Electronic Supplementary Material (ESI) for Dalton Transactions.

Rapid diffusion of H_2 and strong adsorption of D_2 in Ni-4PyC realized the efficient separation of H_2/D_2 by gas chromatography

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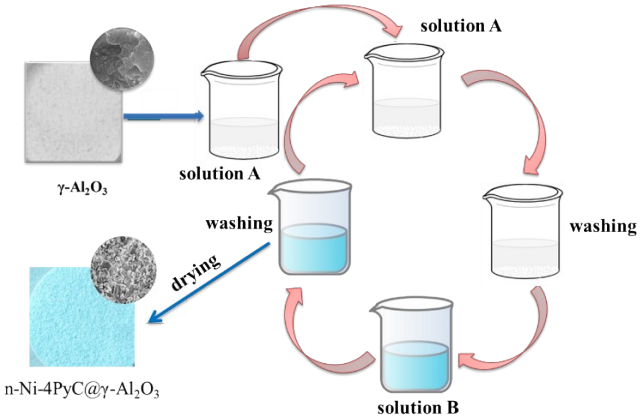

Fig. S1 The synthesis process scheme of Ni-4PyC@γ-Al_2O_3

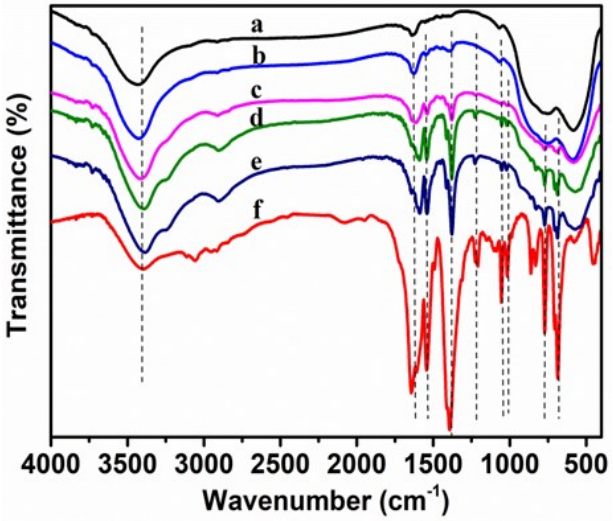

Fig. S2 IR spectra of (a) γ-Al_2O_3, (b) 1-Ni-4PyC@γ-Al_2O_3, (c) 3-Ni-4PyC@γ-Al_2O_3, (d) 5-Ni-4PyC@γ-Al_2O_3, (e) 7-Ni-4PyC@γ-Al_2O_3, (f) Ni-4PyC.

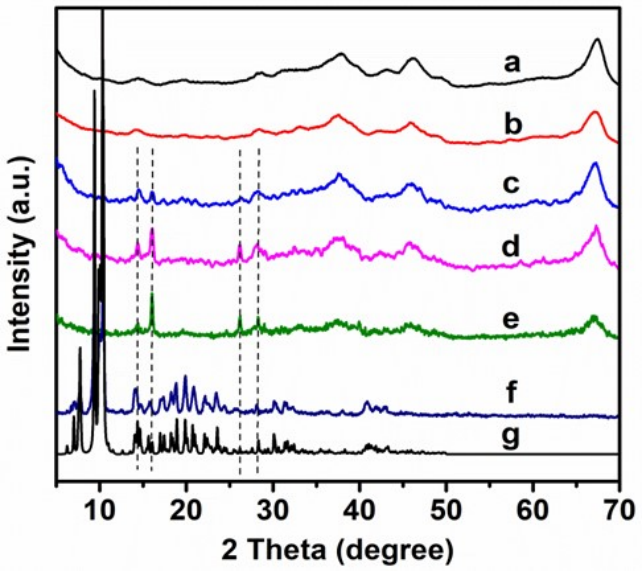

Fig. S3 The PXRD spectra of (a) γ-Al_2O_3, (b) 1-Ni-4PyC@γ-Al_2O_3, (c) 3-Ni-4PyC@γ-Al_2O_3, (d) 5-Ni-4PyC@γ-Al_2O_3, (e) 7-Ni-4PyC@γ-Al_2O_3, (f) Ni-4PyC, (g) Ni-4PyC (simulated).

