Supporting Information

Ruthenium functionalized nickel hydroxide catalyst for highly efficient alcohol oxidations in the presence of molecular oxygen

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1. Experimental Section

1.1. Chemicals

Chemicals used in this work were all commercially available and used without any purification. $RuCl_3 \cdot xH_2O$ was purchased from Sigma-Aldrich. $Ni(NO_3)_2 \cdot 6H_2O$, NaOH and anhydrous Na_2CO_3 were purchased from Showa. Water used for this experiment is of milli Q grade quality.

1.2. X-ray absorption spectroscopic analysis (XAS)

XAS of Ru K edge and Ni K edge were recorded at beam lines 01C1 and 17C1 centres in National Synchrotron Radiation Research Centre, Taiwan. Both beam lines employ a double Si(111)-crystal monochromator for energy selection with a resolution, $\Delta E/E$ better than 2×10^{-4} units. High-order harmonics are rejected by Pt-coated mirrors. The catalyst powder was uniformly distributed on to a Scotch tape, which was then folded several times to reach the optimum thickness. All spectrums were recorded at room temperature either in fluorescence mode (Ru K edge) or transmission mode (Ni K edge) of analysis. X-ray absorption raw data's were analyzed by following standard procedures.[S1]

1.3. Preparation of β_{bc}–Ni(OH)$_2$ powder

The preparation of β_{bc}–Ni(OH)$_2$ was carried out in a two-necked round bottom flask (500 mL) equipped with a mechanical stirrer and it was charged with an aqueous solution (120 mL, pH 13.3) containing a mixture of Na_2CO_3 (6.4 g, 60.38 mmol) and NaOH (7.42 g, 185.5 mmol), and then a solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (17.80 g,

61.21 mmol) in 60 mL H_2O was slowly added by using dropping funnel at the rate of 4 mL/min at RT. The resultant green precipitate was stirred at 65 ºC for 18 h and then filtered off, washed copiously with de-ionized water and dried at 110 ºC for 12 h to afford greenish nickel hydroxide powder (5.56 g).

1.4. Preparation of β_{bc}–Ni(OH)$_2$ powder

An aqueous solution (60 mL) containing $RuCl_3 \cdot xH_2O$ (60 mL, 8.3×10^{-3} mM) was added in drops over 0.5 h to a stirred suspension of β_{bc}-Ni(OH)$_2$ (1 g, 20 mL H_2O) at RT in a two-necked round bottom flask (100 mL). After 12 h, the greenish nickel hydroxide turned into dark gray and the solution became colorless indicating the formation of ruthenium functionalized nickel hydroxide and the resulting gray solid was filtered off, washed with de-ionized water and dried at 110 ºC for 12 h to afford RuNi(OH)$_2$ powder (Ru 0.38 mmol g^{-1} by ICP-MS). A series of Ru/Ni(OH)$_2$ with various concentrations of Ru (0.30, 0.26, 0.15, 0.07 mmole g^{-1} by ICP-MS) were prepared and used for optimization of benzyl alcohol oxidation reaction.

