Supplementary data

Complete Dehydrogenation of $N_2H_4BH_3$ with NiM-Cr_2O_3 (M = Pt, Rh, Ir) Hybrid Nanoparticle

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Chemicals and materials

Potassium tetrachloroplatinate(II) (K_2PtCl_4, J&K Chemical Reagent Co., 99.95%), iridium(III) chloride trihydrate ($IrCl_3 \cdot 3H_2O$, Aladdin Industrial Inc, Ir > 52 wt%), rhodium(III) chloride trihydrate ($RhCl_3 \cdot 3H_2O$, Aladdin Industrial Inc, Rh: 38.5-42.5 wt%), ruthenium(III) chloride hydrate ($RuCl_3 \cdot xH_2O$, Aladdin Industrial Inc, Ru: 38.0-42.0 wt%), sodium tetrachloropalladate (Na_2PdCl_4, Aladdin Industrial Inc, 98%), nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Sinopharm Chemical Reagent Co., 98%), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Sinopharm Chemical Reagent Co., 98%), cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Aladdin Industrial Inc, 98%) chromium(III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Aladdin Industrial Inc, 99.95%), polyvinylpyrrolidone (PVP, Aldrich, 95%), sodium borohydride ($NaBH_4$, Aldrich, 99.9%), sodium hydroxide (NaOH, Nanchang Chemical Works, 96%) 1,4-dioxane (J&K Chemical Reagent Co., Ltd., 99.8%), hydrazine hemisulfate salt ($N_2H_4 \cdot 1/2H_2SO_4$, Aldrich), and n-pentane (Aldrich, 99.5%) were used as received. Ultrapure water with a specific resistance of 18.3 MΩ cm was obtained by reversed osmosis followed by ion exchange and filtration.

Preparation of hydrazine borane (N_2H_4-BH_3, HB)

HB was synthesized according to the previous reports [14,34-35]. Typically, 21.42 g of hydrazine hemisulfate salt ($N_2H_4 \cdot 1/2H_2SO_4$) and 10 g of $NaBH_4$ were added into 80 mL of anhydrous dioxane and stirred at room temperature under an atmosphere of dry Argon for 48 h. The resulting slurry was immediately centrifuged to obtain the clear solution. Subsequently, the filtrate was evaporated by vacuum dryer at 50 ^oC overnight to obtain the raw HB, which was further washed with n-pentene. The obtained material was a white solid, and its purity was verified by our previous reports [44,45].

Calculation method:

$$TOF = \frac{n_{H_2}}{n_{(metal)} \times t} \qquad (S1)$$

Where n_{H2} is the mole number of generated H_2, $n_{(metal)}$ is the total mole number of Ni and Pt in catalyst and t is the completed reaction time in hour.

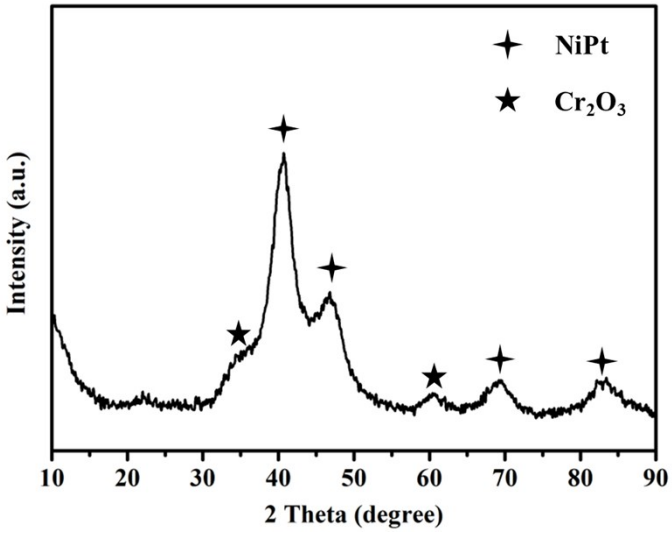

Fig. S1 XRD pattern of the as-synthesized $Ni_{0.9}Pt_{0.1}$-Cr_2O_3 NPs.

