Electronic supplementary information (ESI) for

Effects of Ruthenium Hydride Species on Primary Amine Synthesis

by Direct Amination of Alcohols over Heterogeneous Ru Catalyst

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1. Materials

The following materials were used as received: $Ru(NO)(NO_3)_3$ (Aldrich, 1.5) wt% solution), Mg(NO₃)₂•6H₂O (Aldrich), Sr(NO₃)₂ (Kanto), Ba(NO₃)₂ (Kanto), Ca(NO₃)₂•4H₂O (Wako), aqueous ammonia (Wako), toluene (Kanto), isopropanol (Kanto), monochlorobenzene (Kanto), furfuryl alcohol (TCI), benzyl alcohol (TCI), 4-dimethylaminophenylmethanol (TCI), 4-methoxybenzyl alcohol (TCI), 4-(TCI), chlorophenylmethanol (TCI), 4-trifluoromethylbenzyl alcohol 3methoxybenzyl alcohol (TCI), 2-methoxybenzyl alcohol (TCI), 2,5bis(hydroxymethyl)furan (TCI), benzhydrol (TCI), octanol (TCI), tetrahydrofuran indole-5-methanol (Wako), (+/-)-1-phenylethylalcohol (Wako), (Wako), benzylidene aniline (Wako), benzylalcohol- α , α - d_2 (Aldrich). TiO₂ (ST-01) and Nb₂O₅·nH₂O were supplied from Ishihara Sangyo Kaisha, and Companhia Brasileira de Metalurgia e Mineração, respectively. SiO₂ (Q10) was provided by Fuji Silysia Chemical. Al₂O₃ (JRC-ALO-9) was obtained from the Catalysis Society of Japan as reference catalysts. Metal oxide supports were calcined at 500 °C for 2 h under air before preparation of the supported Ru catalysts.

2. Instruments

Brunauer-Emmett-Teller (BET) specific surface areas of the samples were measured by nitrogen adsorption-desorption at -196 °C (Quantachrome Nova-4200e). Prior to the adsorption measurements, the samples were degassed in situ under vacuum at 150 °C for 1 h. The BET surface area was determined using the multipoint BET algorithm in the P/P_0 range from 0.05 to 0.3. X-ray diffraction (XRD; Ultima IV, Rigaku) patterns of all samples were obtained using Cu Ka radiation (40 kV, 40 mA) in the 20 range of 15-85°. X-ray photoelectron spectroscopy (XPS; ESCA-3200 Shimadzu) measurements were performed using Mg Ka radiation (1486.6 eV). Samples were pressed into pellets and fixed on double-sided carbon tape. The binding energies were calibrated using sputtered C (1s peak at 284.6 eV). Gas titration and temperature programmed reaction/desorption experiments were performed using an automatic measurement instrument (BELCAT-A, BEL Japan) with thermal conductivity (TCD) and mass (Belmass) detectors. CO-pulse titration was performed at 50 °C. Before the measurements the samples were pretreated under 5% H₂ Ar flow at 400 °C for 1 h. The stoichiometry of CO/Ru = 0.6 was assumed. Before temperature-programmed desorption (TPD) of CO₂ and H₂, the sample was pretreated at 400 °C under H₂/Ar flow (5% H_2/Ar , 30 mL min⁻¹) for 1 h and then cooled down to room temperature. CO_2 or H_2 was introduced at 50°C for 1h. The sample was purged with He (30 mL min⁻¹), followed by the TPD process under a He flow (30 mL min⁻¹). Outlet gas was detected with a TCD and mass detector to monitor desorption of CO₂ or H₂ from the samples. Field-emission scanning electron microscopy (FE-SEM; S-5500, Hitachi High-Tech) measurements were conducted at an acceleration voltage of 1, 5 and 20 kV. Transmission electron microscopy (TEM; JEM-2100F, JEOL)-energy dispersive X-ray spectroscopy (EDS, JED-2300T, JEOL) measurements were conducted at an acceleration voltage of 200kV. Fourier transform infrared (FT-IR)

spectra were obtained at a resolution of 4 cm⁻¹ using a spectrometer (FT/IR-6100, Jasco) equipped with an extended KBr beam-splitting device and mercury cadmium telluride (MCT) and a triglycine sulfate (TGS) detectors. The isolation of products was performed with a single channel automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen). ¹H NMR (400 MHz), and ¹³C {¹H} NMR (100 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All ¹H NMR chemical shifts were recorded in ppm (δ) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances (CHCl₃ was used as internal standard, δ 7.26). All ¹³C NMR chemical shifts were recorded in ppm (δ) relative to carbon resonances in CDCl₃ at δ 77.16. The net amounts of metals were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The 5 mg of sample was totally dissolved by aqua regia (10 mL) and HF (0.5 mL). Gas chromatography (GC) analyses were conducted using a gas chromatography (GC-17A, Shimadzu) equipped with an InertCap 17 capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector (FID). The isolation of product was performed with a single channel automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen).

