Supporting information

Experimental

Synthesis of catalyst

The Pd/Al-MCM-41 catalyst was synthesized from tetraethyl orthosilicate (TEOS) (Wako), sodium aluminate (Wako) and $PdCl_2$ in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB, Aldrich). Molar composition of the final gel was SiO_2: x Al: 0.5 NaOH: 0.12 CTAB: 118 H_2O and x can be varied from 0.25 to 0.01. A mixture of 1.05 g of CTAB, 0.48 g of NaOH and 50.9 g of deionized water was stirred at 35 $^{\circ}$C to make a clear solution followed by the addition of required amount of sodium aluminate. After stirring for 1 hr, 10 ml of 1 wt% Pd salt solution was added to the gel and the color turns into brownish yellow. The resulting mixture was again stirred for 1h followed by the addition of 5g of TEOS into the solution. Stirring was continued for another 1h. Finally, the gel was transferred to Teflon-lined stainless steel autoclaves for hydrothermal treatment at 140 $^{\circ}$C for 48 h. After crystallization for 48h, the solid product was filtered, washed with water and dried at 60 $^{\circ}$C. Calcination of the sample was carried out at 550 $^{\circ}$C in air for 8 h to remove the template and the catalyst was characterized by XRD, TEM etc. The analysis shows that the catalyst contains 1 wt % of Pd.

Phase behavior studies

Phase behavior of the reaction mixture is of major concern for understanding the catalytic system in $scCO_2$. The phase behavior of compound **4** (scheme 1b) was studied using a view cell and the details are described elsewhere **(**M. Chatterjee, Y. Ikushima, F. Zhao, *New J. Chem*, **2002**, *27*, 510.**)**. In brief, the cell was placed over a magnetic stirrer for stirring the content and connected to a pressure controller to regulate the pressure inside the view cell. In addition, a temperature controller was also used to maintain the desired temperature of 80 ºC. Substrate was introduced into the view cell followed by hydrogen at the constant pressure of 4 MPa while CO_2 pressure was varied in the range of 7-14 MPa and the phase behavior of substrate-H_2 –CO_2 system was monitored. Figure S2 exhibits the phase behavior of compound **4** (scheme 1b) with the variation of CO_2 pressure.

Figure S1:

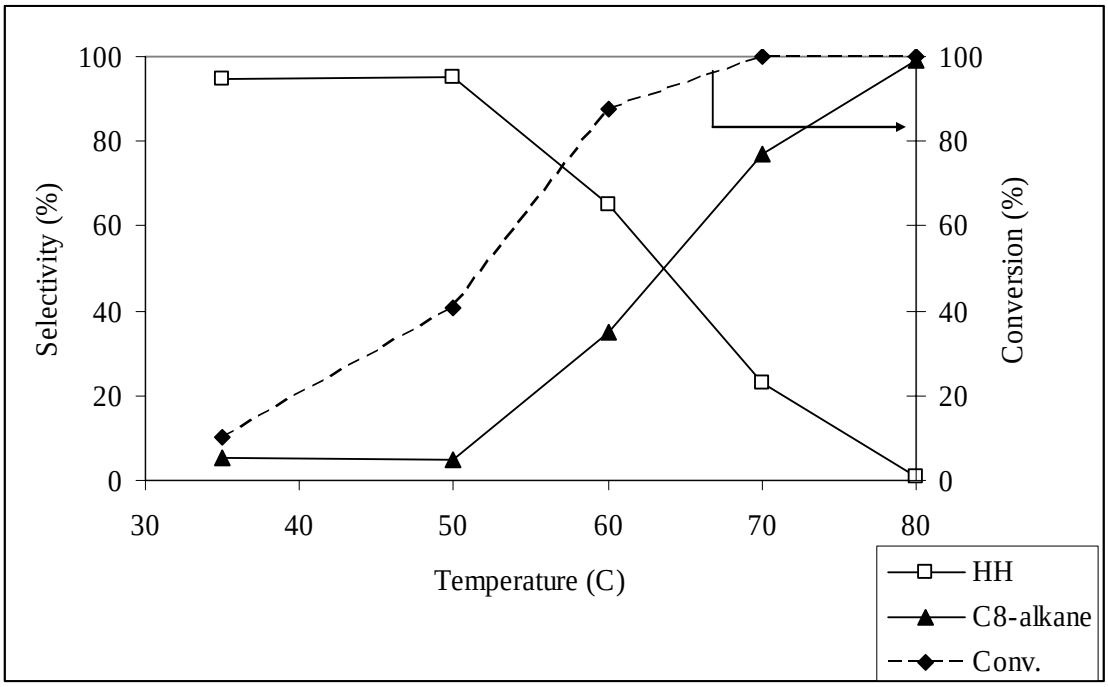
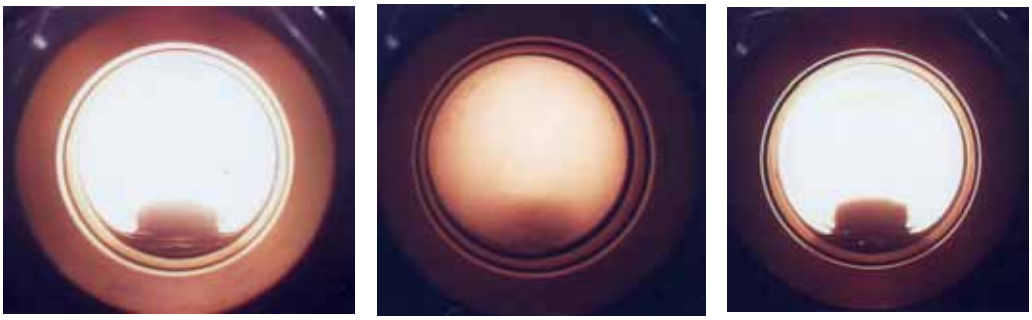


