Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for

Hydrogenation of N-propylcarbazole over supported ruthenium as a new prototype of liquid organic hydrogen carriers

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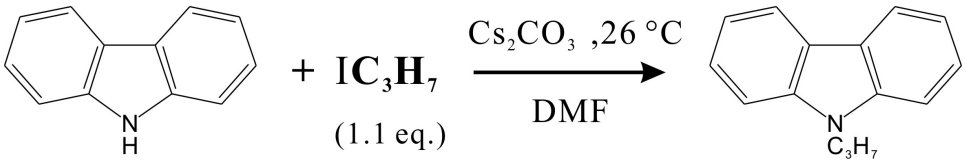
1. Chemicals and materials

The analytical reagent grade (AR) Carbazole, Caesium carbonate, 1-Iodopropane were purchased from Energy Chemical Company. Sichuan Ally High-Tech Company supplied ultra-high purity hydrogen (99.999%). All solvents (N,N-Dimethylformamide and Hexane) were purchased from Sinopharm Chemical Reagent Company. The commercially available 5 wt% Ru on alumina catalyst was purchased from KaiDa Technolgy Limited.

2. N-propylcarbazole synthesis and characterizations



Scheme S1 Alkylation of carbazole with 1-Iodopropane under classical conditions.

N-propylcarbazole was synthesized by solid-liquid phase alkylation of carbazole with 1-Iodopropane, as shown in Scheme S1. Caesium carbonate was used as a phase transfer catalyst. A solution of 10 mmol of the reagent carbazole and 11 mmol of 1-Iodopropane and 11 mmol of anhydrous Cs_2CO_3 in 100 ml of dry Dimethylformamide (DMF) was poured into a

round-bottomed flask, the reaction mixture was stirred at the temperature of 26 °C. The completion of the reaction required reaction time of 30 hours. Isolated yield of final product N-propylcarbazole was in the range of 95-98 %. GC-MS analysis was carried out on an Agilent 7890A-GC-5975C-MSD instrument with a capillary column of BD-17ms (30m×320μm×0.25μm) and He as carrier gas. Melting Point System (Mettler-Toledo, M50) was used to check the melting point (m.p.) of N-propylcarbazole. The melting range was detected to be 47.2 °C to 49.6 °C.

3. Experimental details of hydrogenation

The catalytic hydrogenation reaction of N-propylcarbazole was carried out at 120, 130, 140 and 150 °C and a hydrogen pressure of 7 MPa in a 600 mL stainless steel autoclave batch reactor (Parr Instrument Company 4568) with continuous monitoring and control of stirrer speed, temperature and hydrogen pressure. The schematic diagram of the hydrogenation reactor is shown in Fig. S1. The reaction mixture was stirred using a magnetic stirrer at the speed of 600 rpm. In a typical experiment, 10 gram of N-propylcarbazole and 1 gram of Ru catalyst were added to the reactor. The reactor was then sealed, flushed with hydrogen and heated to the certain temperature. The system was charged with 7 MPa ultra-high pure hydrogen after the desired temperature was reached. To obtain catalytic information such as the concentration versus time profile, small liquid samples were removed periodically (every 2 min for the first 10 min; every 5 min for 10-60 min; every 15 min for 60-120 min) from the reactor for composition analysis using GC-MS (Agilent 7890A-GC-5975C-MSD instrument with a capillary column of BD-17ms).