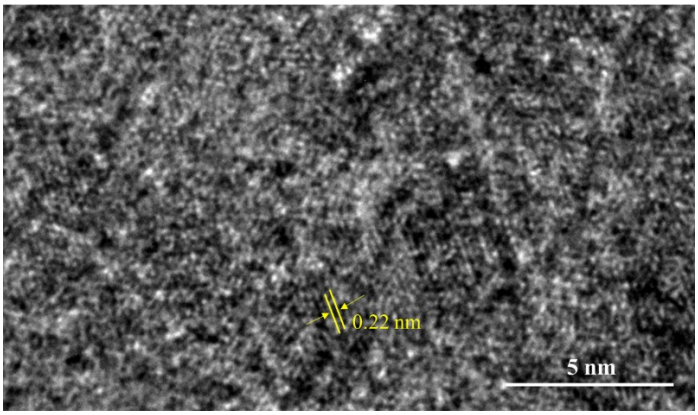

Fig. S4 HRTEM image of 7-Ni-4PyC@γ-Al_2O_3

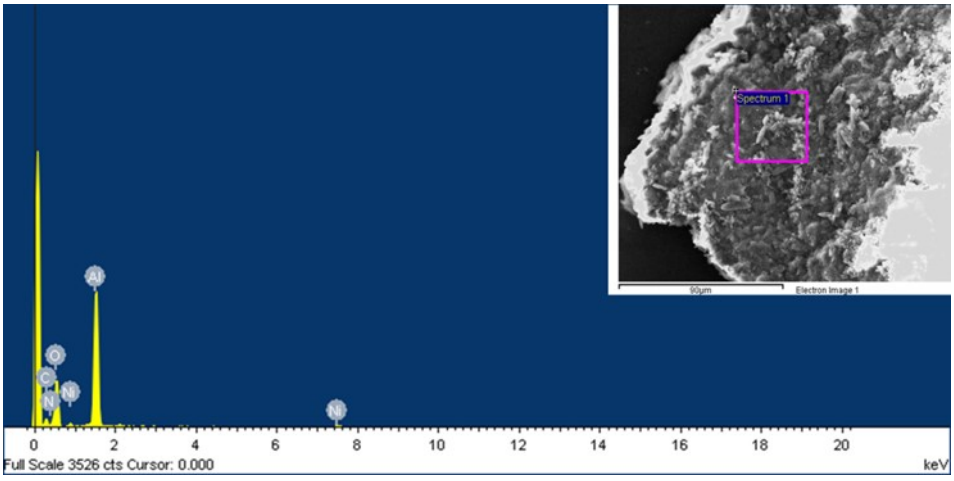

Fig. S5 The EDS spectrum of 3-Ni-4PyC@γ-Al_2O_3.