Figure S1. Effect of reaction temperature on the ring opening in $scCO_2$; Reaction conditions: P_{CO2}= 14 MPa, P_{H2}= 4 MPa, Time=20 h; Temp. = 80 ºC; HH= half hydrogenated product; compound **5** and C8 alkane= compound **6** from scheme 1b

Figure S2



Initial biphasic system

Transition state 10-11 MPa

Single phase at 14 MPa

Figure S3

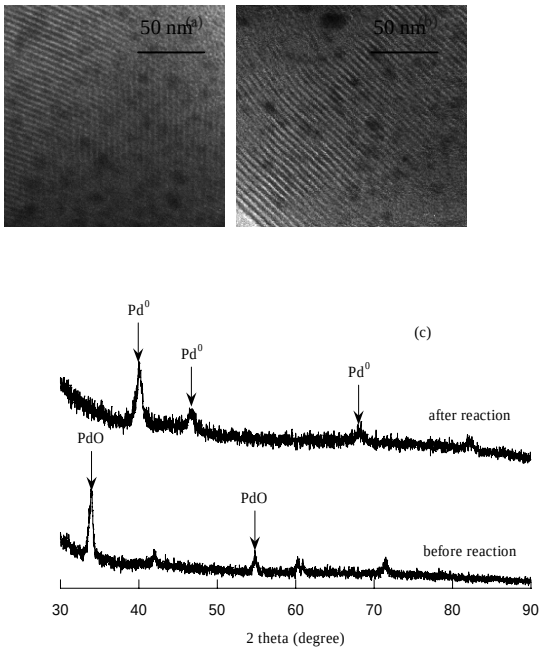


Figure S3. TEM image of the Pd/Al-MCM-41 catalyst (a) before and (b) after the reaction; (c) wide angel XRD pattern of the catalyst before (below) and after the reaction (above).

Table S1. Hydrogenation and dehydration/hydrogenation of N and S containing compounds in $scCO_2$

Substrate	Catalyst	Conv. (%)	HH (%)	Alkane product (%)
Imidazole	Pd/C	90.0	N.D.	-
	Pd/Al_2O_3	71.2	N.D.	-
	Pd/Al-MCM-41	94.8	N.D.	-
Thiophene	Pd/C	no reaction	-	-
	Pd/Al_2O_3	no reaction	-	-
	Pd/Al-MCM-41	no reaction	-	-
	Pd/Al-MCM-41[a]	no reaction	-	-

[a)] Thiophene + Compound **4** from scheme 1b; N. D. = not detected, No reaction for thiophene carbaxaldehyde because of the catalyst poisoning, Reaction conditions: Temp.= 80 °C, P_{CO2}=14 MPa, P_{H2}= 4 MPa, Time =20h