sub>		KO'Bu		47		28 (60)
8	RuCl <sub>3</sub> · <i>n</i> H <sub>2</sub> O		KO'Bu		40		33 (83)
9	Ru NPs		None		<1		n.d.
10	None		KO'Bu		5		Trace

<sup>a</sup> Reaction conditions: 1a (2 mmol) was reacted in the presence of a Ru catalyst (0.05 mol%) and base (0.2 mmol) at 150 °C for 24 h. <sup>b</sup> GC yield based on 1a. Numbers in square brackets show isolated yields. n.d. = not detected by GC. Numbers in parentheses show selectivity of 2a = [yield (%) 1a]/[conv. (%) 1a].



simultaneously with  $\text{CO}_2$  and DMF, at approximately  $280\text{ }^\circ\text{C}$  and above  $400\text{ }^\circ\text{C}$ . These results suggest partial CO desorption from the Ru NPs.

Next, we investigated the Guerbet reaction of 1-dodecanol (**1a**) as a model substrate under various conditions (Table 1). The reaction of **1a** (2 mmol) was performed in the presence of Ru NPs (0.05 mol%), with  $\text{KO}^\text{t}\text{Bu}$  (0.2 mmol) as a base, at  $150\text{ }^\circ\text{C}$  for 24 h; the main  $\beta$ -alkylated product **2a** was obtained in a moderate yield of 93% and with 98% selectivity (Table 1, entry 1). The effect of the base was then determined. A strong base such as KOH gave the desired **2a** in 83% yield, whereas weak inorganic bases such as  $\text{Cs}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  were ineffective (Table 1, entries 2–4). Other Ru complexes gave the desired product in moderate yields (Table 1, entries 5–7). Use of the M NP precursor ( $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ ) as the catalyst resulted in a low yield and selectivity (Table 1, entry 8). At this time, the metal black formation significantly decreased catalytic activity. The reaction did not proceed in the absence of a base (Table 1, entry 9) and Ru NPs (Table 1, entry 10). This shows that the catalyst and base are both necessary for alkylation.

The reaction scope was investigated under the optimal reaction conditions (Table 1, entry 1); the results are shown in Fig. 3. The reaction with any C16 to C4 aliphatic primary alcohols gave the corresponding Guerbet alcohols (**2b**–**2i**). Aliphatic alcohols with short carbon chains resulted in low yields. Similarly, 1-cyclohexylpropanol and tetrahydrogeraniol were efficiently alkylated to give **2j** and **2k** in good yields (74% and 64%, respectively).

The reusability of the Ru NPs was investigated (Fig. 4). The substrates and desired products were removed by distillation (40 Pa,  $130\text{ }^\circ\text{C}$ ). The base was then removed from the mixture by filtering through a cotton plug (for details see Fig. S6†). The Ru NPs retained their catalytic activity and selectivity over several cycles without the need for preactivation.

The feasibility of this transformation was demonstrated by the gram-scale synthesis of **2a** (Fig. 5). Specifically, **1a** (8.8

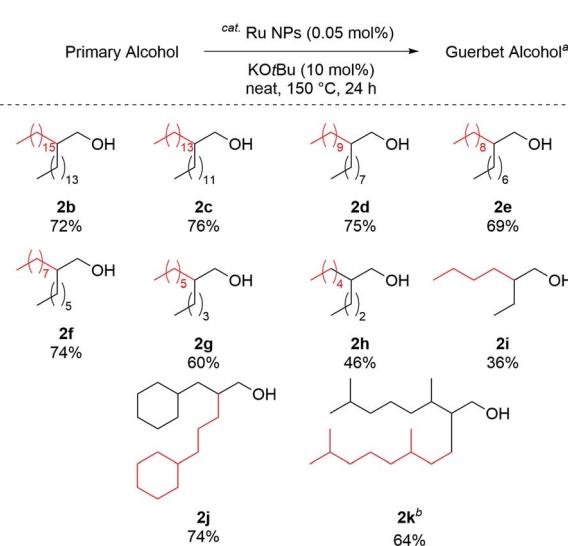


Fig. 3 Substrate scope. <sup>a</sup> Reaction conditions, Table 1, entry 1. <sup>b</sup> 72 h.

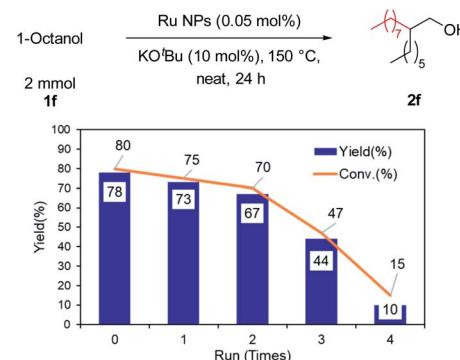


Fig. 4 DMF-stabilized Ru NP reuse in Guerbet reaction of 1-octanol.