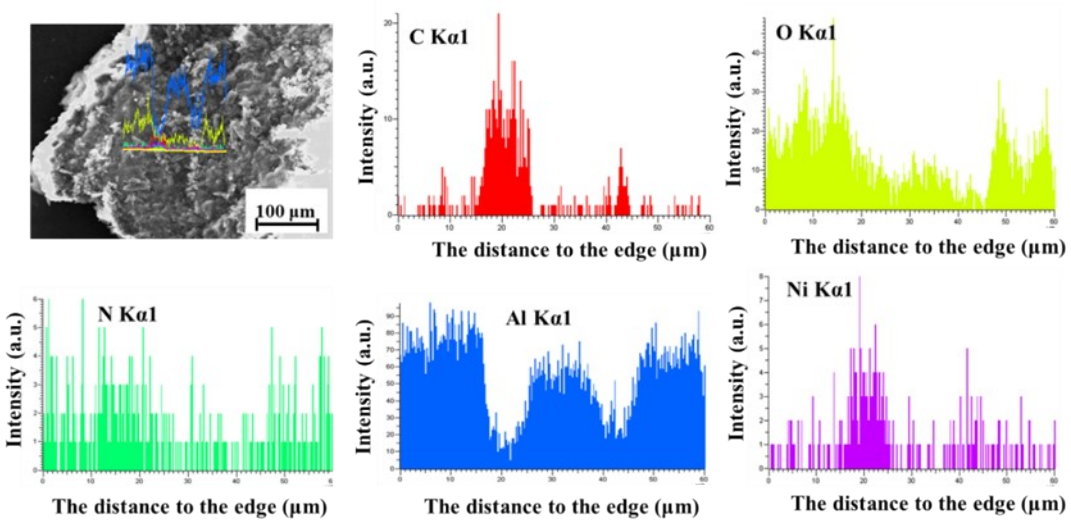

Fig. S6 EDS line scan of 3-Ni-4PyC@γ-Al_2O_3.

Table S1. BET surface area, pore volume and average aperture of γ-Al_2O_3, 3-Ni-4PyC@γ-Al_2O_3.

Chromatographic packing	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore size (nm)
γ-Al_2O_3	205.2	0.484		7.64
3-Ni-4PyC@γ-Al_2O_3	207.2	0.174	0.039	3.35

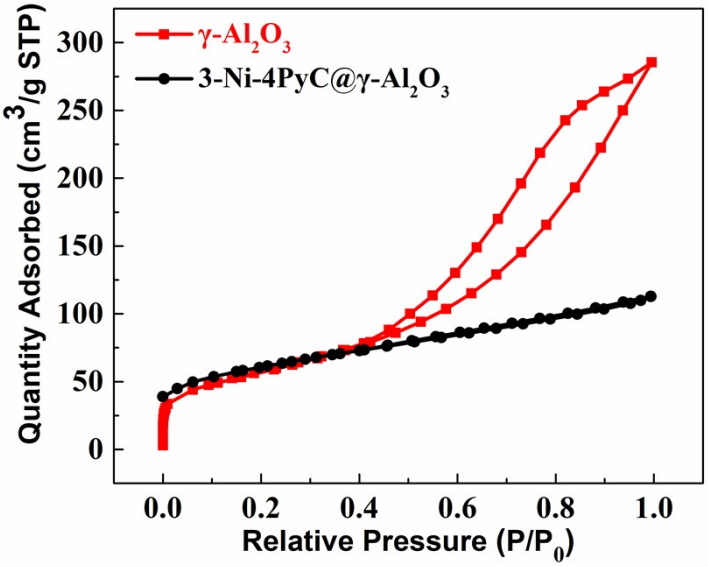

Fig. S7 N_2 adsorption-desorption isotherms of γ-Al_2O_3 and 3-Ni-4PyC@γ-Al_2O_3.

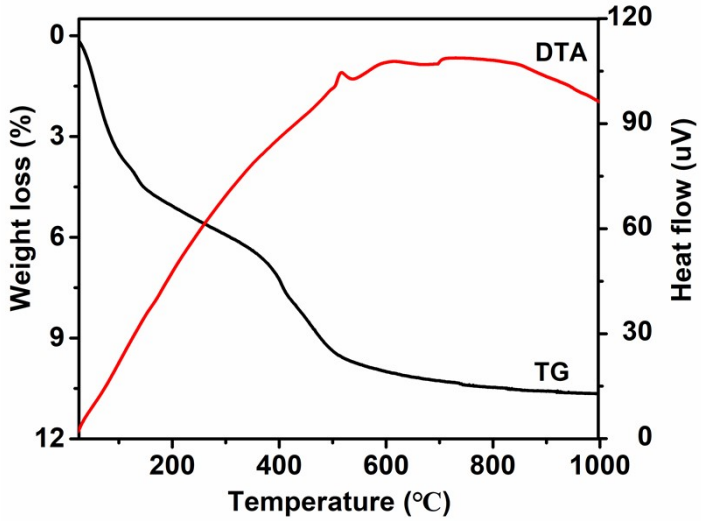

Fig. S8 TG-DTA curves of 3-Ni-4PyC@γ-Al_2O_3.