3. Preparation of Ru-MgO/TiO₂

Ru(NO)(NO₃)₃ solution (1.5 wt%, 3.33 g) was diluted with H₂O (20 mL). TiO₂ was added to the solution and the resulting suspension was stirred at r.t. for 1 h. The volatile was removed by evaporation. The solid is dried at 90 °C overnight. To a plastic bottle, he dried sample, Mg(NO₃)₂•6H₂O, and H₂O (100 mL) were added. The solution was stirred at r.t. for 1 h. The pH was adjusted to 10.5 by aqueous ammonia. The additional stirring was conducted for 2 h. The solid was corrected by filtration and washed with H₂O (100 mL). The corrected sample was dried at 90 °C overnight. The sample was treated in 5% H₂/Ar (flow rate = 30 mL/min) at 400 °C for 2 h and transferred to Ar glove box without exposure to air to give Ru-MgO/TiO₂. The net amounts of Ru and MgO were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be 4.8 and 22.7 wt%, respectively.

4. Preparation of supported Ru catalysts

The 5 wt% Ru/support catalysts were prepared by wet impregnation method.^{S1} Ru(NO)(NO₃)₃ solution (1.5 wt%, 3.33 g) was diluted with H₂O (20 mL), and the mixture was evaporated at 60 °C until dryness. The obtained solid was further dried at 90 °C overnight. The dried sample was reduced with 5% H₂/Ar (30 mL/min) at 400 °C for 2 h.

5. Catalytic direct amination

The catalytic reaction was conducted in a 30 mL stainless-steel autoclave equipped with a magnetic stirrer. 200 mg of catalyst was loaded into the reactor with 0.5 mmol of alcohol and 5 mL of toluene in Ar glove box. The autoclave was purged with NH_3 several times to remove Ar and then pressurized with NH_3 at 0.7

MPa. The autoclave was heated at 110 °C for 20 h.

6. Reuse experiments

The catalytic reaction was conducted according to the general procedure. For reuse experiments, the catalyst was recovered by filtration, washed with MeOH (20 mL) and H₂O (200 mL). The corrected sample was suspended in NaOH solution (1 M, 100 mL). The resulting solution was stirred at room temperature for 2 h. The sample was corrected by filtration, washed with H₂O (200 mL). The corrected sample was dried at 90 °C overnight and treated with H₂/Ar (flow rate = 30 mL/min) at 400 °C for 2 h and transferred to Ar glove box without exposure to air.

7. Deuterium labeling experiments

The catalytic reaction was conducted according to the general procedure. After the reaction, the catalyst is separated by filtration. The filtrate was diluted with THF (10 mL). To the solution, added Et_3N (1 mL) and acetyl chloride (2 mmol), then the mixture was stirred overnight at room temperature. H₂O (50 mL) was added to the mixture. The organic layer was extracted with EtOAc (15 mL × 3). The combined organic layer was evaporated. The resulting crude product was purified by silica gel column chromatography. The deuterium content is calculated based on benzylic proton as against acetyl proton.

8. Procedure for IR measurements

Isopropanol-adsorbed IR measurements were conducted using self-supported disks (20 nm diameter, ca. 20 mg) and placed in an IR cell attached to a closed glass-circulation system. Prior to measurements, the disks were dehydrated by heating at 200 °C for 1 h under vacuum. Isopropanol as a probe molecule was then introduced into the IR system at room temperature under 5000 mT. The temperature was increased from 60 to 150 °C. The disk was exposed to a vacuum at 150 °C.

