Supporting information for

Barium-promoted ruthenium catalysts on yittria-stabilized zirconia supports for ammonia synthesis

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Figures: 3

CHEMKIN Input Files: 4

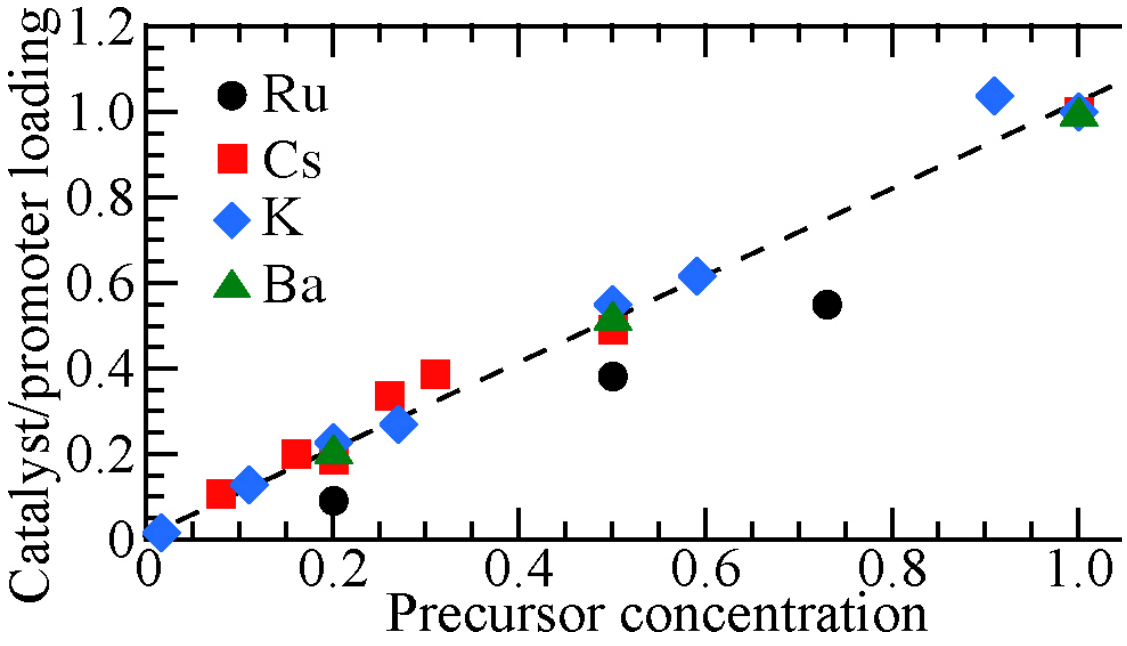

Figure S1: Normalized loading of catalyst/promoters as a function of normalized precursor concentration for Ru, Cs, K, and Ba displaying the nominally linear relationship between loading and precursor concentration.

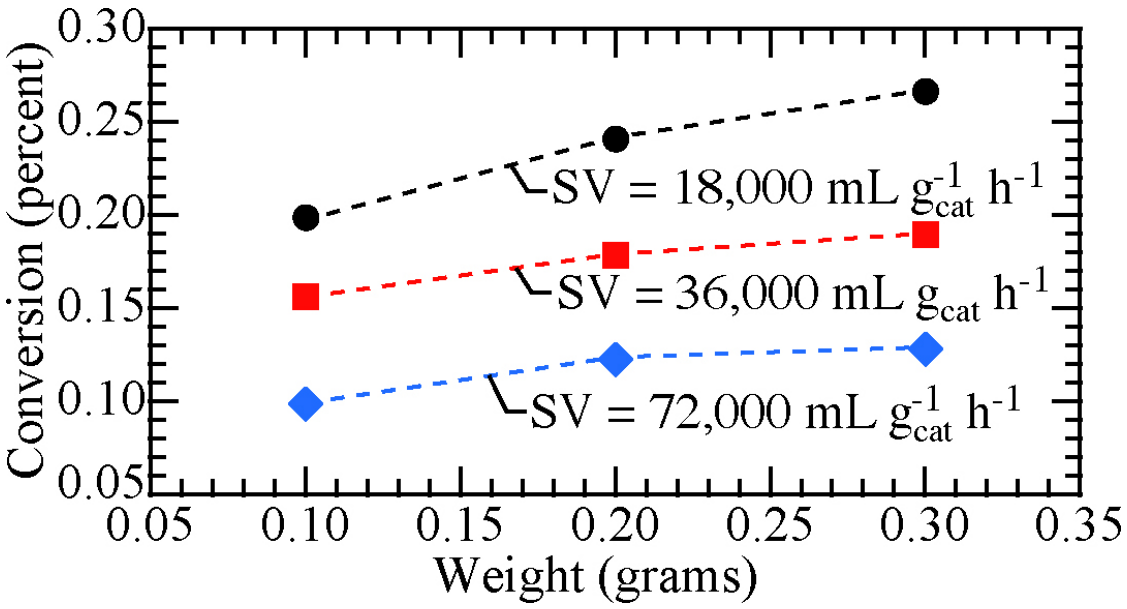

Figure S2: Conversion as a function of the catalyst weight. Flowrate is adjusted to keep space velocity constant including 18,000, 36,000, and 72,000 mL $gcat^{-1}$ h^{-1}, for 0.1, 0.2, and 0.3 g in catalyst weight, separately. At 18,000 and 36,000 the rate slowly increases with catalysts wright whereas at 72,000 mL $gcat^{-1}$ h^{-1} the rate saturates with mass. Reaction conditions: P = 10 bar (gauge), H_2/N_2 = 3, T = 450ºC.

