Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Material

Metal-organic Frameworks Immobilized RhNi Alloy Nanoparticles for Complete H_2 Evolution from Hydrazine Borane and Hydrous Hydrazine

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Calculation method for TOF

The total turn-over frequency (TOF) reported in this work is an apparent TOF value based on the number of metal (Rh + Ni) atoms in catalysts, which is calculated from the equation as follows:

$$TOF = \frac{n_{H_2}}{n_{(Rh+Ni)} \times t} \qquad \text{(Eq. S1)}$$

Where n_{H2} is the mole number of generated H_2, $n_{(Rh+Ni)}$ is the total mole number of Ni and Rh in catalyst and *t* is the completed reaction time in hour. The TOF values of all the cited catalysts shown in Table 1 and Table S2 are the total TOF values and are normalized to the mass of metals.

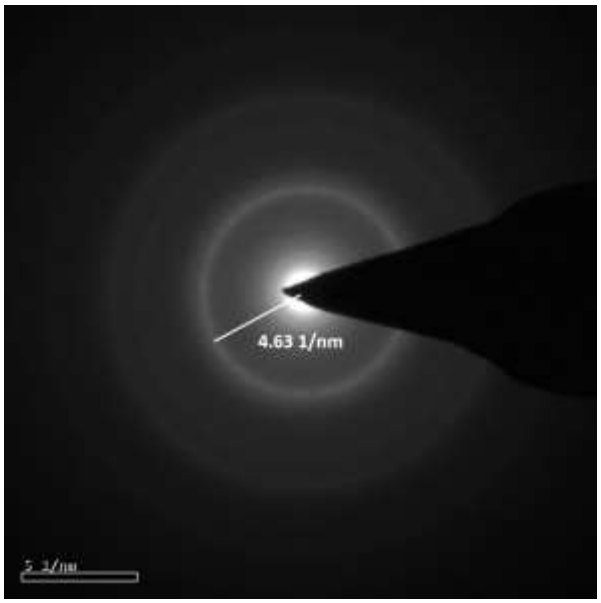

Fig. S1 SAED image of $Rh_{0.8}Ni_{0.2}$/MIL-101 catalyst.

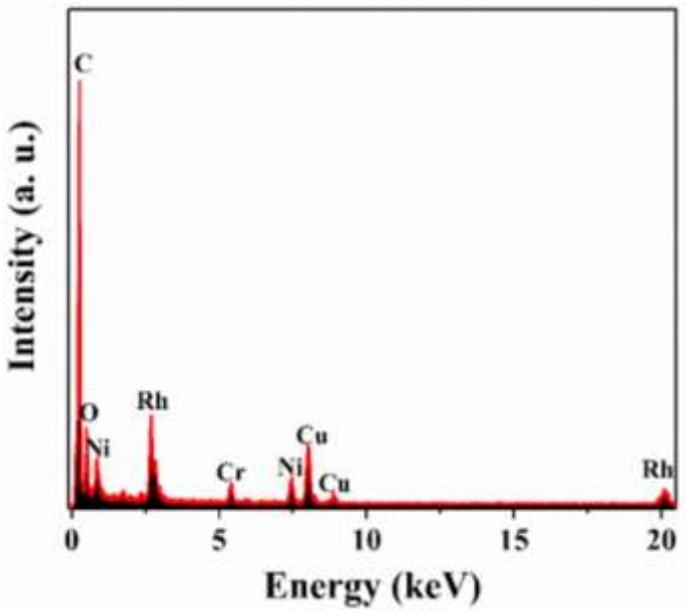

Fig. S2 EDX spectrum of $Rh_{0.8}Ni_{0.2}$/MIL-101 catalyst.