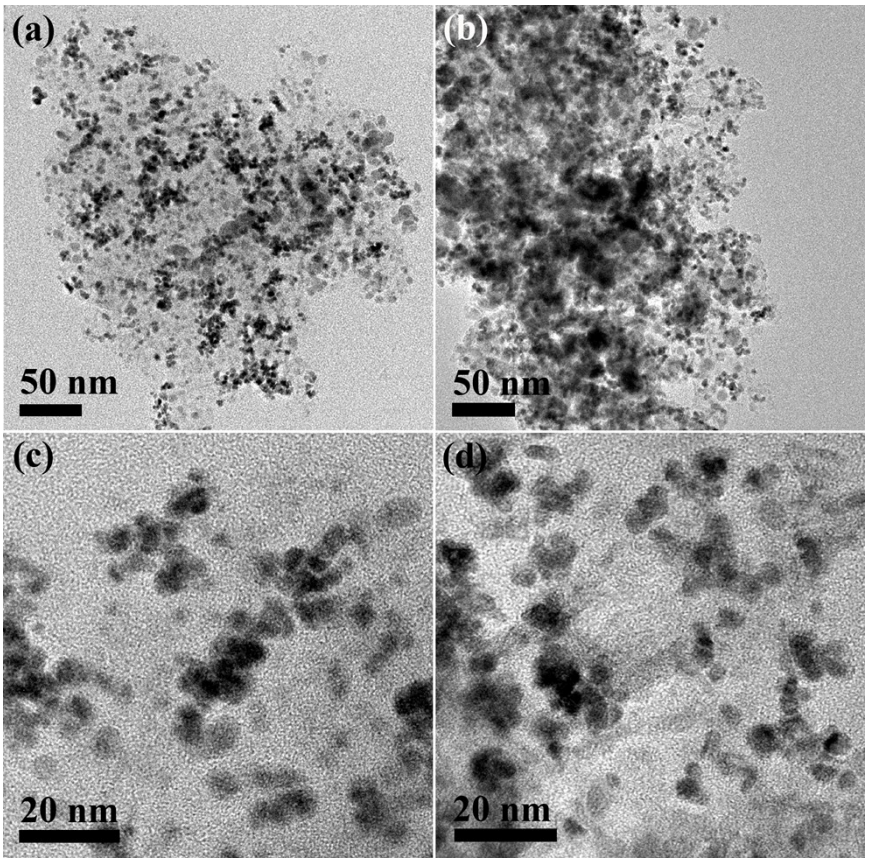

Fig. S2 TEM images of $Ni_{0.9}Pt_{0.1}$-Cr_2O_3 nanocatalysts before (a and c) and after (b and d) six catalytic runs.

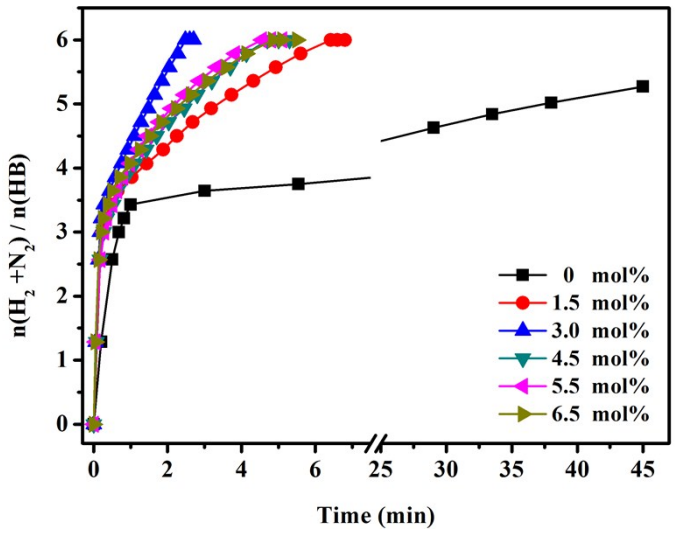

Fig. S3 Time course plots for the dehydrogenation of aqueous solution HB catalyzed by $Ni_{0.9}Pt_{0.1}$-$(Cr_2O_3)_x$ with different molar contents (x = 1/2*[Cr/(Ni + Pt+ Cr)]) of Cr_2O_3 (n_{NiPt} : n_{HB} = 0.1, NaOH = 0.5 M, T = 50 ^oC).

