Experimental Section (Electronic Supplementary Information)

In a general procedure, a batch of 5 wt% ruthenium-doped tantalum oxide catalysts were prepared by impregnating mesoporous Ta oxide (2g, synthesized according to ref.11 with an additional 48 h soxhlet extraction in MeOH followed by vacuum drying at 300 °C for 4 h. Template removal was confirmed by IR inspection of the C-C and C-N regions and C,H, N analysis.) with $Ru_3(CO)_{12}$ (0.22g, Aldrich) in tetrahydrofuran (THF). After stirring overnight, the mixture was evaporated in a rotary evaporator and dried in situ at 70°C for 4h. The yellow powders were then moved to a reaction tube and evacuated at 300°C for 3h. The temperature ramping time was 60 minutes.

To obtain the barium-promoted ruthenium catalyst with the molar ratio of Ba:Ru=1:1, the thermally decomposed 5% Ru-Ta oxide(0.5g) was stirred in a solution of Ba(NO₃)₂ (0.065g, Aldrich) and solvent (H₂O: EtOH=50:50; 20ml) for 4h and subsequently dried in oven at 120°C overnight. The grey powders were then moved to a U-shaped Pyrex reactor with a sintered glass frit as the fixed bed, and further dried at 100°C in vacuo overnight.

Ultra-High-Purity (99.999%) H₂ and low oxygen (99.999%) N₂ were used as synthesis gases. Higher purity gasses were not used as they gave no observed performance advantage in our system. To determine the activities at low temperatures ($\leq 250^{\circ}$ C), the catalysts were first activated by H₂ at 350°C for 4h, then pumped in Schlenk line (10⁻³ torr) at 300°C for 2h to remove any residual surface ammonia. After cooling to reaction temperature in vacuum, a mixture of H₂+N₂ (3:1) was immediately fed into the reactor. The NH₃ produced was adsorbed by 0.01N HCl aqueous solution and analyzed by the indophenol blue method (ref.18). The activities at 350°C were determined in a stream of synthesis gas from the beginning.

XRD patterns (Cu K α) were recorded on a Siemens D5000-20 diffractometer. XPS data were obtained on a Physical Electronics PHI-5500 using charge neutralization and all peaks were referenced to the carbon C-(C, H) peak at 284.8 eV. TEM picture was obtained by using a H9000 HR-TEM operated at 300 kV. Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010.



ESI 1 X-ray powder diffraction patterns for: (a) mesoporous Ta oxide starting material, (b) parent catalyst Ba-Ru/Ta oxide, (c) catalyst after catalytic run at 175°C, 3h, (d) catalyst after H₂ regeneration at 350°C, 2h.



ESI 2 Natural log of incremental activity versus time at 350°C of the catalyst Ba-Ru/Ta oxide.



ESI 3 TEM of 5% Ru-doped mesoporous Ta oxide.



ESI 4 EDS spectrum of 5% Ru-doped mesoporous Ta oxide.



ESI 5 XPS spectra of the Ru 3p region for: (a) parent catalyst Ba-Ru/Ta oxide, (b) after catalytic run at 175°C, 3h, (c) catalyst after H₂ regeneration at 350°C, 2h.

Temperature (Kelvin)	Activity k (µmolg ⁻¹ , 1h)	lnk (k: μmolg ⁻¹ h ⁻¹)
295	0.64	-0.446
328	0.85	-0.163
373	0.97	-0.030
398	1.36	0.307
448	1.38	0.322
523	2.28	0.824
573	2.69	0.990
623	5.52	1.708

Table 1 Activities at different reaction temperatures (ESI †)

No.	Catalyst processing conditions	BET surface area (m^2g^{-1})
1	Mesoporous Ta oxide starting material	541
2	5% $Ru_3(CO)_{12}$ -doped Ta oxide after decomposition in	470
	vacuo at 300°C, 3h	
3	Parent catalyst Ba-Ru/Ta, Ru=5 wt %, Ba/Ru=1	370
4	Parent catalyst after H ₂ reduction at 350°C, 4h	242
5	Material from 4 after vacuum treatment at 300°C, 2h	237
6	Material from 5 after catalytic run at 175°C, 3h	229
7	Material from 6 after H ₂ regeneration at 350°C, 2h	220

Table 2 Surface areas of catalyst from ESI 2 after subsequent steps in the catalytic process (ESI †)