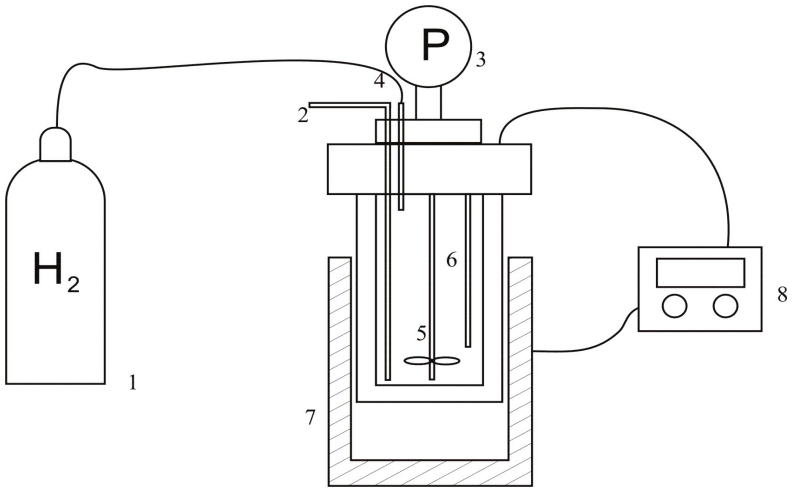


Fig. S1 Schematic diagram of the hydrogenation reactor. 1 H_2 tank; 2 In situ sampling; 3 Pressure gauge; 4 H_2 to reactor; 5 stirring; 6 Thermocouple; 7 heater; 8 controller (connected to computer)

4. Computational details of perhydro-N-propylcarbazole isomers

The DFT calculations were performed using DMol[3] program. The electronic structure calculations were done using a double-numeric atomic basis set (DNP) with the gradient-corrected GGA functional of PBE to account for the exchange-correlation effects. Full geometry optimization on all molecular structures was carried out without symmetry constraints.

For the full hydrogenation products, we optimized the structures of all possible conformations to identify the most stable isomers. The lowest energy isomers were found to be 12H-NPCZ-a and 12H-NPCZ-b shown in Scheme 1 (Table S1).

Table S1 The calculated relative energies of perhydro-N-propylcarbazole isomers with the energy of 12H-NPCZ-b set to 0 kcal/mol..

Isomer Name	Total Energy (kcal/mol)
12H-NPCZ-a	0.2
12H-NPCZ-b	0
12H-NPCZ-c	2.1
12H-NPCZ-d	1.1
12H-NPCZ-e	2.1
12H-NPCZ-f	1
12H-NPCZ-g	4.6
12H-NPCZ-h	2.1
12H-NPCZ-i	2
12H-NPCZ-j	5.8
12H-NPCZ-k	1

5. Catalyst properties

The commercially available 5 wt% Ru on alumina catalyst was received in a reduced state. It was re-reduced prior to use as the hydrogenation catalyst. The catalyst was characterized to determine BET surface area, pore volume and pore size using a Micromeritics ASAP 2020 analyzer. Table S2 summarizes the characterization data for the Ru/alumina catalyst. BET surface area, pore volume and average pore size were also measured for the 5 wt% reduced Ru/alumina catalyst.

Table S2 Catalyst properties of the re-reduced Ru/alumina.

Catalyst	BET surface area, m^2g^{-1}	Pore volume, cm^3g^{-1}	Average pore size, nm	Tap density, g ml^{-1}	Metal dispersion, %
Ru/Al_2O_3	108.2	0.35	12.3	0.76	11.4

Table S3 N-propylcarbazole conversion obtained by GC-MS analysis of the samples at 120 °C.

Time, min	Concentration, mol/L				
	NPCZ	4H-NPCZ	8H-NPCZ	12H-NPCZ-a	12H-NPCZ-b
0	4.8416	0	0	0	0
2	2.90496	1.01674	0.33891	0.09683	0
4	1.95659	1.50777	1.0024	0.47167	0
6	1.16198	1.93664	1.06515	0.67782	0
8	0.72624	1.5009	1.59773	1.01674	0.04842
10	0.49016	0.80898	1.91689	1.35817	0.1222
15	0.14651	0.49438	2.35762	1.74801	0.19197
20	0	0.28774	1.84906	2.45256	0.25225
25	0	0.10744	1.37366	3.06894	0.32637
30	0	0	1.17796	3.26551	0.39812
35	0	0	0.83029	3.46567	0.5457
40	0	0	0.56952	3.62229	0.64979
45	0	0	0.43632	3.67981	0.72547
50	0	0	0.2016	3.65943	0.98057
55	0	0	0.10211	3.64137	1.11294
60	0	0	0	3.55654	1.28506
75	0	0	0	3.45927	1.38233
90	0	0	0	3.38854	1.45306
105	0	0	0	3.14704	1.69456
120	0	0	0	3.00179	1.83981

Table S4 N-propylcarbazole conversion obtained by GC-MS analysis of the samples at 130 °C.