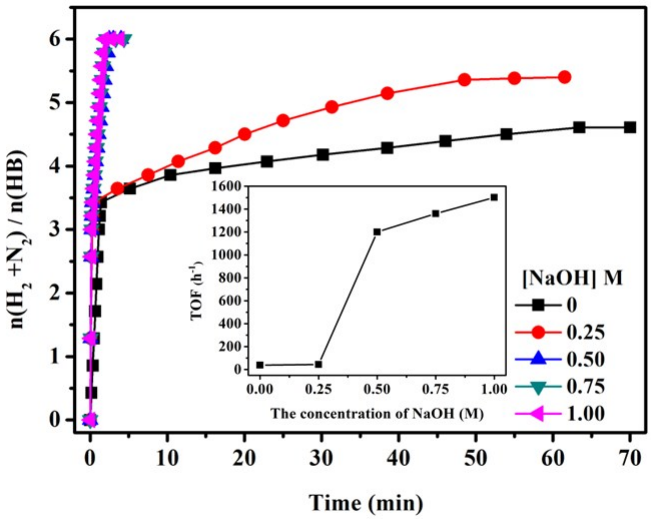

Fig. S4 Time course plots for the dehydrogenation of aqueous solution HB over $Ni_{0.9}Pt_{0.1}$-Cr_2O_3 NPs with different concentration of NaOH. The insert is the corresponding TOF over $Ni_{0.9}Pt_{0.1}$-Cr_2O_3 NPs with different concentration of NaOH (n_{NiPt} : n_{HB} = 0.1, T = 50 ^oC).

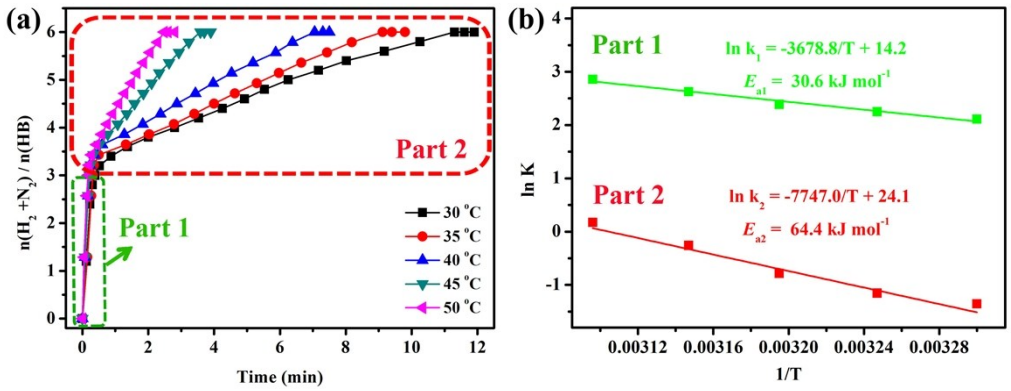

Fig. S5 (a) Time course plot for the dehydrogenation of aqueous solution HB over $Ni_{0.9}Pt_{0.1}$-Cr_2O_3 NPs at 30, 35, 40, 45, and 50 ^oC (n_{NiPt} : n_{HB} = 0.1, NaOH = 0.5 M); (b) Plot of ln k versus 1/T for hydrogen generation from hydrolysis of the BH_3 group (Part 1) and decomposition of the N_2H_4 moiety (Part 2) of $N_2H_4BH_3$.