1.5. Typical procedures for the aerobic oxidation of alcohols

Benzyl alcohol (0.108 g, 1 mmol) was mixed with 0.1 g of RuNi(OH)$_2$ (Ru 0.03 mmol) in 2 mL toluene with slow purging of O_2 and constant stirring at T = 363 K. Gas chromatography was used to monitor the progress of the reaction. Reaction product was analyzed by GC, NMR and GC-MS. After the reaction, RuNi(OH)$_2$ catalyst was separated by filtration and regenerated by successive washing with toluene, aqueous solution of Na_2CO_3 and water and then dried in oven. Finally, the solvent was removed from the filtrate and the residue was subjected to column chromatography on silica gel to obtain 97% pure benzaldehyde.
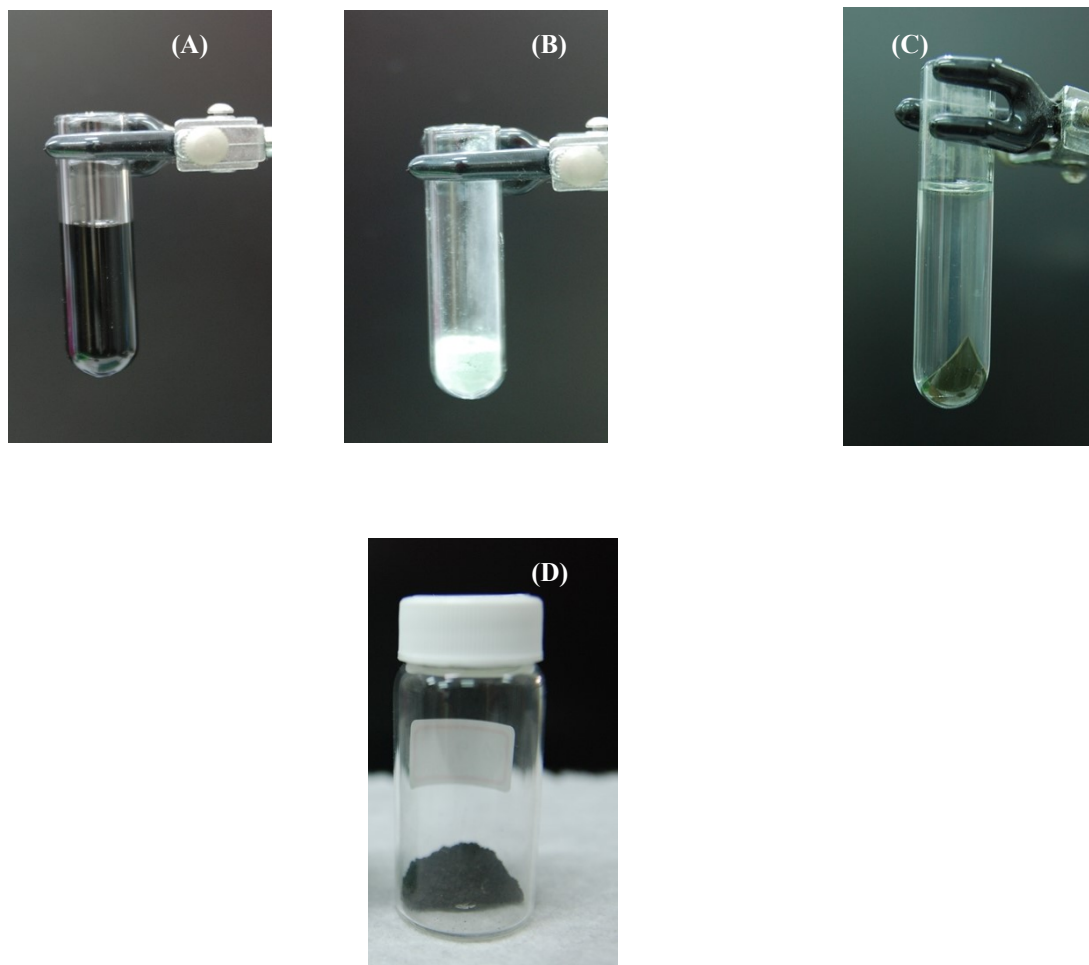
Fig. S1 Photographs of (A) aqueous $RuCl_3$ solution, (B) as prepared $Ni(OH)_2$ without and (C) with $RuCl_3$ solution. Note: there is an obvious color change in the photograph indicates that there is a reaction between the Ru^{3+} and $Ni(OH)_2$. (D) $RuNi(OH)_2$ catalyst.
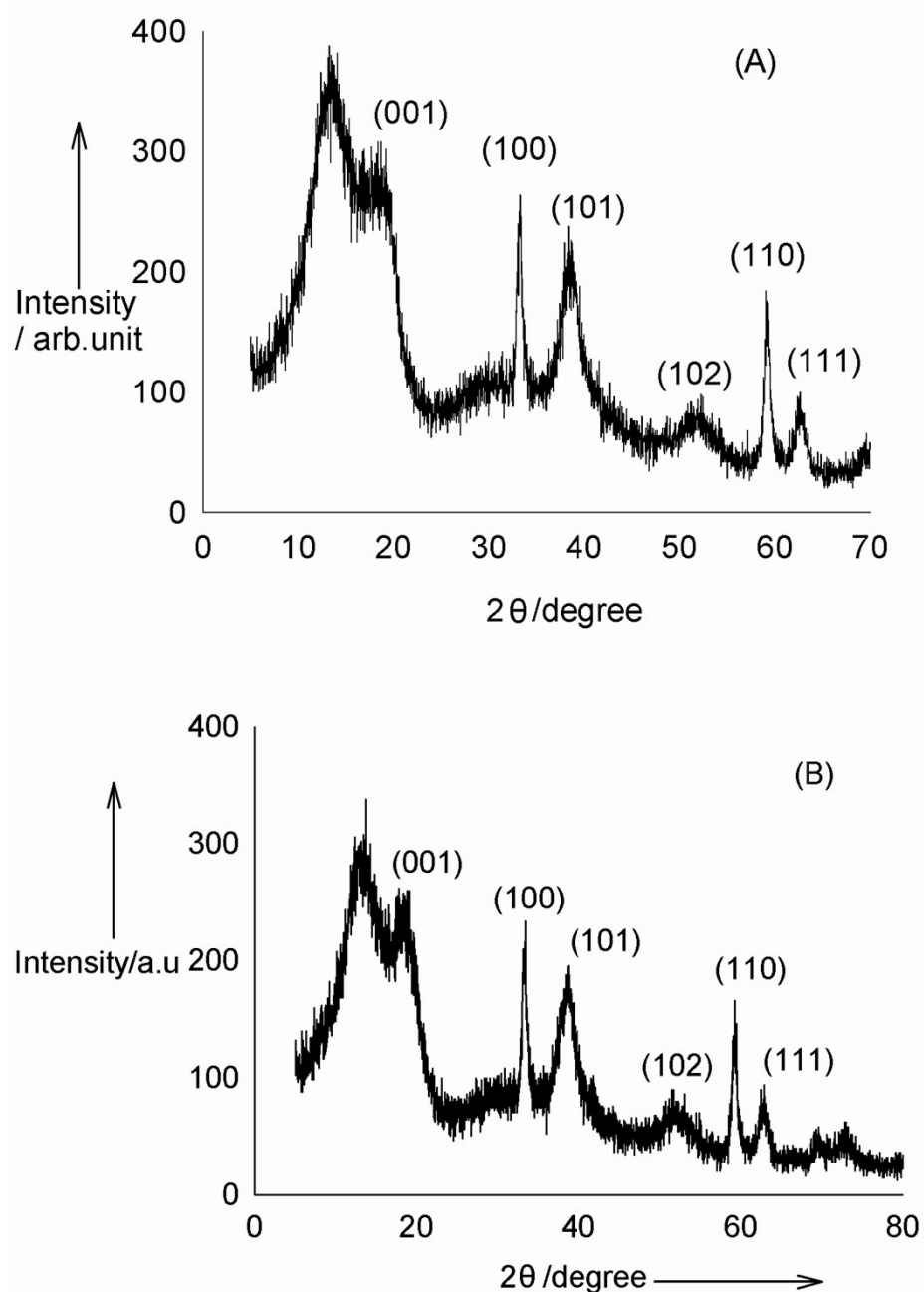
Fig. S2 XRD patterns of (A) $Ni(OH)_2$ and (B) $RuNi(OH)_2$ powder samples. XRD measurements were performed using (Shimadzu XRD-6000) a Cu Kα (1.54060 Å) radiation source.