The amounts of Lewis and Brønsted acid sites on metal oxides and supported catalysts were estimated using FT-IR measurements for pyridine-adsorbed samples at 25 °C. Sample was pressed into self-supporting disks (20 mm diameter, ca. 20 mg) and placed in an IR cell attached to a closed glass-circulation system. Prior to pyridine adsorption, the sample was dehydrated by heating at 200 °C for 1 h under vacuum. The intensities of the bands at 1450 cm⁻¹ (pyridine coordinatively bonded to Lewis acid sites) and 1540 cm⁻¹ (pyridinium ions formed by Brønsted acid sites) were plotted against the amounts of pyridine adsorbed on the Lewis and Brønsted acid sites of the samples, respectively. The intensities of both bands increased with the amount of chemisorbed pyridine, reaching plateaus with the appearance of the band due to physisorbed pyridine (1440 cm⁻¹). While the band at 1440 cm⁻¹ disappeared after evacuation at room temperature for 4 h, there was no significant difference in intensity of the bands at 1450 and 1540 cm⁻¹ before and after evacuation, which indicated that the maximum intensities of the bands at 1450 and 1540 cm⁻¹ correspond to the amounts of Lewis and Brønsted acid sites available to chemisorb pyridine to saturation, respectively. The amounts of Brønsted and Lewis acid sites on samples were estimated from the maximum band intensities and molecular absorption coefficients at 1450 and 1540 cm^{-1} .

9. Spectral Data

Furfuryl amine (**3a**)^{S2}

After the reaction was completed, the catalyst was separated by filtration. ¹H NMR (400 MHz, CDCl₃): δ = 7.35 (d, *J* = 0.8 Hz, 1H), 6.32–6.30 (m, 1H), 6.13 (d, *J* = 3.2 Hz, 1H), 3.83 (s, 2H), 1.58 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 156.6, 141.6, 110.2, 105.1, 39.3.

Benzylamine (3b) S2

After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.36–7.25 (m, 5H), 3.87 (s, 2H), 1.70 (br s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 156.6, 141.6, 110.2, 105.1, 39.3.

4-(Aminomethyl)-N,N-dimethylaniline (3c) S3



After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.18 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 2H), 2.93 (s, 6H), 1.56 (br s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 149.9, 130.0, 128.4, 112.9, 45.4, 40.8.

4-Methoxybenzylamine (3d)^{S3}



After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc eluent) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.78 (br s, 5H), 1.77 (br s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 157.6, 135.5, 128.3, 114.0, 55.3, 45.9.

4-Chlorobenzylamine (3e) S2

After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 2H), 1.51 (br s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 141.7, 132.5, 128.6, 128.5, 45.8.

(4-(Trifluoromethyl)phenyl)methanamine (3f)^{S4}

After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.59 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 2H), 1.55 (br s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 147.1, 129.1 (q, *J* = 32.5 Hz), 127.3, 125.4 (q, *J* = 3.2 Hz), 124.3 (q, *J* = 270.2 Hz), 45.9.

2-Methoxybenzylamine (3g) S5

After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.26–7.20 (m, 2H), 6.91 (t, *J* = 14.8 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 2H), 1.66 (br s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 114.9, 89.3, 86.0, 85.5, 78.0, 67.8, 34.5, 12.6.

(1*H*-indol-5-yl)methanamine (**3h**)^{S6}

After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.52$ (s, 1H), 7.55 (s, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.17 (t, J = 2.7 Hz, 1H), 7.13 (dd, J = 8.3, 1.4 Hz, 1H), 6.51 (m, 1H), 3.94 (s, 2H), 1.62 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 135.0, 135.0, 128.1, 124.6, 121.8, 118.9, 111.2, 102.4, 47.0.

1-Phenylethan-1-amine (3j)^{S7}

 NH_2

After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 70:30) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.31 (m, 4H), 7.26–7.22 (m, 1H), 4.11 (q, *J* = 6.8 Hz, 1H), 1.73 (br s, 2H), 1.39 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 147.8, 128.6, 127.0, 125.8, 51.4, 35.7.

Diphenylmethanamine (3k)^{S8}



After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 100:0 to 50:50) to give the pure title compound.

¹H NMR (400 MHz, CDCl₃): δ =7.38–7.36 (m, 3H), 7.32–7.29 (m, 3H), 7.25–7.20 (m, 2H), 5.21 (s, 1H), 1.74 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 145.6, 128.5, 126.9, 77.3, 77.0, 76.7, 59.8.

Furan-2,5-diyldimethanamine (31)^{S9}

After the reaction was completed, the catalyst was separated by filtration. ¹H NMR (400 MHz, CDCl₃): δ = 6.18 (s, 2H), 3.78 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 155.7, 103.9, 38.2.