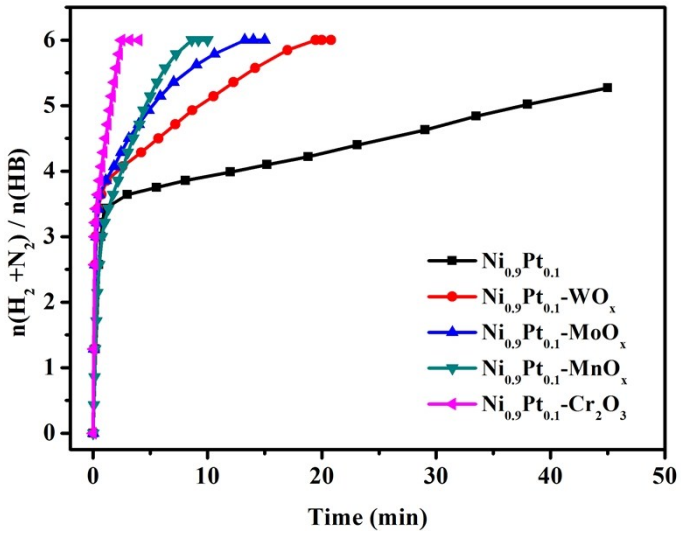

Fig. S6 Time course plots for the dehydrogenation of aqueous solution HB over $Ni_{0.9}Pt_{0.1}$ and $Ni_{0.9}Pt_{0.1}$-MO_x NPs (M = Cr, Mo, W, and Mn) (n_{NiPt} : n_{HB} = 0.1, n_{MOx} : $n_{(NiPt + MOx)}$ = 0.06, NaOH = 0.5 M, T = 50 ^{o}C).

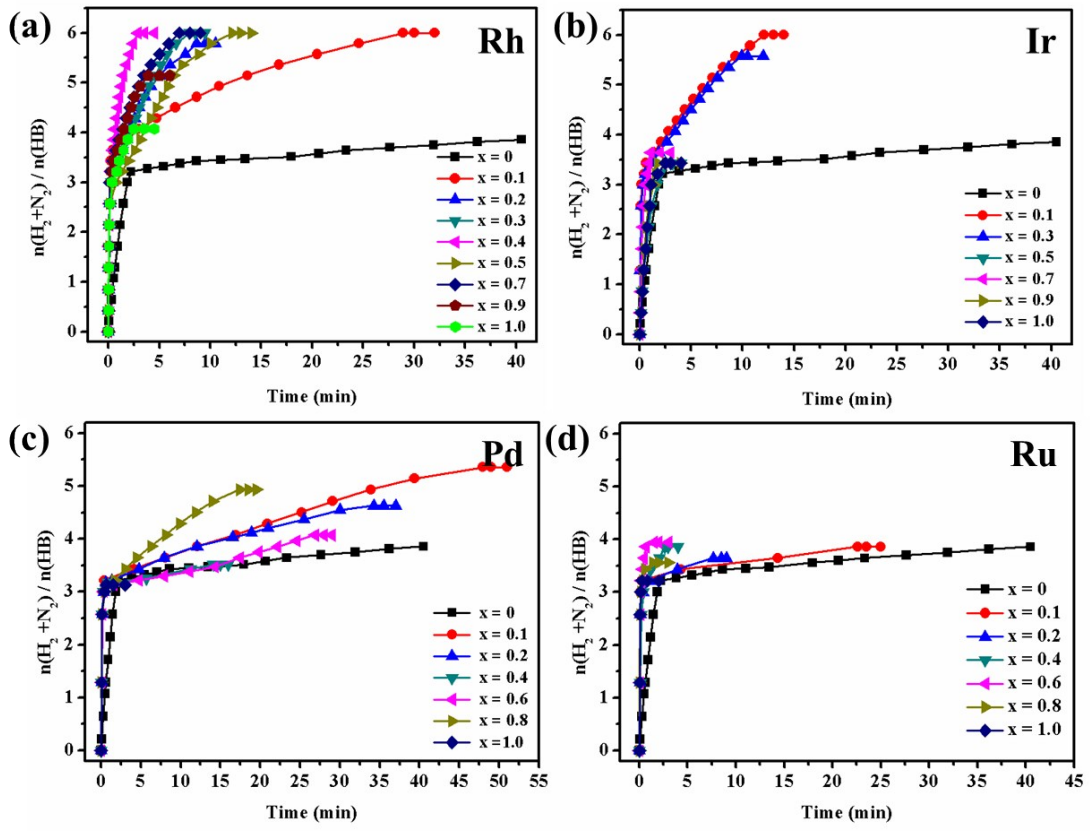

Fig. S7 Time course plots for the dehydrogenation of aqueous solution HB catalyzed by (a) $Ni_{1-x}Rh_x$-Cr_2O_3, (b) $Ni_{1-x}Ir_x$-Cr_2O_3, (c) $Ni_{1-x}Pd_x$-Cr_2O_3, and (d) $Ni_{1-x}Ru_x$-Cr_2O_3 NPs (n_{metal} : n_{HB} = 0.1, NaOH = 0.5 M, T =50 °C, Cr_2O_3 : 3.0 mol%).