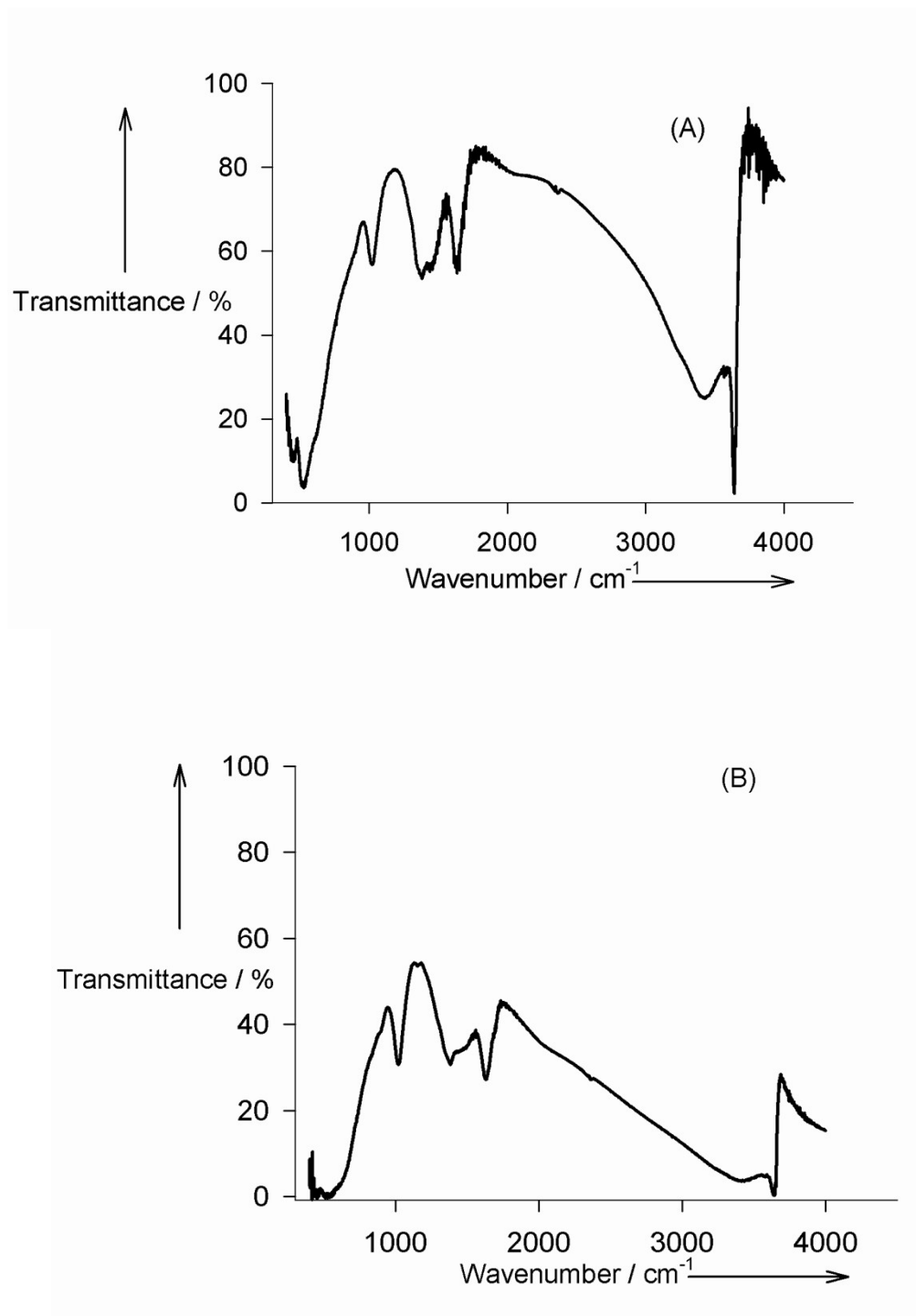**Fig. S3A** IR spectrum of (A) Ni(OH)$_2$ and (B) RuNi(OH)$_2$. IR spectrum were recorded with a JASCO FTIR-410 instrument (KBr method).
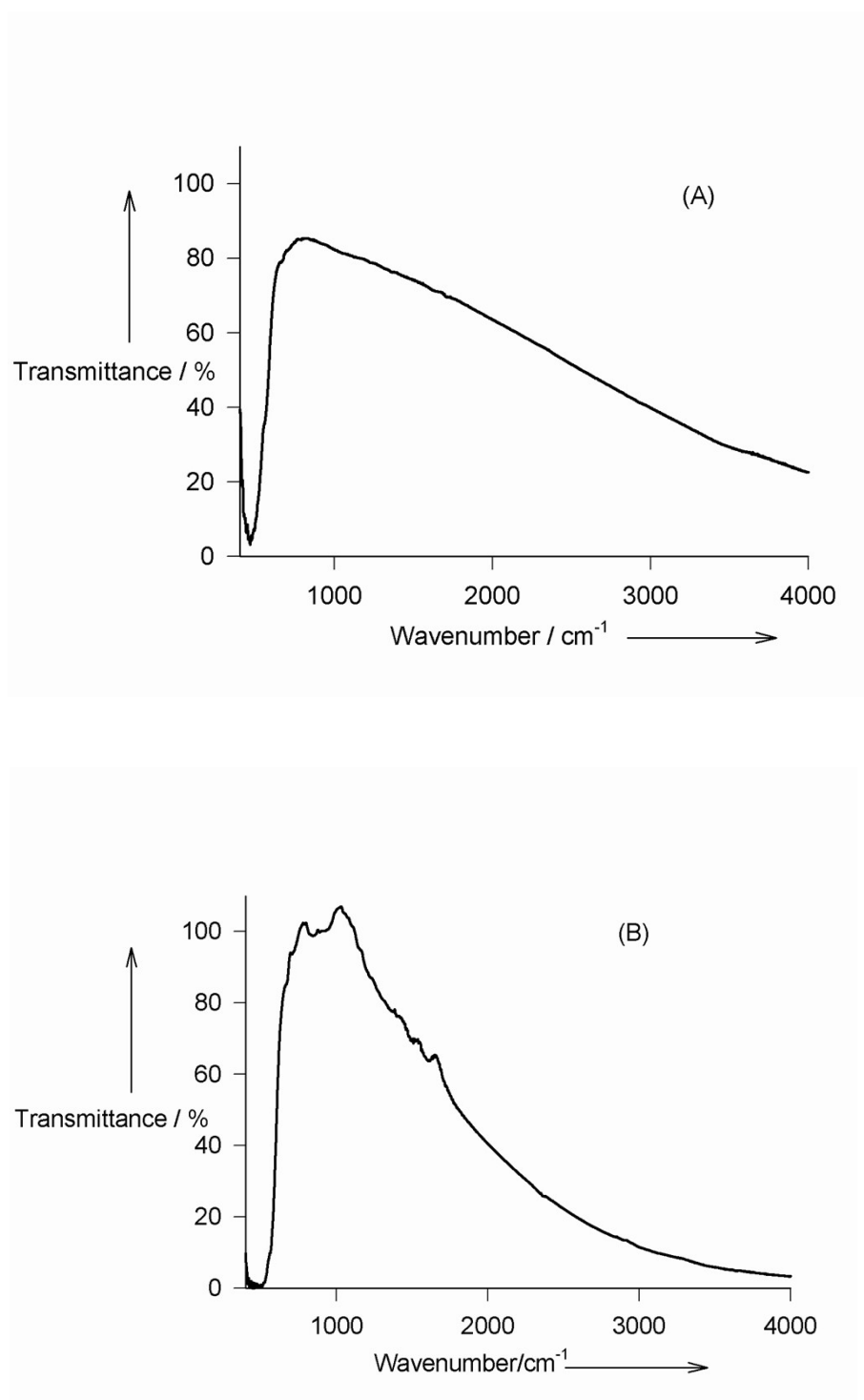
Fig. S3B IR spectrum of (A) NiO and (B) RuNiO. IR spectrum were recorded with a JASCO FTIR-410 instrument (KBr method). Note: No sign for any functional groups in the finger print region.
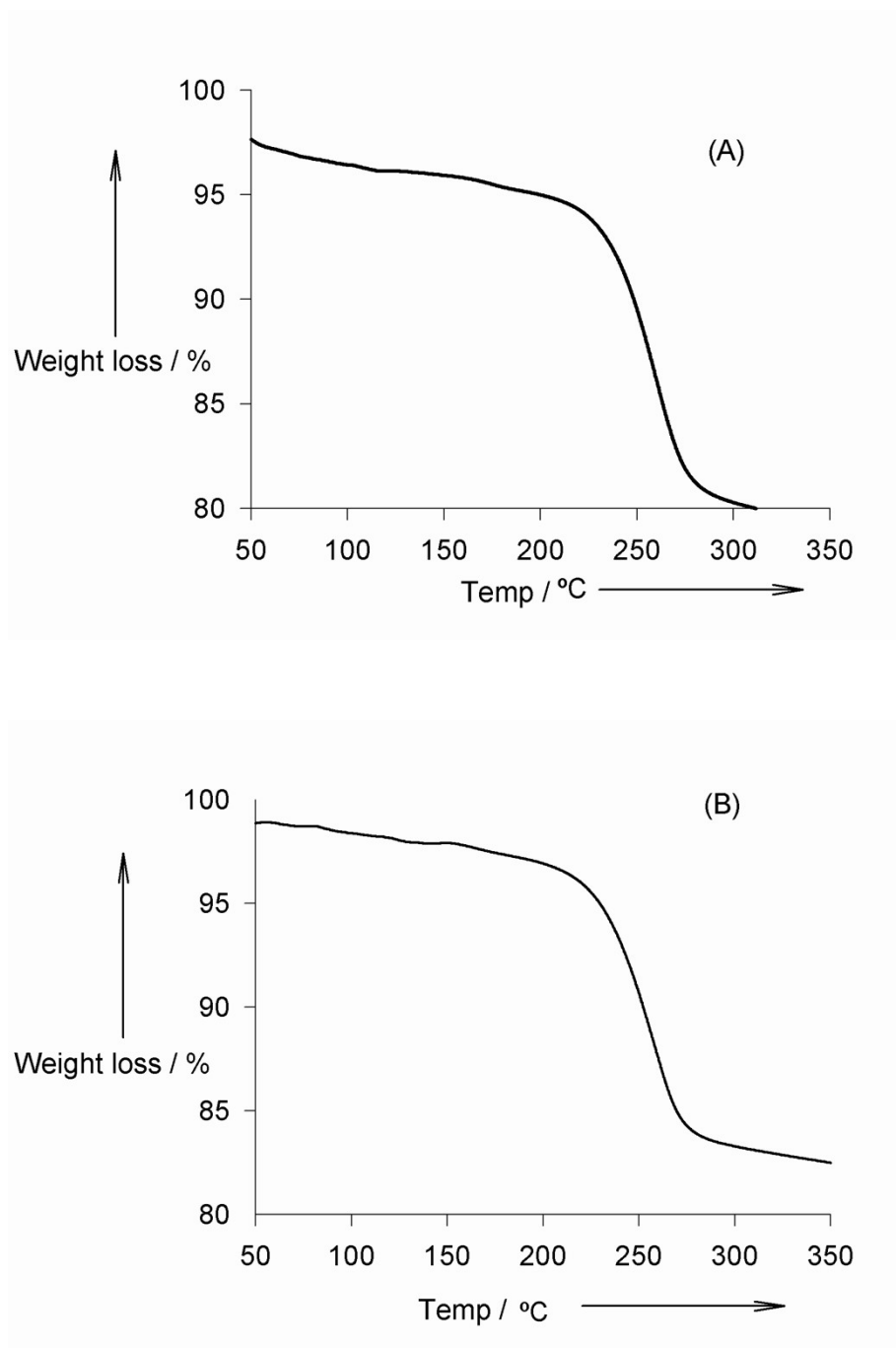