S8



S9











































catalyst	substrate	product	H ₂	temp. (°C)	yield (%)	ref
	ОМ	NH ₂	_	110	86 (0.6 h ⁻¹)	This work
	PhOH	Ph NH ₂	—	150	87 (9.0 h ⁻¹) ^a	
Ru/C		H ₂ N H	10 bar	170	18	S10
Ru/C	C ₁₂ H ₂₅ -OH	$C_{12}H_{25}-NH_{2}$	2 bar	150	83.8 (5.1 h ⁻¹)	S11
Ru/SiO ₂	C ₁₂ H ₂₅ -OH	$C_{12}H_{25}-NH_{2}$	1 bar	150	69 (37.1 h ⁻¹)	S12
Ru/Al ₂ O ₃	ОН	NH ₂ NH ₂	1 MPa	220	38.4 (242 h⁻¹)	S13
RuNPs	C ₈ H ₁₇ -OH	C ₈ H ₁₇ -NH ₂	2 bar	180	80 (20.9 h ⁻¹)	S14
Co/SiO ₂	C₂H₅−OH	C ₂ H ₅ -NH ₂	80 mL/min (40 equiv.)	210	37	S15
Co/Al ₂ O ₃	C ₃ H ₇ -OH	C ₃ H ₇ -NH ₂	90 mL/min (12 equiv.)	190	79	S16
Co/Al ₂ O ₃	C ₈ H ₁₇ -OH	C ₈ H ₁₇ -NH ₂	1 bar	140	(104.8 h ⁻¹)) S17
Pt-Co/CeO ₂	PhOH	Ph NH ₂	0.2 MPa	180	55	S18
Cu(OH) _x /Al ₂ O ₃	Ph OH	Ph NH ₂	—	135	80	S19
Ni/Al ₂ O ₃			_	160	88	S20
Ni/CaSiO ₃			_	160	86	S21
Raney Ni	ОМ	NH ₂	—	180	76.5	S22
Ni-Re/Al ₂ O ₃	H ₂ N OH	H ₂ N NH ₂	—	175	41.3	S23
Ni/Ce-Al	C ₈ H ₁₇ -OH	C ₈ H ₁₇ -NH ₂	—	180	54	S24
Ni-Al ₂ O ₃ /SiO ₂	PhOH	Ph NH ₂	—	160	96	S25
Ni-Pd/Al ₂ O ₃ -CD	C ₈ H ₁₇ -OH	C ₈ H ₁₇ -NH ₂	—	160	66	S26
Raney Ni	PhOH	Ph NH ₂	—	180	50.6	S27
Ni/HAP	C ₃ H ₇ -OH	C ₃ H ₇ -NH ₂		150	9.9	S28

Table S1 Reported Catalytic Systems for Direct Amination of Alcohols with ammonia.

^a Reaction conditions: benzyl alcohol (0.5 mmol), Ru-MgO/TiO2 (0.05 g), toluene (1mL), NH3 (0.7 MPa), 150 °C, 2 h. The values in the parentheses were TOF values. $CD = \beta$ -cyclodextrine, HAP = hydroxyapatite

¢ () () () () () () () () () ()	$PH + NH_3 - \frac{catalyst}{toluene}$	NH ₂	+	N O	
1a		2a		3a	
		Conv.	Yield (%)		
Entry	Catalyst	(%)	2a	3a	
1^b	Ru/MgO-a	15	0	0	
2^c	Ru/MgO-w	77	56	trace	
2	Ru/Al_2O_3	95	trace	trace	
3	Ru/Mg(OH) ₂	45	27	trace	
4	Ru/Al(OH) ₃	46	0	0	
5	Ru/La(OH) ₃	7	0	0	
6	Ru/Ce(OH) ₄	26	5	trace	
7	Ru/Zr(OH) ₄	27	0	0	

 Table S2 Screening of Ru-based catalyst^a

^{*a*} Reaction conditions: catalyst (0.2 g), **1a** (0.5 mmol), NH₃ (0.7 MPa), toluene (5 mL), 110 °C, 20 h. Conversion and yield were determined by GC analysis. ^{*b*} The catalyst was prepared by impregnation method using acetone as a solvent.^{S29 *c*} The catalyst was prepared by impregnation method using water as a solvent.^{S1}

Table S3 Specific surface area and CO-pulse titration results of supported Ru catalysts

Entry	Catalyst	Specific surface	Dispersion	Ru particle
Linuy	Cuturyst	area (m ² g ^{-1})	(%) ^a	size $(nm)^b$
1	Ru-20MgO/TiO ₂	217	43	3.2
2	Ru/TiO ₂	193	18	7.6
3	Ru/MgO-a	46	n.d.	n.d.
4	Ru/MgO-w	179	2.5	53

^{*a*} The dispersion was determined with CO-pulse titration technique. The stoichiometry of CO/Ru = 0.6 was assumed.^{S30} ^{*b*} The Ru particle size was estimated from the dispersion. n.d. = not determined

Table S4 Amounts of acid and base sites on supported Ru catalysts.