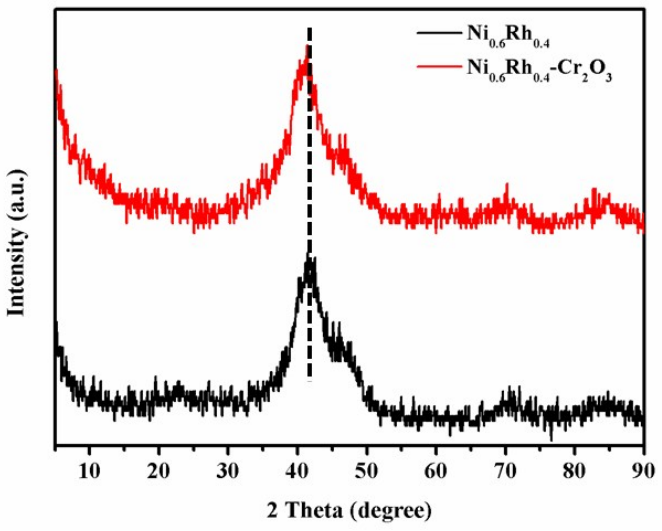

Fig. S8 XRD patterns of the as-synthesized $Ni_{0.6}Rh_{0.4}$ and $Ni_{0.6}Rh_{0.4}$-Cr_2O_3 samples.

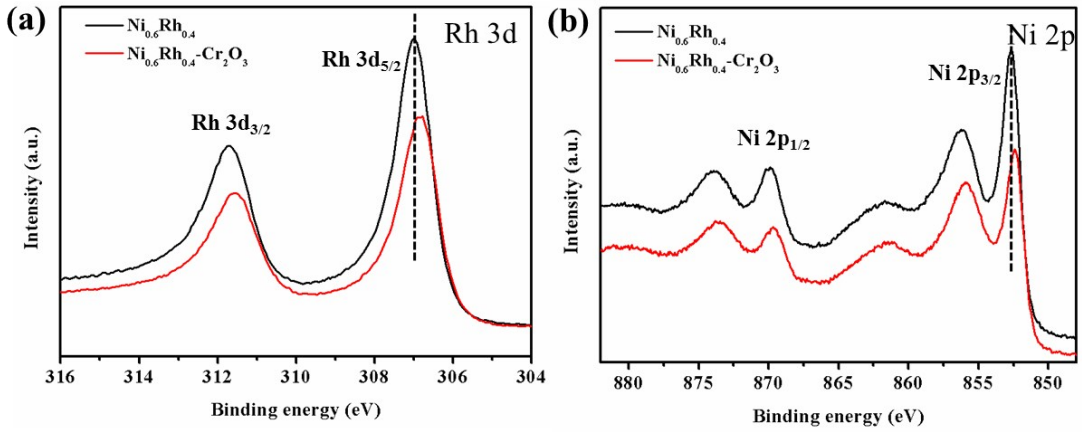

Fig. S9 The high resolution XPS spectra of (a) Rh 3d, (b) Ni 2p for $Ni_{0.6}Rh_{0.4}$ and $Ni_{0.6}Rh_{0.4}$-Cr_2O_3 nanocatalyst after argon etching 5 min, respectively.