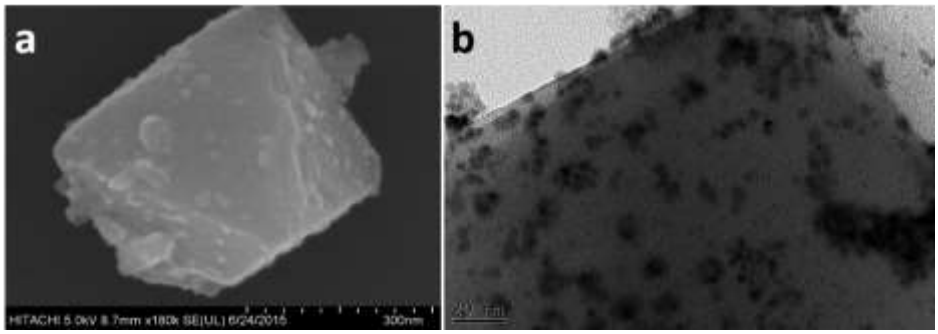

Fig. S3 The typical SEM (a) and TEM (b) images of the $Rh_{0.8}Ni_{0.2}$/MIL-101 catalyst obtained via a slow reduction process with a low molar ratio of reductant ($NaBH_4/(Rh^{3+}+Ni^{2+}) = 4$).

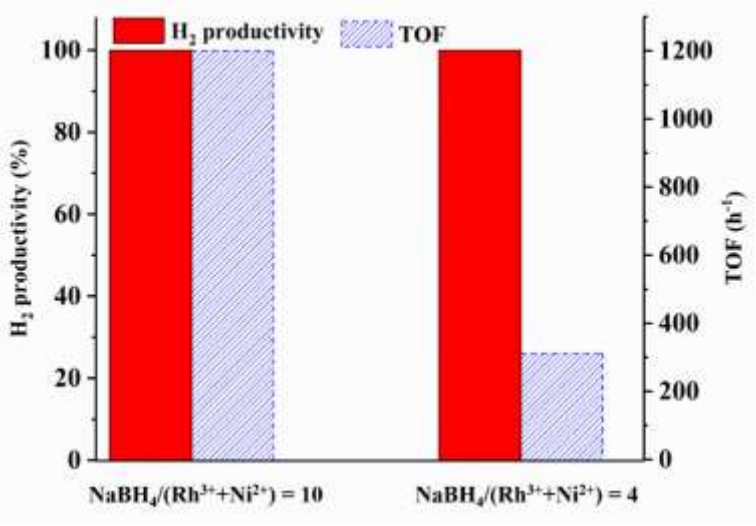

Fig. S4 Catalytic performance of $Rh_{0.8}Ni_{0.2}$/MIL-101 catalysts obtained with different molar ratio of reductant ($NaBH_4$/(Rh^{3+}+Ni^{2+}).