Fig. S4 TGA of the (a) Ni(OH)$_2$ and (b) RuNi(OH)$_2$ samples. Analyses were performed (Versa Therm UTHS) with a heating rate of 5ºC/min in the presence of air (gas flow rate 50 sccm). The weight loses in the range 180–250 ºC due to decomposition of RuNi(OH)$_2$ and Ni(OH)$_2$ into corresponding NiO, RuO$_x$ and NiO respectively.[S2]
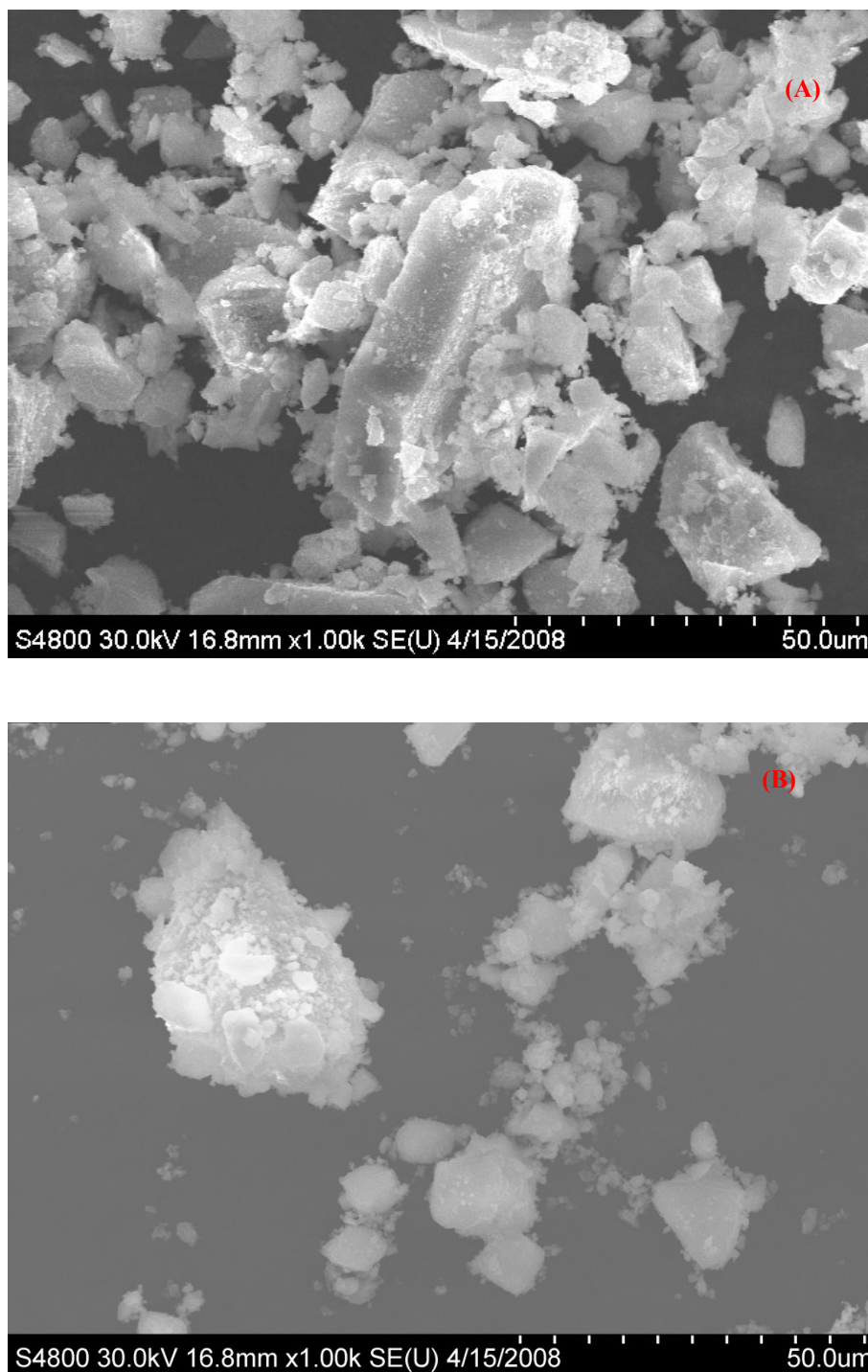