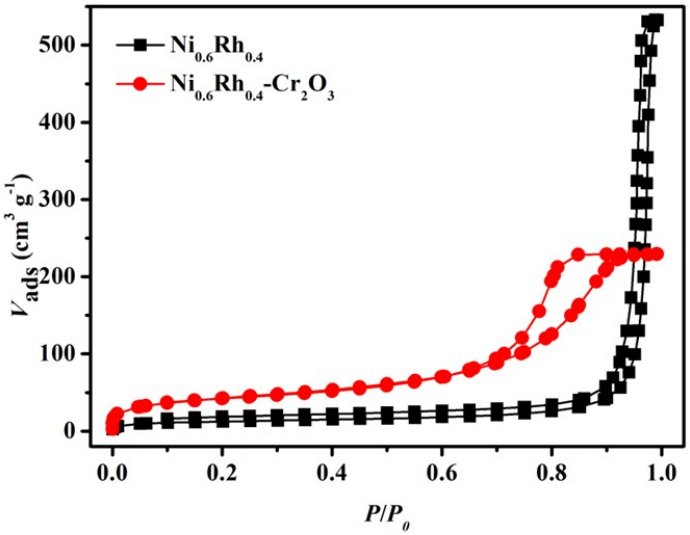

Fig. S10 Nitrogen isotherms recorded at 77 K for $Ni_{0.6}Rh_{0.4}$ and $Ni_{0.6}Rh_{0.4}$-Cr_2O_3 NPs.

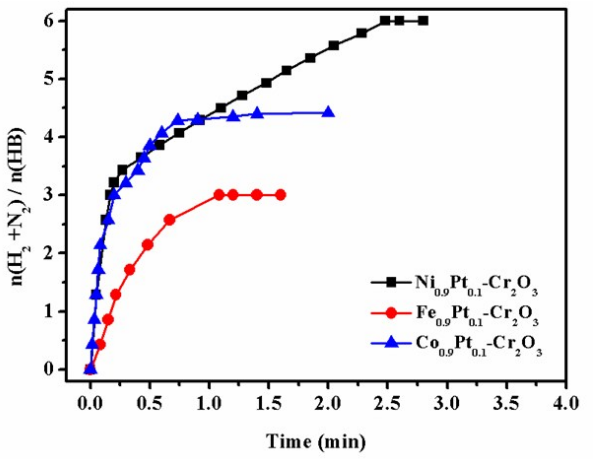

Fig. S11 Time course plots for the dehydrogenation of aqueous solution HB catalyzed by $M_{0.9}Pt_{0.1}$-Cr_2O_3 (M = Ni, Fe, and Co) (n_{metal} : n_{HB} = 0.1, NaOH = 0.5 M, T = 50 ^oC).

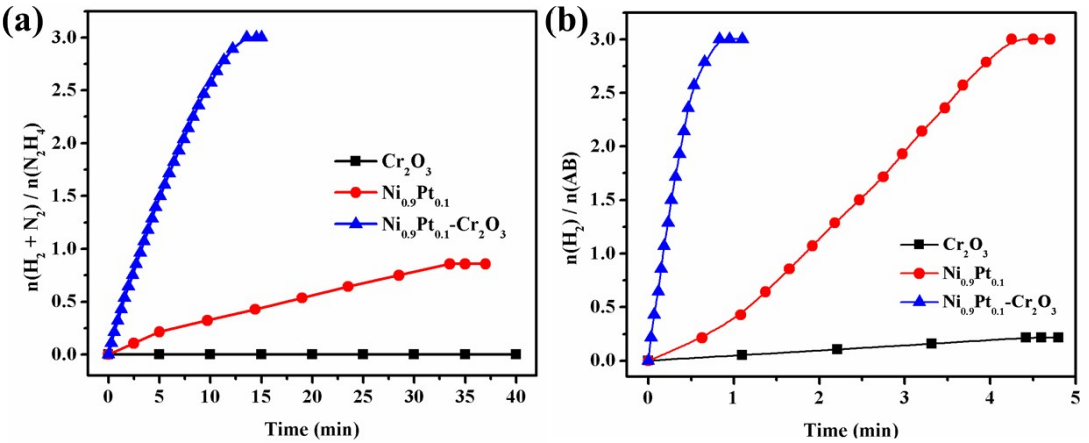

Fig. S12 Time course plots for the dehydrogenation of aqueous solution of (a) N_2H_4 and (b) AB catalyzed by Cr_2O_3, $Ni_{0.9}Pt_{0.1}$, and $Ni_{0.9}Pt_{0.1}$-Cr_2O_3 (n_{metal} : n_{N2H4} = 0.1, n_{metal} : n_{AB} = 0.1).