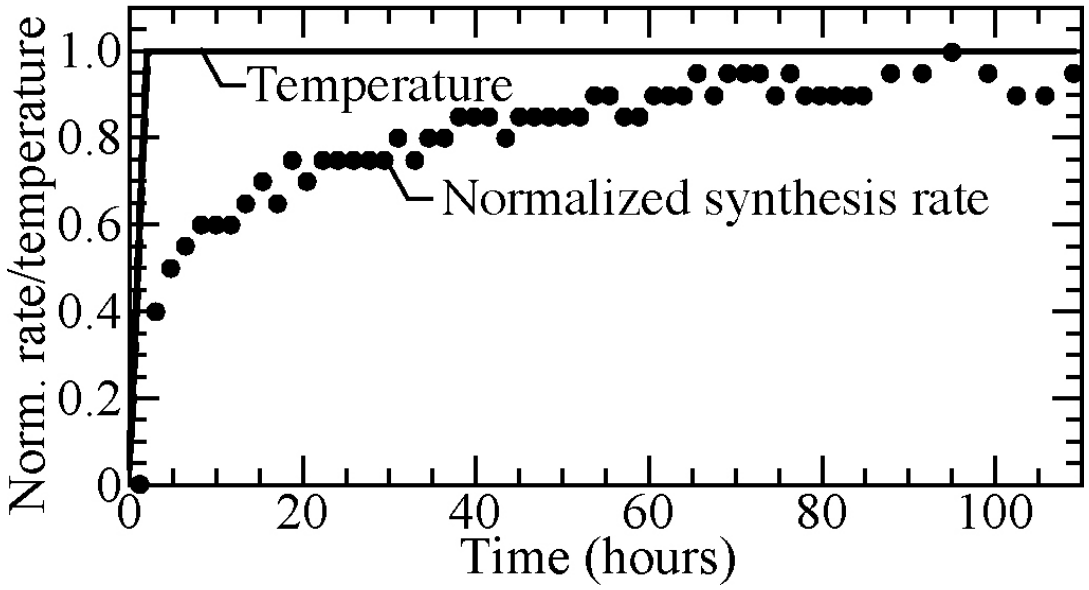

Figure S3: Normalized NH_3 synthesis rate of Ru/YSZ over time at 450°C. Reaction conditions: p = 0 bar (gauge), H_2/N_2 = 3, SV = 72,000 mL $gcat^{-1}$ h^{-1}. The Ru/YSZ takes up to 60 hours of activation to approach its maximum rate but then remains stable

The supplementary data include required input files in Chemkin format. The files include:

1- surf.inp: The file contains the surface species, side densities and the elementary step reaction mechanism for Ba-Ru/YSZ catalysts.

The mechanism uses the units of cm, s, kJ, mol.

2- chem.inp: Contains the gas phase species and element lists

3- therm.dat: Contains NASA constants of gas-phase and surface species to calculate the thermodyamic properties.

The gas-phase species thermodynamic data are taken from Burcat (http://garfield.chem.elte.hu/Burcat/burcat.html). The surface species NASA constants are based on

Gibbs free energy calculations after the adjustment procedure.

4- Trans.dat: Gas-phase speices transport properties are listed.

The data are taken from CURRAN, H. J., GAFFURI, P., PITZ, W. J., AND WESTBROOK, C. K. "A COMPREHENSIVE MODELING STUDY OF ISO-OCTANE OXIDATION"