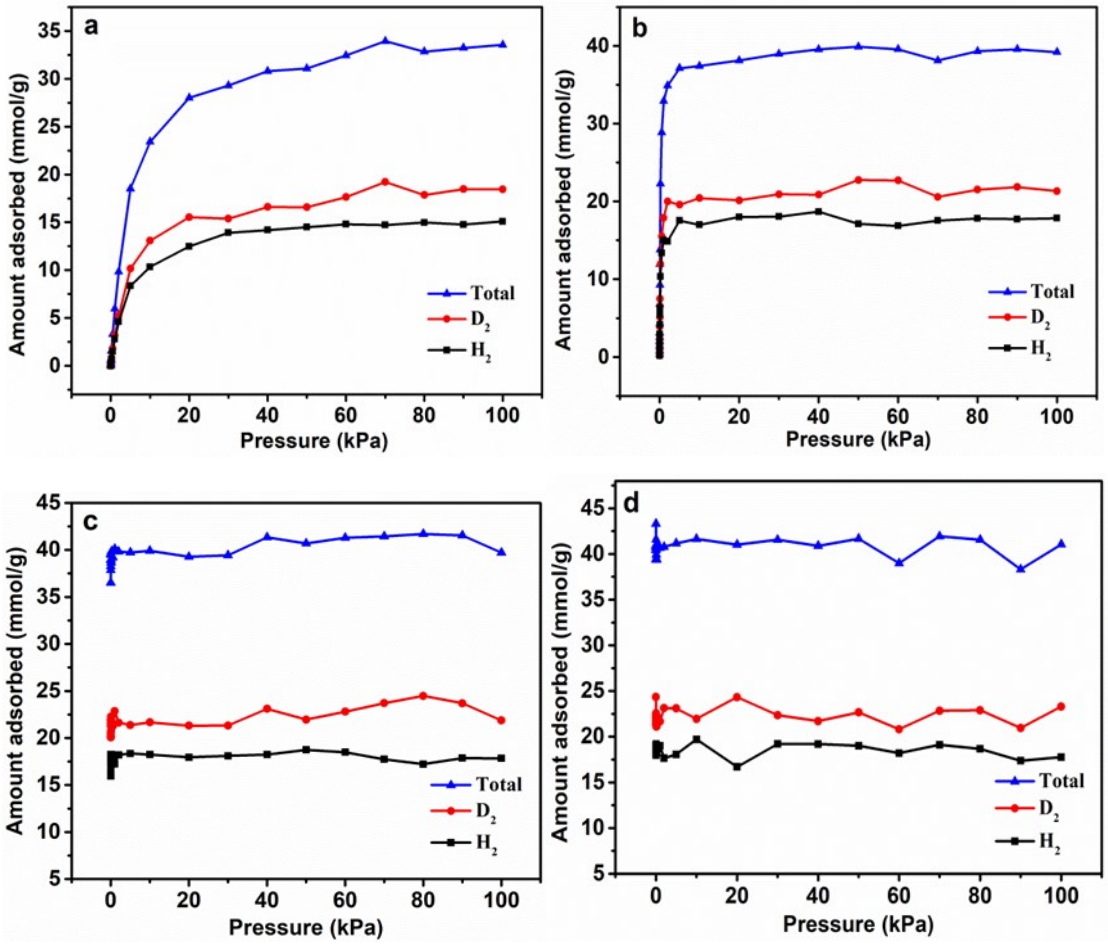

Fig. S9 Variations with pressure of each adsorption amount and total adsorption amount of the mixed gas (H_2:D_2 = 1:1) in the Ni-4PyC at different temperatures: (a) 77 K, (b) 60 K, (c) 40 K, (d) 20 K.