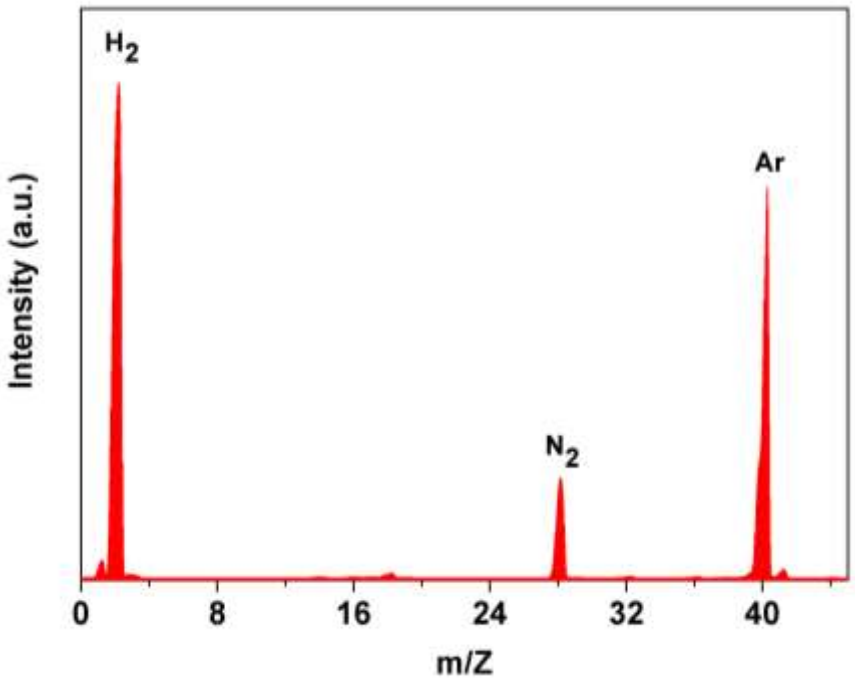

Fig. S5 Mass spectral profile for gases released from the aqueous $N_2H_4BH_3$ solution using $Rh_{0.8}Ni_{0.2}$/MIL-101 catalyst under an argon atmosphere.

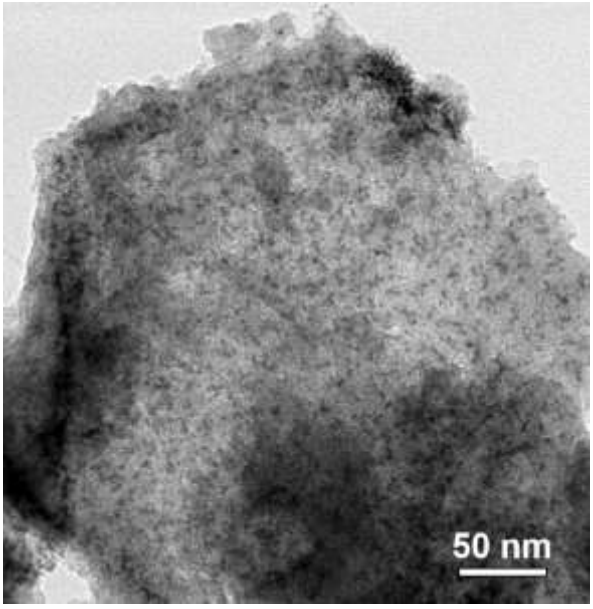

Fig. S6 TEM image of the $Rh_{0.8}Ni_{0.2}$/MIL-101 catalyst after the durability test.

Table S1. Catalysts composition determined by inductively coupled plasma atomic emission spectroscopic (ICP-AES).

Catalysts	Ni (wt%)	Rh (wt%)	Rh:Ni (atomic ratio)
Ni/MIL-101	10.0	~	~
Rh/MIL-101	~	16.7	~
$Rh_{0.8}Ni_{0.2}$/MIL-101	1.9	13.5	80.2:19.8

Table S2 Activities in terms of selectivity, activation energy and *TOF* values of different catalysts tested in H_2 generation from hydrous hydrazine.

Catalyst	T (^{o}C)	Selectivity (%)	E_a (kJ/mol)	*TOF* (h^{-1})[a]	Ref.
Rh	25	44	-	2.9	38
Rh_4Ni	25	100	-	6.0	39
$Rh/Ni@SiO_2$	25	99.4		66	40
RhNi@graphene	25	100	-	20.1	41
$Ni_{0.90}Pt_{0.05}Rh_{0.05}/La_2O_3$	25	100	-	45.9	42
Rh-Cu NOHFs/C	25	31.4	-	33.7	43
$Rh_{51}Ni_{19}P_{30}$/rGO	25	100	58.8	101	49
RhNiB	30	100	-	54.5	44
$Rh_{0.8}Ni_{0.2}@CeO_x$/rGO	30	100	58.0	36.4	21
Ni_3Rh_7/NPC-900	50	100	-	156	46
$Ni_{66}Rh_{34}$@ZIF-8	50	100	58.1	140	47
$Rh_{58}Ni_{42}$@MIL-101	50	100	33.0	344	50
$Rh_{55}Ni_{45}/Ce(OH)CO_3$	50	100	38.8	395	45
$Rh_{0.8}Ni_{0.2}$/MIL-101	**50**	**100**	**48.4**	**428.6**	**This study**
$Rh_{92.6}P_{7.4}$/rGO	50	100	50.5	843.9	48

[a]The total *TOF* values were calculated according to the original data provided by the reports.