Fig. S5A SEM of (A) Ni(OH)$_2$ and (B) RuNi(OH)$_2$ samples (JEOL, JSM-6330F). Respective SEM-EDX analysis responses were given in **Figure S5B**.
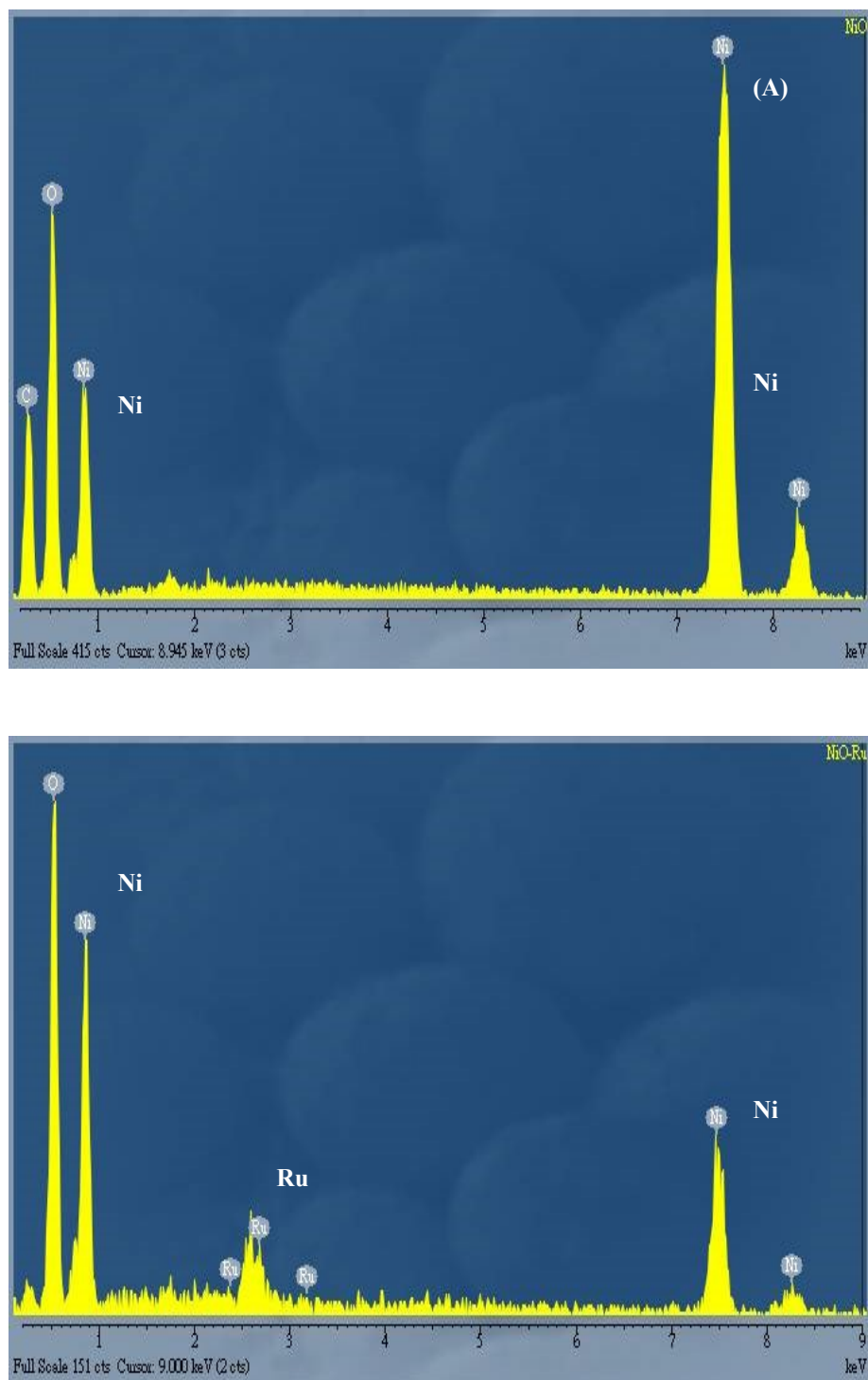
Fig. S5B Typical SEM-EDX analysis responses of the Figure S5A for the (A) Ni(OH)$_2$ and (B) RuNi(OH)$_2$ samples.
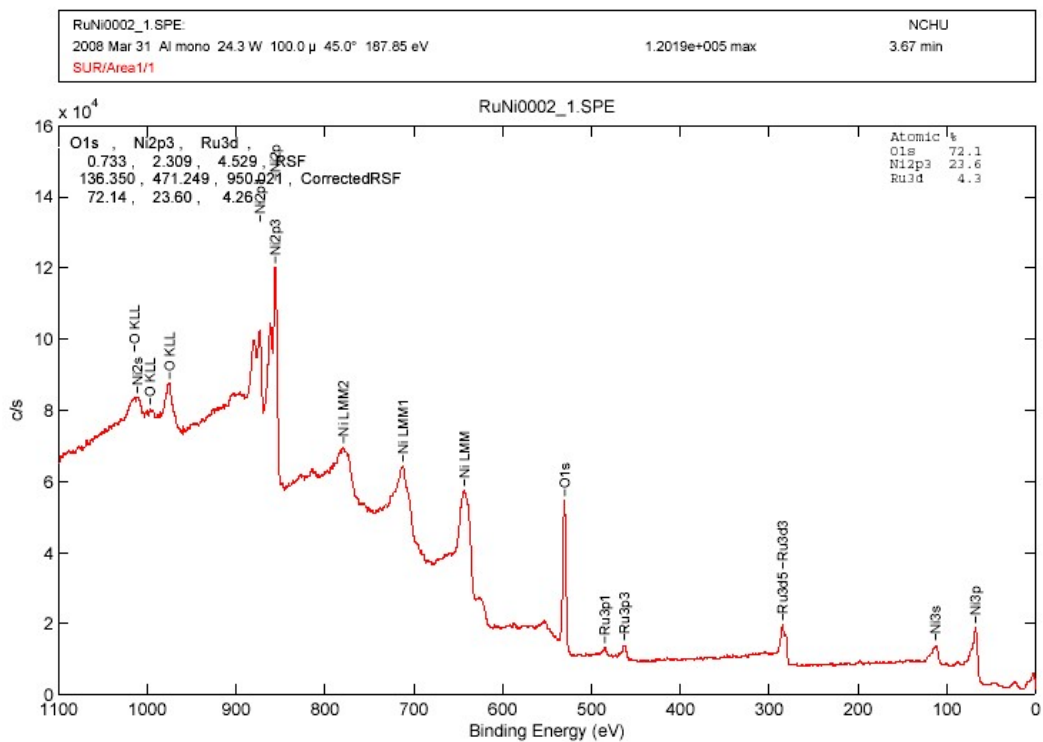
Fig. S6 XPS survey scan response of RuNi(OH)$_2$ sample. Experiment was performed using PHI 5000 Versa Probe (E-Beam = 100 μm, 25 W, 15 Kv)