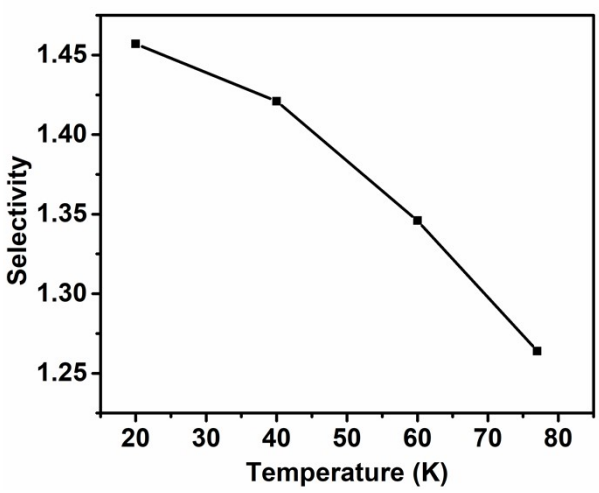

Fig. S10 The best adsorption selectivity of mixed D_2/H_2(D_2:H_2 = 1:1) obtained under different temperature in Ni-4PyC

Table S2. The selectivity of D_2/H_2 at Ni-4PyC at different temperatures and pressures

pressure（kPa）	Selectivity（D_2/H_2）			
	77K	60K	40K	20K
0.001	1.167	1.134	1.289	1.202
0.002	1.182	1.139	1.153	1.180
0.004	1.257	1.147	1.338	1.283
0.006	1.139	1.115	1.220	1.186
0.008	1.217	1.124	1.243	1.207
0.01	1.165	1.125	1.210	1.159
0.02	1.093	1.146	1.244	1.255
0.04	1.074	1.321	1.168	1.169
0.06	1.155	1.235	1.295	1.138
0.08	1.184	1.196	1.160	1.145
0.1	1.182	1.182	1.213	1.156
0.2	1.112	1.155	1.183	1.157
0.5	1.215	1.159	1.184	1.183
1	1.141	1.188	1.326	1.140
2	1.139	1.345	1.188	1.311
5	1.217	1.117	1.165	1.279
10	1.264*	1.202	1.187	1.114
20	1.245	1.119	1.187	1.457*
30	1.106	1.159	1.178	1.164
40	1.170	1.117	1.267	1.131

50	1.144	1.330	1.171	1.193
60	1.192	1.346*	1.233	1.144
70	1.250	1.174	1.337	1.195
80	1.192	1.209	1.421*	1.227
90	1.252	1.233	1.326	1.205
100	1.223	1.195	1.226	1.312

*Indicates the maximum selectivity at each temperature

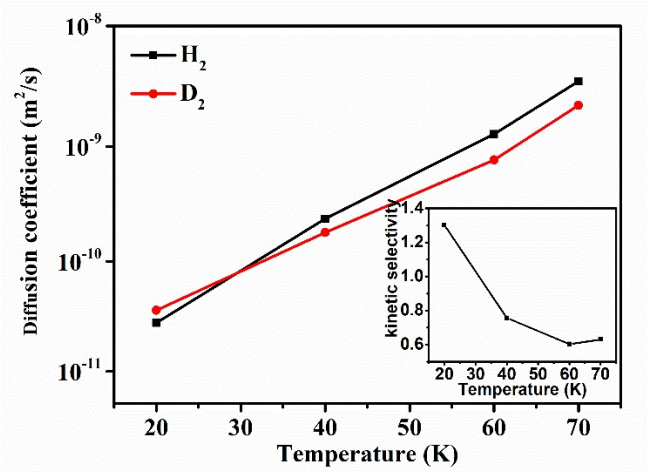

Fig. S11. The effect of temperature on the diffusion coefficients of H_2 and D_2 in Ni-4PyC. Inset: Kinetic selectivity of D_2 to H_2 at different temperatures. Temperature: 20, 40, 60, 77 K.