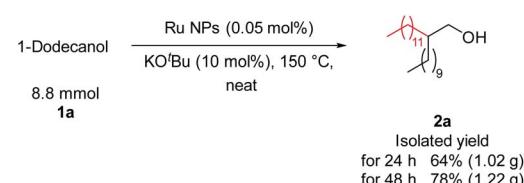


Fig. 5 1 g scale synthesis of **2a**.

mmol) was stirred at  $150\text{ }^\circ\text{C}$  for 48 h in the presence of Ru NPs (0.05 mol%),  $\text{KO}^\text{t}\text{Bu}$  (0.88 mmol, 10 mol%), which afforded **2a** in good yield (1.22 g). This result supports the scalability of the process.

The Ru NPs were characterized by STEM, X-ray absorption spectroscopy, and XPS to elucidate the reasons for their high catalytic activity. After the 1st reaction, the Ru NP mean diameter had increased slightly to 4.4 nm (Fig. 6a and S7†). The XANES spectrum of the used Ru NPs was similar to that of the fresh Ru NPs (Fig. 6b, green). The Ru  $3\text{p}_{3/2}$ , Ru  $3\text{p}_{1/2}$ ,  $3\text{d}_{5/2}$  peaks of the used Ru NPs appeared at 461.4, 483.7, 280.1 eV, respectively (Fig. S8†). These results suggest that the Ru species in the DMF-stabilized Ru NPs were retained after several uses. The DLS analysis showed that the size of Ru NPs increased after 4th reuse (Fig. S9†). The size increase and aggregation of the metal nanoparticles would decrease the catalytic activity during the recycling process.<sup>19,20</sup>

Fig. 7 shows the time-dependent production of intermediates and the desired products during the Guerbet reaction. The yield of **2a** gradually increased, with low yields of reaction

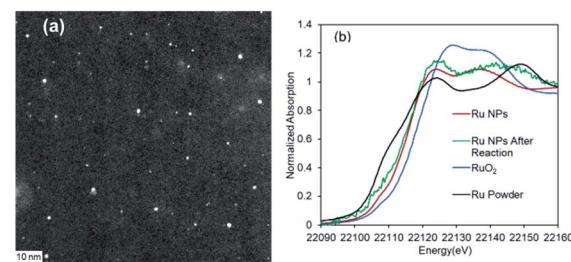


Fig. 6 (a) ADF-STEM image of Ru NPs after reaction and (b) Ru K-edge XANES spectra of Ru NPs before (red) and after reaction (green).



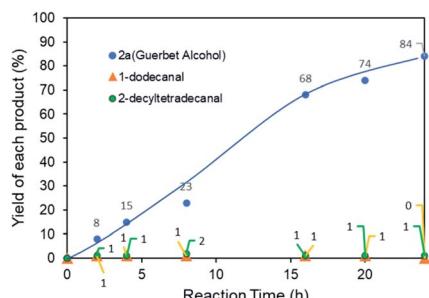


Fig. 7 Time course of reaction with DMF-stabilized Ru NPs.

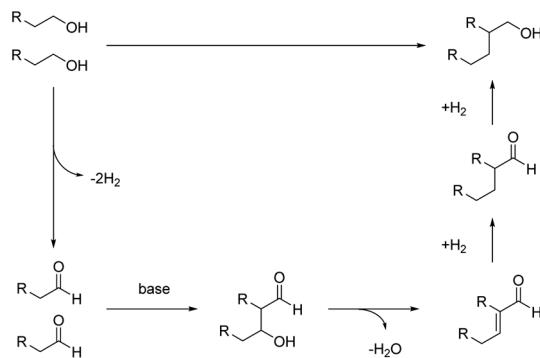


Fig. 8 Plausible reaction pathway for Guerbet reaction with DMF-stabilized Ru NPs.

intermediates such as 1-dodecanal and 1-decyldodecanal. The produced aldehyde intermediates were immediately consumed. Use of the Ru NP catalyst minimized byproduct formation because of their high dehydrogenation/hydrogenation properties in the Guerbet reaction.<sup>7a,b</sup>

Based on our experiments, a plausible catalytic mechanism is proposed for the  $\beta$ -alkylation of primary alcohols. As shown in Fig. 8, the primary alcohol is oxidized to give an aldehyde. In the presence of a base, the initially formed aldehydes condense to give the unsaturated aldehyde (aldol condensation). The  $\alpha,\beta$ -unsaturated aldehyde then undergoes hydrogenation in the presence of Ru NPs to generate the desired Guerbet alcohol.

## Conclusions

$\beta$ -Alkylation of primary alcohols to branched alcohols under mild reaction conditions was achieved by using a DMF-stabilized Ru NP catalyst. The Ru NP catalyst promoted the Guerbet reaction under external ligand- and solvent-free conditions. Various primary alcohols were converted into the corresponding branched alcohols in high yields. This catalytic system has significant advantages, namely mild operating conditions, a simple catalyst preparation procedure, high catalyst reusability, and a broad substrate scope. Its use will enable green sustainable Guerbet reactions to be performed.

## Conflicts of interest

There are no conflicts to declare.

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