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                               Print Spectrum

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     Operator           : WEN
     Acquired           :  5 Mar 2008  03:08 pm using AcqMethod RU_CE.M
     Acq Mode           : Spectrum
     Sample Type        : Sample
     Sample Name        : Fillrate
     Misc Info          :
     Prep Dilution      : 200.0 = ( 200.0 / 1.000 ) * 1.000
     Auto Dilution      : Undiluted
     Total Dilution     : 200.0
     Method             : C:\ICPCHEM\1\METHODS\RU_CE.M
     ISTD Conc          : Level 1
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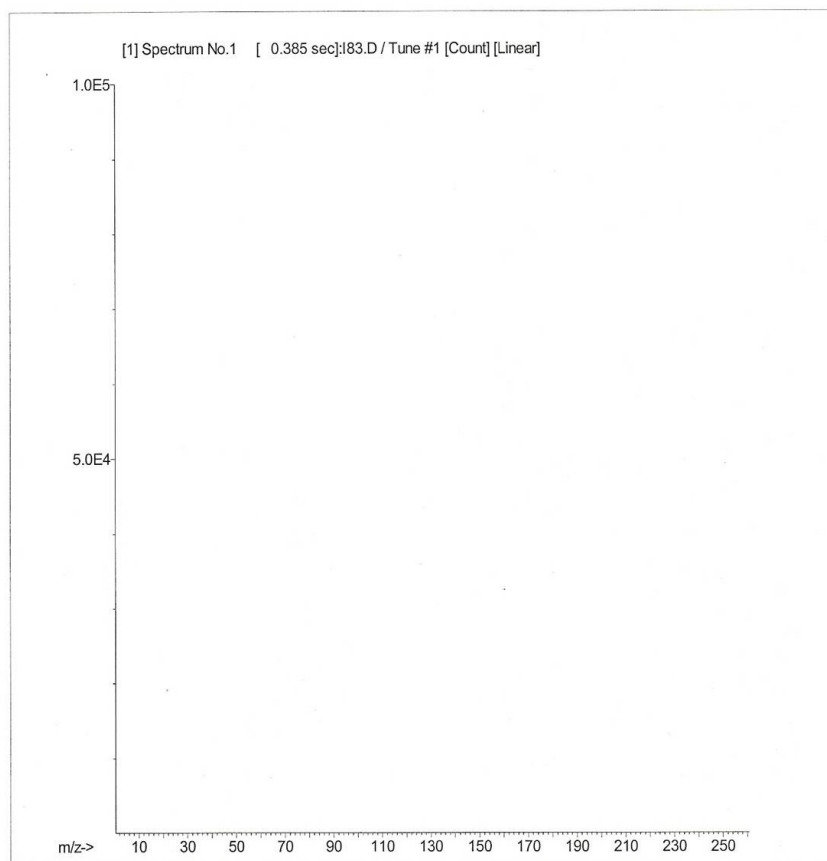