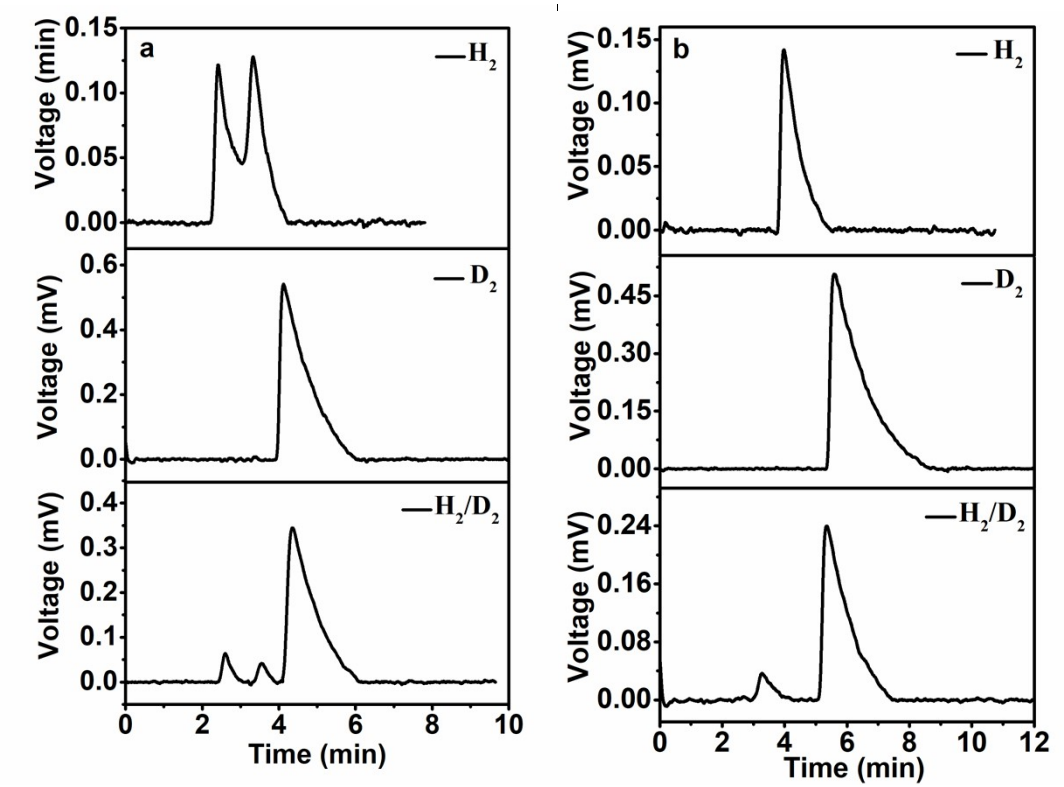

Fig. S12 The gas chromatogram of H_2, D_2 and H_2/D_2 (1:1) separation on stationary phase packing

(a) γ-Al_2O_3 and (b) 3-Ni-4PyC@γ-Al_2O_3. Experimental conditions: column length 60 cm; injection volume 50 μL; carrier gas flow rate 30 mL/min.

Table S3. Various parameters for chromatographic separation of H_2 and D_2 on 3-Ni-4PyC@γ-Al_2O_3 at different carrier gas flow rates.

Carrier gas flow rate (mL/min)	Retention time (min)		Resolution	Separation time (min)
	H_2	D_2		
10	9.692	15.272	1.75	24.74
20	5.239	8.520	1.81	12.59
30	3.292	5.355	1.84	7.47
60	2.025	3.443	1.79	5.62
90	1.497	2.488	1.74	3.61

Table S4. Under different injection volume, the separation parameters of H_2/D_2 on 3-Ni-4PyC@γ-Al_2O_3.

Injection volume	Retention time (min)		Peak height (mv)		Peak area (mV·min)		Resolution	Separation time (min)
(μL)	H_2	D_2	H_2	D_2	H_2	D_2		
50	3.292	5.355	37.84	244.109	742.2	8797.4	1.84	7.47
100	3.112	5.272	102.633	390.191	2118.9	18945	1.79	8.42
150	2.931	4.986	162.856	543.658	3784.6	29560.201	1.76	7.67
200	2.961	4.912	218.518	720.192	5223.4	42026.898	1.64	8.41
250	3.313	5.416	278.492	843.886	6393.4	56517.699	1.59	9.97