COMBUSTION AND FLAME 129:253-280 (2002)

```
                                        surf
SITE  /Ru_surface/    SDEN/2.6079E-9/
Ru(s)
N(s)
H(s)
NH(s)
NH2(s)
NH3(s)
END

THERMO
  300.0   1000.0   3000.0
Ru(s)                    Ru  1H   0          G  0300.00   5000.00  1000.00      1
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    2
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00                   4
N(s)                     N   1H   ORu  1     G  0300.00   5000.00  1000.00      1
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    2
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00                   4
H(s)                     O   0H   1Ru  1     G  0300.00   5000.00  1000.00      1
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    2
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00                   4
NH(s)                    N   1H   1Ru  1     G  0300.00   5000.00  1000.00      1
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    2
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00                   4
NH2(s)                   H   2N   1Ru  1     G  0300.00   5000.00  1000.00      1
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    2
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00                   4
NH3(s)                   H   3N   1Ru  1     G  0300.00   5000.00  1000.00      1
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    2
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00-0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.00000000E+00 0.00000000E+00                   4
END

REACTIONS  KJOULES/MOLE  MWOFF
N2 +Ru(s) +Ru(s) =>N(s) +N(s)             2.892E-06  0.000      38.949
    STICK
N(s) +N(s) =>Ru(s) +Ru(s) +N2             2.015E+17  -0.279     148.027
    COV/N(s)                                0.000E+00  0.000      -14.000/
H2 +Ru(s) +Ru(s) =>H(s) +H(s)             4.007E-03  0.000      0.000
    STICK
H(s) +H(s) =>Ru(s) +Ru(s) +H2             3.600E+20  0.658      91.948
    COV/H(s)                                0.000E+00  0.000      -2.000/
NH3 +Ru(s) =>NH3(s)                         1.247E-05  0.000      0.000
    STICK
```

```
                                                surf
NH3(s) =>Ru(s) +NH3                              2.235E+11  0.083      83.536
H(s) +N(s) =>NH(s) +Ru(s)                       8.424E+20  0.000      83.620
    COV/N(s)                                     0.000E+00  0.000      -7.000/
NH(s) +Ru(s) =>H(s) +N(s)                       6.813E+19  0.207      30.972
    COV/H(s)                                     0.000E+00  0.000       1.000/
NH(s) +H(s) =>NH2(s) +Ru(s)                     4.949E+19  0.083      75.236
NH2(s) +Ru(s) =>NH(s) +H(s)                     8.321E+19  -0.083     15.767
    COV/H(s)                                     0.000E+00  0.000       1.000/
NH2(s) +H(s) =>NH3(s) +Ru(s)                    3.886E+19  0.083      17.036
NH3(s) +Ru(s) =>NH2(s) +H(s)                    1.478E+20  0.000      64.980
    COV/H(s)                                     0.000E+00  0.000       1.000/
END
```

chem

```
ELEMENTS
  H  N  Ru  AR
END

SPECIES
H2    NH3    N2   AR

END

REACTIONS    KJOULES/MOLE

END
```

therm2

```
!DetchemDatabase
THERMO
0300.00  1000.00  5000.00
! FROM GRI MECHANISM
AR                120186AR  1               G  0300.00   5000.00  1000.00      1
 0.02500000E+02 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-0.07453750E+04 0.04366000E+02 0.02500000E+02 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.07453750E+04 0.04366000E+02                   4
NH3               121386N   1H   3          G  0300.00   5000.00  1000.00      1
 0.02461904E+02 0.06059166E-01-0.02004976E-04 0.03136003E-08-0.01938317E-12    2
-0.06493269E+05 0.07472097E+02 0.02204351E+02 0.10114765E-01-0.14652648E-04    3
 0.14472350E-07-0.05328509E-10-0.06525488E+05 0.08127138E+02                   4
N2                121286N   2               G  0300.00   5000.00  1000.00      1
 0.02926640E+02 0.01487977E-01-0.05684761E-05 0.01009704E-08-0.06753351E-13    2
-0.09227977E+04 0.05980528E+02 0.03298677E+02 0.01408240E-01-0.03963222E-04    3
 0.05641515E-07-0.02444855E-10-0.01020900E+05 0.03950372E+02                   4
H2                121286H   2               G  0300.00   5000.00  1000.00      1
 0.02991423E+02 0.07000644E-02-0.05633828E-06-0.09231578E-10 0.15827519E-14    2
-0.08350340E+04-0.13551101E+01 0.03298124E+02 0.08249441E-02-0.08143015E-05    3
-0.09475434E-09 0.04134872E-11-0.10125209E+04-0.03294094E+02                   4
END
```

tran2

```
!Methyl Formate Oxidation: Speciation Data, Laminar Burning Velocities, Ignition
Delay Times and a Validated Chemical Kinetic Model
!S. Dooley, M.P. Burke, M. Chaos, Y. Stein, F.L. Dryer, V.P. Zhukov, O. Finch, J.M.
Simmie and H.J. Curran.
!Comments to Stephen Dooley, Princeton University, dooleys@princeton.edu
! Base transport parameters from, CURRAN, H. J., GAFFURI, P., PITZ, W. J., AND
WESTBROOK, C. K.
! "A COMPREHENSIVE MODELING STUDY OF ISO-OCTANE OXIDATION"
! COMBUSTION AND FLAME 129:253-280 (2002).
! UCRL-WEB-204236
! REVIEW AND RELEASE DATE: MAY 19, 2004.
! MANY OF THE TRANSPORT DATA ARE TAKEN FROM
! KEE, R.J., DIXON-LEWIS, G., WARNATZ, J., COLTRIN, M.E., AND MILLER, J.A,
! A FORTRAN COMPUTER CODE PACKAGE FOR THE EVALUATION OF GAS-PHASE MULTICOMPONENT
! TRANSPORT PROPERTIES, SANDIA REPORT SAND86-8246, 1986.
!
NH3                2   481.000     2.920     1.470     0.000    10.000
AR                 0   136.500     3.330     0.000     0.000     0.000
H2                 1    38.000     2.920     0.000     0.790   280.000
N2                 1    97.530     3.621     0.000     1.760     4.000
END
```