Time, min	Concentration, mol/L				
	NPCZ	4H-NPCZ	8H-NPCZ	12H-NPCZ-a	12H-NPCZ-b
0	4.8416	0	0	0	0
2	2.75971	1.30723	0.58099	0.09712	0
4	1.73402	1.89428	1.37976	0.31771	0
6	0.9199	1.74298	1.64614	0.48416	0
8	0.58099	1.45248	1.88822	0.77466	0.04842
10	0.24208	1.22037	2.1334	1.30283	0.09683
15	0	0.20388	2.3092	1.99009	0.19197
20	0	0.11378	1.3649	2.79147	0.54274
25	0	0	0.8895	3.31102	0.64108
30	0	0	0.59697	3.36235	0.83387
35	0	0	0.39454	3.46567	0.98144
40	0	0	0.1925	3.41648	1.23078
45	0	0	0	3.22872	1.60412
50	0	0	0	2.93319	1.90841
55	0	0	0	2.51763	2.32397
60	0	0	0	2.03347	2.80813
75	0	0	0	1.35565	3.48595
90	0	0	0	0.67782	4.16378
105	0	0	0	0.19366	4.64794
120	0	0	0	0.09683	4.74477

Table S5 N-propylcarbazole conversion obtained by GC-MS analysis of the samples at 140 °C.

Time, min	Concentration, mol/L				
	NPCZ	4H-NPCZ	8H-NPCZ	12H-NPCZ-a	12H-NPCZ-b
0	4.8416	0	0	0	0
2	2.4208	1.11357	0.77466	0.43574	0
4	1.46681	1.68347	1.05213	0.63919	0
6	0.72624	1.59773	1.45248	0.96832	0.09683
8	0.2905	1.25882	1.83981	1.39922	0.16946
10	0	1.08345	1.65772	1.84509	0.26837
15	0	0.09688	0.96629	2.9604	0.81804
20	0	0	0.42863	3.25452	1.15845
25	0	0	0.20591	3.33272	1.30297
30	0	0	0	3.28275	1.55885
35	0	0	0	2.90496	1.93664
40	0	0	0	2.46922	2.37238
45	0	0	0	1.93664	2.90496
50	0	0	0	1.35565	3.48595
55	0	0	0	0.87149	3.97011
60	0	0	0	0.33891	4.50269
75	0	0	0	0	4.8416
90	0	0	0	0	4.8416
105	0	0	0	0	4.8416
120	0	0	0	0	4.8416

Table S6 N-propylcarbazole conversion obtained by GC-MS analysis of the samples at 150 °C.

Time, min	Concentration, mol/L				
	NPCZ	4H-NPCZ	8H-NPCZ	12H-NPCZ-a	12H-NPCZ-b
0	4.8416	0	0	0	0
2	2.22714	1.16198	0.96832	0.48416	0
4	1.25882	1.74646	1.19922	0.6968	0
6	0.67782	1.30723	1.79139	0.91927	0.13556
8	0	0.96832	2.46922	1.2104	0.21787
10	0	0.79935	2.32377	1.42358	0.31679
15	0	0.19284	1.42929	2.43741	0.7687
20	0	0	0.59968	2.69222	1.5497
25	0	0	0.41531	2.47038	1.95591
30	0	0	0	2.55191	2.28969
35	0	0	0	1.85525	2.98635
40	0	0	0	1.45248	3.38912
45	0	0	0	0.9199	3.9217
50	0	0	0	0.48416	4.35744
55	0	0	0	0.19366	4.64794
60	0	0	0	0	4.8416
75	0	0	0	0	4.8416
90	0	0	0	0	4.8416
105	0	0	0	0	4.8416
120	0	0	0	0	4.8416