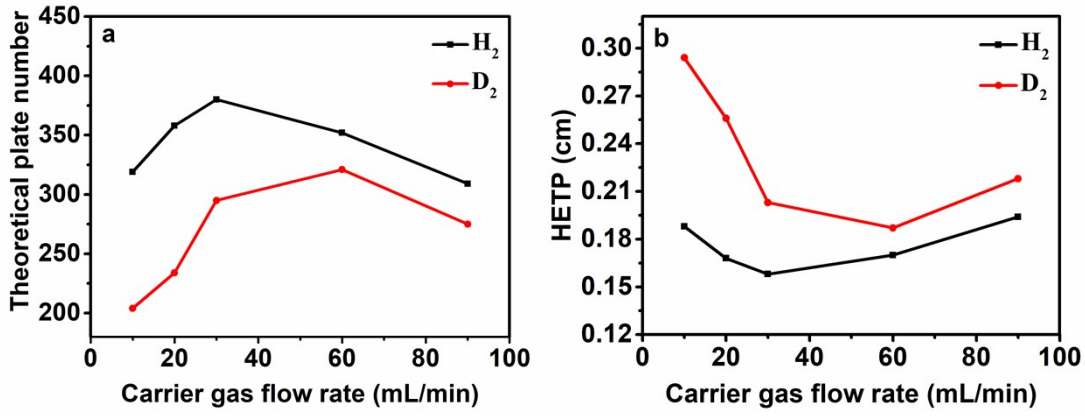

Fig. S13 (a) The relationship between the n of H_2/D_2 and the carrier gas flow rate, (b) the relationship between the HETP of H_2/D_2 and the carrier gas flow rate.