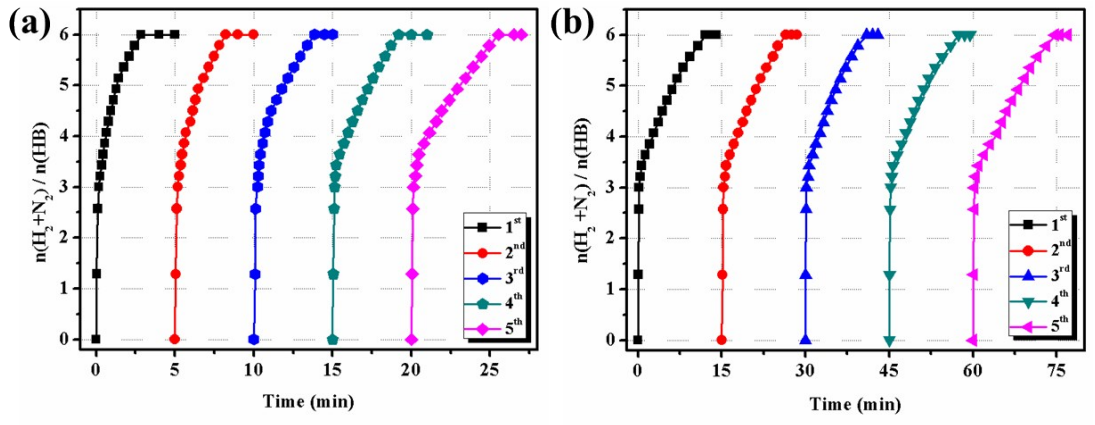

Fig. S13 Time course plots for the dehydrogenation of aqueous solution HB over (a) $Ni_{0.6}Rh_{0.4}$-Cr_2O_3 and (b) $Ni_{0.9}Ir_{0.1}$-Cr_2O_3 (n_{metal} : n_{HB} = 0.1, NaOH = 2.0 M, 50 °C) at sequential runs by the addition of equivalent molar amounts of HB.

Table S1. Catalytic activities for dehydrogenation of hydrazine borane catalyzed by different catalysts.

Catalyst	**Tem. (^oC)**	**n(metal)/ n(HB)**	**$n(H_2+N_2)/n$ (HB)**	**TOF (h^{-1})**	**Ref.**
$Ni_{0.6}Pt_{0.4}$/MSC-30	30	0.1	5.95 ± 0.05	662[a]	46
Ni_5@Pt	50	0.04	4.4	2.3[a]	43
$Ni_{0.89}Ir_{0.11}$	50	0.14	4.9	9.5[a]	42
$Ni_{0.89}Rh_{0.11}$	50	0.16	5.1	9.9[a]	42
$Ni_{0.89}Pt_{0.11}$	50	0.14	5.79	18[a]	40
$Ni_{0.77}Ru_{0.23}$	50	0.15	4.0	23.3[a]	42
Ni@Rh_4Ni	50	0.1	5.74	72[a]	45
Rh_4Ni NPs	50	0.1	5.8	90[a]	44
CuNiMo	50	0.2	6.0	108[b]	56
NiPt-CeO_2	50	0.1	5.74	234[b]	50
$Ni_{0.9}Pt_{0.1}$/graphene	50	0.1	6.0	240[b]	51
$Rh_{0.8}Ni_{0.2}$@CeOx/rGO	50	0.1	6.0	667[b]	49
$Ni_{0.9}Pt_{0.1}$-Cr_2O_3	50	0.1	6.0	1200	This study
$Ni_{0.3}Pt_{0.7}$-Cr_2O_3	50	0.1	6.0	3093	This study
$Ni_{0.5}Fe_{0.5}$-CeO_x/MIL-101	70	0.2	6.0	351.3[b]	57
CuNiMo	70	0.2	6.0	484[b]	56

[a]The total TOF values were calculated according to the original data provided by the reports, in which the TOF values were not provided.

[b]The total TOF values were provided by the reports.