[1] Spectrum No.1   [0.385 sec]:I83.D / Tune #1 [Count] [Linear]

Fig. S7 ICP-MS analysis data for filtrate of the 0.1 g of RuNi(OH)$_2$ (3 mol% Ru) catalyzed benzyl alcohol oxidation reaction in toluene at T = 363 K. Note that there is no signal for Ru in the filtrate solution.
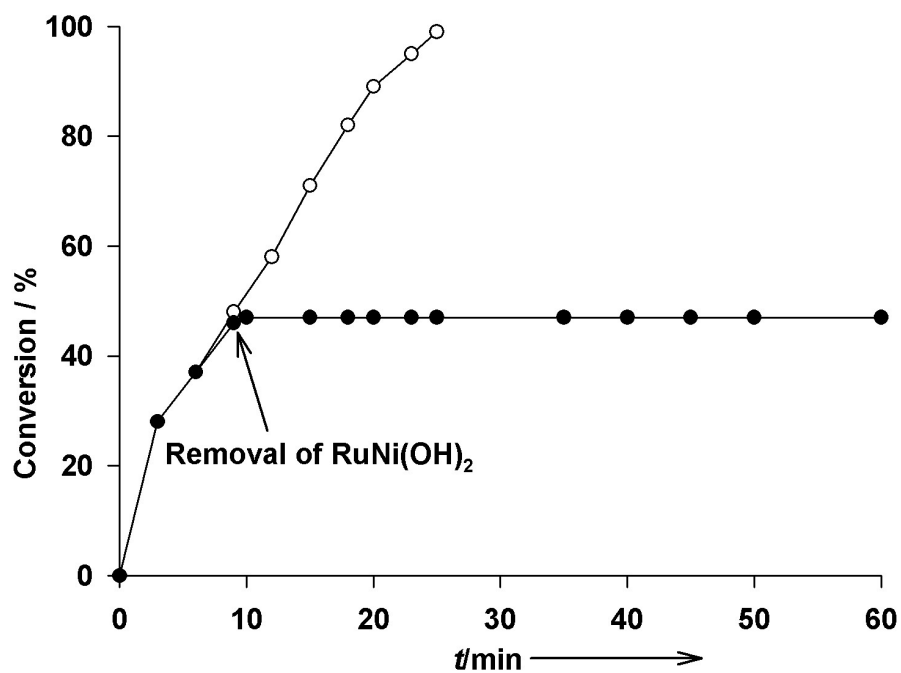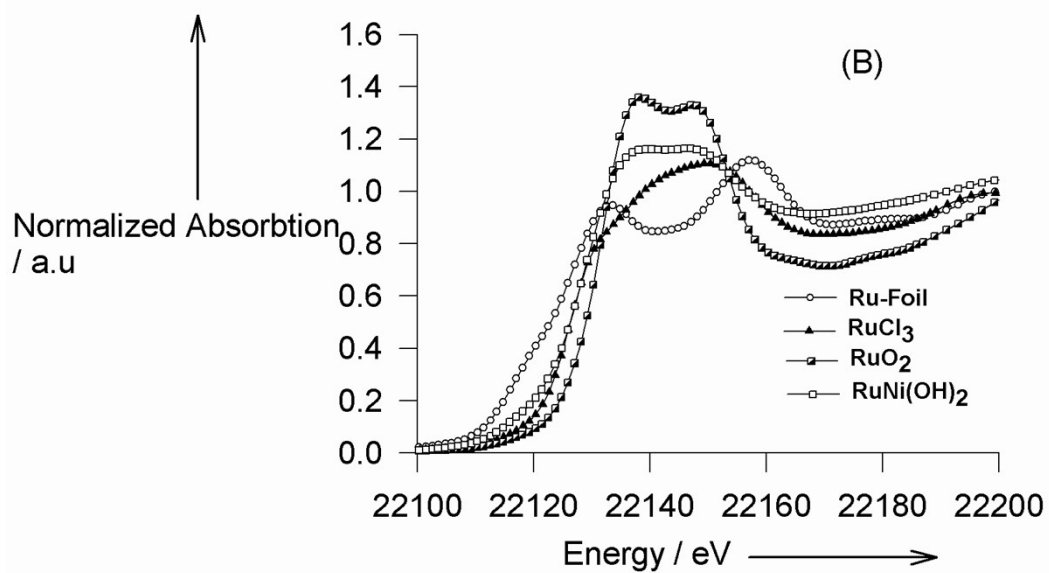
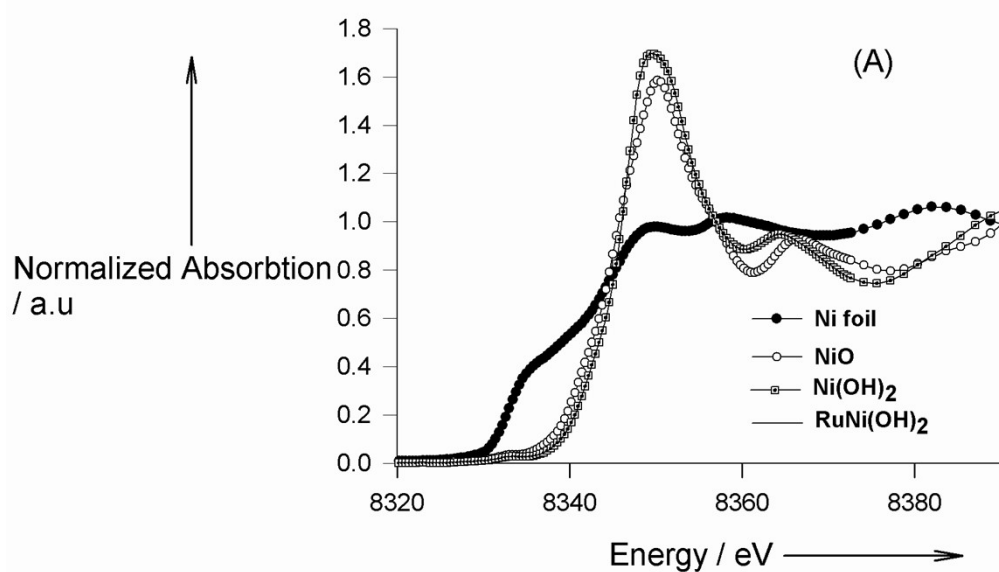**Fig. S8** Effect of removal of $RuNi(OH)_2$ in the oxidation of benzyl alcohol. With $RuNi(OH)_2$ (3 mol% Ru) (○); an arrow indicates the removal of $RuNi(OH)_2$ (●). Reaction conditions: Benzyl alcohol (1 mmol), toluene (2 mL), 363 K, O_2 flow.
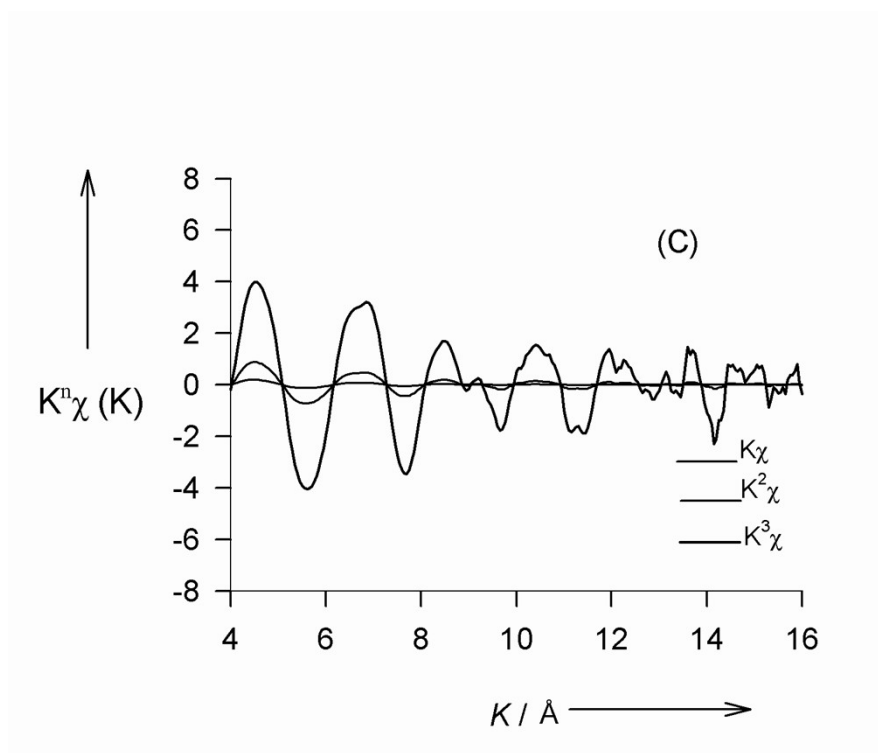
Fig. S9 (A) Comparative Ni K edge XANES responses of $Ni(OH)_2$ with other reference samples. (B) Comparative Ru K edge XANES responses of $RuNi(OH)_2$ with other reference samples. (C) k^n–weighted EXAFS data of Ru K edge $RuNi(OH)_2$.
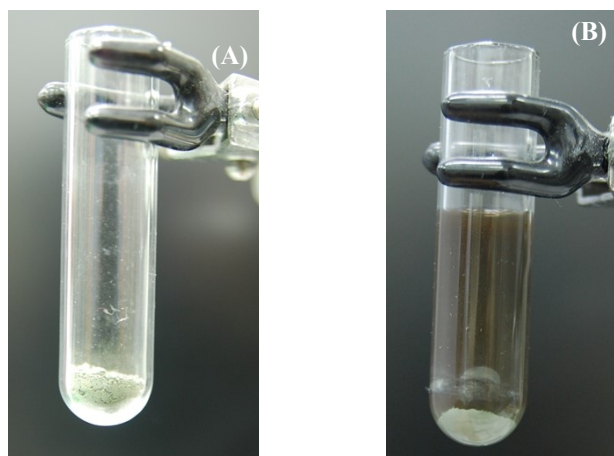
Fig. S10 Photographs of NiO (A) and NiO + RuCl3 (B): Note that there is no obvious colour change of the NiO powder indicating no reaction between the Ru^{3+} and NiO, unlike to the case of Ru^{3+} and $Ni(OH)_2$ as shown in **Fig. 1**.

Table S1. TOFs of various Ru catalyzed alcohol oxidation reactions with molecular oxygen.

Entry	Catalyst	Ru (mmol)	Temp (K)	4-methoxy benzyl alcohol	4-methyl benzyl alcohol	4-chloro benzyl alcohol	2-bromo benzyl alcohol	Benzhydrol	Cyclopropyl (phenyl) methanol)
1	**RuNi(OH)$_2$**	**0.03**	**363**	**82.5 h^{-1}**	**100 h^{-1}**	**55 h^{-1}**	**33 h^{-1}**	**66 h^{-1}**	**100 h^{-1}**
2.	Ru-Al-Mg-HT[S3]	0.22	333	1.07 h^{-1}	----	0.7 h^{-1}	----	1.1 h^{-1}	----
3	Ru-Co-Al-Mg-HT[S4]	0.23	333	----	11 h^{-1}	5.60 h^{-1}	----	9.3 h^{-1}	----
4	Ru-Co-HAP[S5]	0.02	363	46.5 h^{-1}	78 h^{-1}	78 h^{-1}	----	----	----
5.	Ru/ Co/CeO$_2$[S6]	0.20	333	-----	20 h^{-1}	20 h^{-1}	----	12 h^{-1}	----
6	Ru/HAP[S7]	0.33	353	1.97 h^{-1}	-	1.97 h^{-1}	----	2.95 h^{-1}	----
7	Ru/Alumina[S8]	0.025	356	40 h^{-1}	40 h^{-1}	40 h^{-1}	----	5.7 h^{-1}	40 h^{-1}
8	Ru/Fe$_2$O$_3$[S9]	0.038	378	----	26 h^{-1}	26 h^{-1}	----	----	26 h^{-1}
9.	RuMnMn/HT[S10]	0.02	333	----	----	----	----	23.5 h^{-1}	7.83 h^{-1}