Entry	Catalyst	Lewis acid $(\text{mmol } \text{g}^{-1})^a$	Brønsted acid $(\text{mmol } \text{g}^{-1})^a$	Base $(\text{mmol } \text{g}^{-1})^b$
1	Ru-20MgO/TiO ₂	0.90	<1	0.072
2	Ru/TiO ₂	0.62	<1	0.082

^{*a*} Amounts of acid sites were estimated from pyridine-adsorbed FT-IR measurements.^{S31} ^{*b*} Amounts of base sites were calculated from CO₂-TPD measurements.^{S31}

Table S5 Optimization study^a

	OH + NH ₃ 5Ru	-20MgO/TiO ₂	H ₂ +	N O	
	1a	2a	2a 3a		
Eatar	Calvant		Yield (%)		
Entry	Solvent	Conv. (%) —	2a	3 a	
1	Toluene	96	85	trace	
2^b	Toluene	>99	94	0	
3	THF	77	43	trace	
4	CH ₃ CN	51	5	trace	
5	Methanol	31	0	trace	
6	Ethanol	29	0	0	
7	t-amyl alcohol	88	23	trace	
8	CH_2Cl_2	53	0	trace	
9	DMA	>99	9	trace	
10	cyclohexane	>99	33	trace	

^{*a*} Reaction conditions: Ru-20MgO/TiO₂ (0.2 g), **1a** (0.5 mmol), NH₃ (0.7 MPa), solvent (5 mL), 110 °C, 20 h. Conversion and yield were determined by GC analysis. ^{*b*} 0.4 g catalyst was used.

Table S6 Hydrogenation of benzylidene aniline over supported Ru catalyst^a

P	h N ^{-Ph} + H ₂ 4	catalyst toluene 40 °C, 2 h	∽N ^{Ph} H 5
Entry	Catalyst	Conv. (%)	Yield (%)
1	Ru-20MgO/TiO ₂	>99	63
2	Ru/TiO ₂	63	54

^{*a*} Reaction conditions: catalyst (0.05 g), benzylidene aniline (0.5 mmol), H_2 (0.5 MPa), toluene (5 mL), 40 °C, 2 h. Conversion and yield were determined by GC analysis.

Table S7 Reductive amination of furfural over supported Ru catalyst^a

	0 0 0	NH ₃ + H ₂ - .1 MPa x MPa	catalyst	N N	H ₂
Entry	Catalyst	pH ₂ (MPa)	Solvent	Conv. (%)	Yield (%)
1 ^b	Ru-20MgO/TiO ₂	4	Toluene	>99	0
2^b	Ru-20MgO/TiO ₂	1	Toluene	>99	68
3	Ru/Nb ₂ O ₅	4	MeOH	>99	99
4	Ru/Nb ₂ O ₅	4	Toluene	>99	73

^{*a*} Reaction conditions: catalyst (0.02 g), furfural (0.5 mmol), NH₃ (0.1 MPa), H₂ (1 or 4 MPa), solvent (5 mL), 90 °C, 4 h. Conversion and yield were determined by GC analysis. ^{*b*} Complex mixture of other products (e.g., furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofurfuryl amine, secondary amine, etc.) was obtained.



Fig. S1 FE-SEM images of Ru-20MgO/TiO₂ (a) Secondary electron image with 30k EI-BCM, (b) Secondary electron image with 100k EI-BCM, (c) Backscatted electron image with 100k EI-BCM.

X-ray photoelectron spectroscopy (XPS) measurements for Ru 3d of the catalyst showed that Ru^0 coexists with Ru^{4+} (Fig. S1), which was consistent with the IR results (Fig. 3).



Fig. S2 Ru 3d XPS spectrum for Ru-20MgO/TiO₂. Peak position of Ru⁰: 279.9 eV, RuO₂: 280.7 eV.^{S32}



Fig. S3 CO₂-TPD profiles of Ru-20MgO/TiO₂ and Ru/TiO₂



Fig. S4 H_2 -TPD profiles of Ru-20MgO/TiO₂ and Ru/TiO₂



Fig. S5 XRD patterns for (a) Ru-20CaO/TiO₂, (b) Ru-20SrO/TiO₂, (c) Ru-20BaO/TiO₂



Fig. S6 Difference IR spectra of isopropanol-adsorbed 5Ru-20MgO/TiO₂



Fig. S7 Difference IR spectra of isopropanol-adsorbed 5Ru/TiO₂



Fig. S8 Difference IR spectra of isopropanol- d_8 -dsorbed 5Ru-20MgO/TiO₂

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