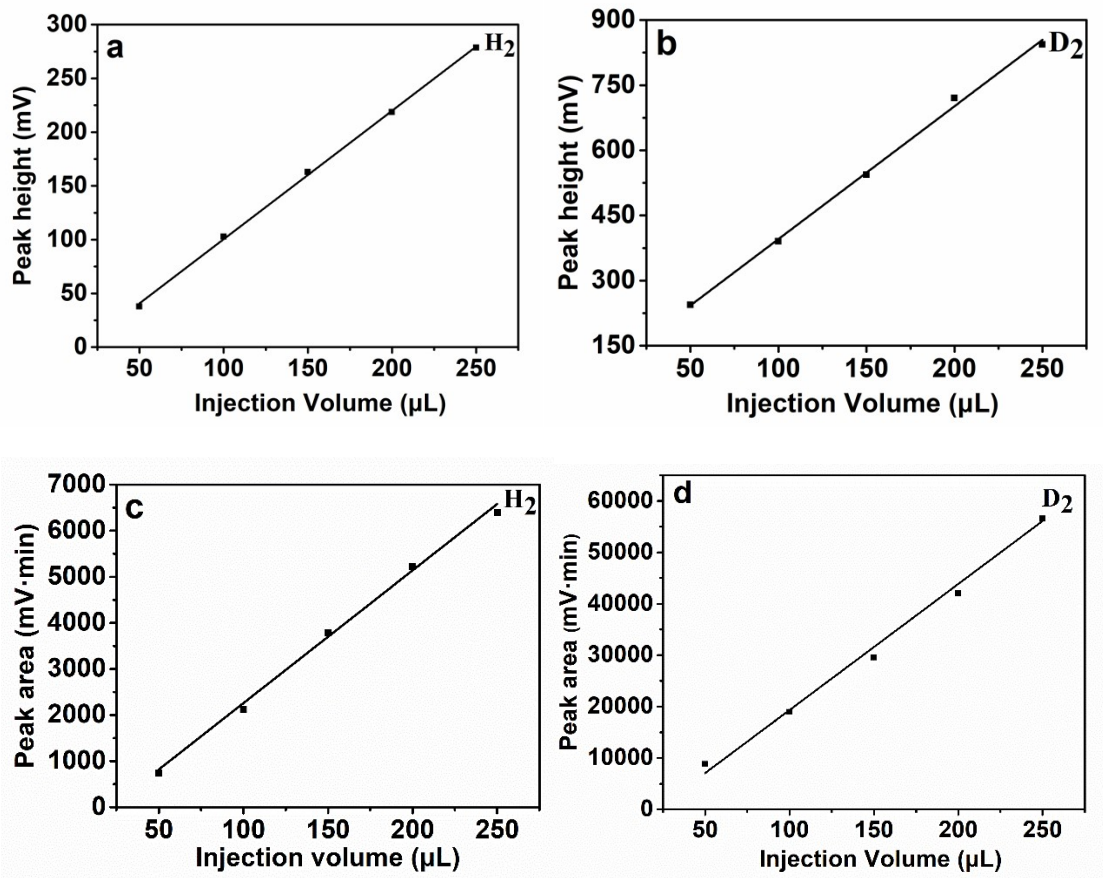

Fig. S14 Relationship between peak height (a, b), peak area (c, d) of H_2/D_2 and H_2/D_2 injection volume (H_2:D_2 = 1:1)

Table S5. Reproducibility of retention time, peak height and peak area of pure H_2 and D_2 component, and the corresponding relative standard deviation percentage (%RSD) with 3-Ni-4PyC@γ-Al_2O_3 packed column.

Times	H_2			D_2		
	Retention time (min)	Peak height	Peak area (mV. min)	Retention time (min)	Peak height	Peak area (mV· min)
1	3.324	78.839	1702.043	5.392	466.935	22524.670
2	3.343	82.111	1711.186	5.404	464.715	20316.460
3	3.348	73.780	1698.600	5.379	483.739	22001.070
4	3.341	78.959	1700.471	5.388	468.482	21605.870
5	3.326	76.862	1649.029	5.299	464.103	20973.870
6	3.290	82.799	1648.314	5.319	508.373	21875.270
7	3.288	78.809	1646.900	5.338	497.823	21516.570

8	3.272	87.097	1565.543	5.310	478.767	20455.200
9	3.276	77.576	1640.500	5.327	514.994	22331.400
10	3.372	79.067	1683.767	5.372	481.108	21816.370
Average	3.318	79.590	1664.635	5.353	482.904	21541.675
SD	0.033	3.466	41.948	0.036	17.520	706.857
RSD(%)	0.983	4.354	2.520	0.723	3.628	3.281

Table S6. Reproducibility of H_2/D_2 (25 μL:25 μL) separation and the corresponding standard deviation (SD), relative standard deviation percentage (%RSD), relative deviation percentage (%) under optimal conditions* with 3-Ni-4PyC@γ-Al_2O_3 packed column.

Times	Retention time (min)		Peak Area (S_{H2} and S_{D2}) of components in mixed samples (mV· min)		Content determined（%）		Relative deviation （%）	
	H_2	D_2	H_2	D_2	H_2	D_2	H_2	D_2
1	3.522	6.027	798.548	10412.098	47.97	48.33	-4.06	-3.331
2	3.572	6.080	848.677	10905.917	50.98	50.63	1.97	1.254
3	3.500	6.045	836.387	11265.221	50.24	52.30	0.49	4.590
4	3.577	5.980	838.177	10482.799	50.35	48.66	0.70	-2.674
5	3.545	5.988	833.645	11217.903	50.08	52.08	0.16	4.151
6	3.597	6.072	799.516	10408.211	48.03	48.32	-3.94	-3.367
7	3.577	6.065	867.048	10833.448	52.09	50.29	4.17	0.581
8	3.567	5.998	849.516	10390.544	51.03	48.23	2.07	-3.531
9	3.585	5.978	866.468	11041.525	52.05	51.26	4.10	2.513
10	3.578	5.996	825.952	10729.270	49.62	49.81	-0.76	-0.386
Average	3.562	6.023	836.394	10768.694	50.24	49.99	0.49	-0.02
SD	0.029	0.038	22.537	320.809	1.354	1.492	/	/
RSD(%)	0.810	0.629	2.695	2.979	2.695	2.985	/	/

*Peak area (mV· min) of pure H_2 and D_2 was 1664.635 and 21541.675, and their corresponding theoretical content was 50% respectively.