Product analysis:

GLC measurements were all carried out using (GLC, China chromatography 9800, Taiwan) a home made stainless steel column containing 10% sp-2100 on a chromosorb W HP (80/100 mesh) support. The optimized GLC conditions are injection = 200 ºC, FID = 200 ºC and the oven was kept at 150 ºC for 4 min, then the temperature was increased at a rate of 10 ºC/ min to 250 ºC as a final temperature for 5 min. Selectivity was determined by GC MS (Varian Saturn 2200 GC/MS equipped with capillary column (HR-1, 30 m, 0.25mmID). ^{1}H NMR (Varian Mercury 400) spectrometer at 400 MHz in CDCl$_3$ with TMS as an internal standard.
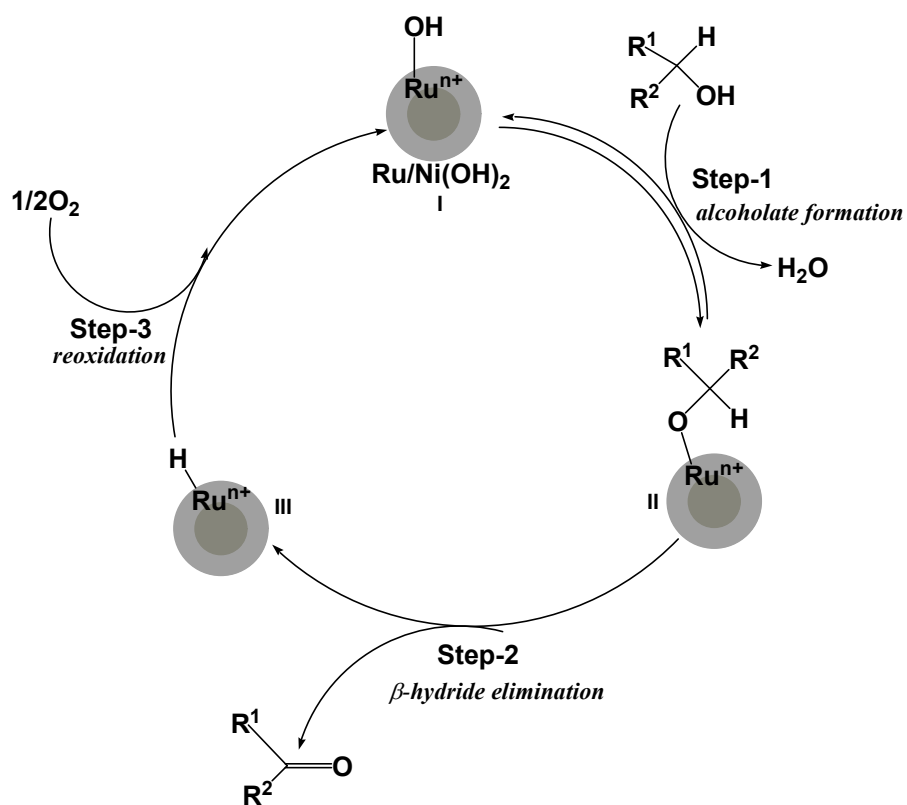
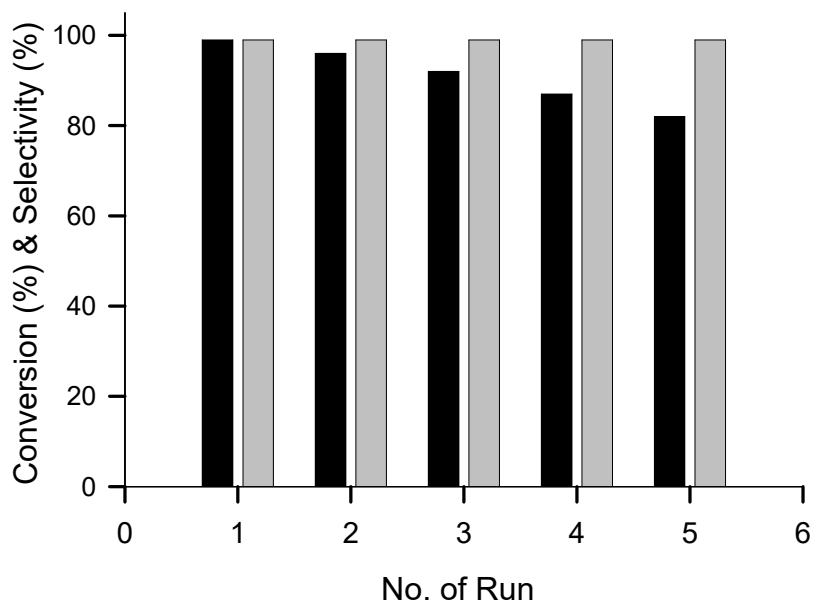**Scheme S1. Proposed cyclic mechanism for Ru/Ni(OH)$_2$ catalyzed AOR.**

Fig. S11. Results of Ru/Ni(OH)$_2$ catalyst recycling in the selective benzyl alcohol oxidation. (■) Conversion (%) (▢) Selectivity (%). Reaction conditions: Benzyl alcohol (1 mmol), toluene (2 mL), 363 K, O$_2$ flow.

References.

[S1] *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS,* (Eds.: D. C. Koningsberger and R. Prins, Wiley, New York, **1988**.

[S2] (a) Q. Song, Z. Tang, H. Guo and S. L. I. Chan, *J. of Power Sour.*, 2002, **112,** 428; (b) Z.-H. Liang, Y.-J. Zhu and X.-L. Hu, *J. Phys. Chem. B.,* 2004, **108**, 3448.

[S3] K. Kaneda, T. Yamashita, T. Matsushita and K. Ebitani, *J. Org. Chem.*, 1998, **63**, 1750.

[S4] T. Matsushita, K. Ebitani and K. Kaneda, *Chem. Commun.*, 1999, **265**.

[S5] Z. Opre, J-D. Grunwaldt, M. Maciejewski, D. Ferri, T. Mallet and A. Baiker, *J. of Catal.*, 2005, **230**, 406.

[S6] H. B. Ji, T. Mizugaki, K. Ebitani and Kaneda, *Tetrah. Lett.*, 2002, **43**, 7179.

[S7] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2000, **122***,* 7144.

[S8] K. Yamaguchi and N. Mizuno, *Chem. Eur. J.*, 2003, **9***,* 4353-4361; *Angew. Chem. Int. Ed.*, 2002, **41***,* 4538-4542.

[S9] M. Kotani, T. Koike, K. Yamaguchi and N. Mizuno., *Green Chem.*, 2006, **8**, 735.

[S10] K. Ebitani, K. Motokura, T. Mizugaki and T. Kaneda, *Angew. Chem. Int. Ed.*, 2005, **44***,* 3423.