Electroactive mesoporous tantalum oxide catalysts for nitrogen activation and ammonia synthesis†

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A new mesoporous Ta oxide catalyst for conversion of dinitrogen to ammonia shows strong evidence for a novel mechanism involving low valent Ta on the surface, supporting recent work in organometallic chemistry using low valent early transition metals for dinitrogen cleavage.

After decades of intense research, the activation of dinitrogen by transition metals and their compounds is still one of the frontiers of inorganic chemistry.[1–6] The Haber–Bosch ammonia synthesis is one of the most widely used catalytic processes in industry, however the selective functionalization of dinitrogen and its use as a feedstock in the synthesis of nitrogen-containing organics has remained a challenge. Extensive research in the field of organometallic chemistry has shown that low valent early transition metal complexes can either stoichiometrically,[7,8] or catalytically[9] cleave dinitrogen as long as the ligand environment around the metal is bulky enough to stabilize the coordinatively unsaturated metal center while still allowing access to the active site.[10] The main challenge in the selective functionalization of dinitrogen is to couple a strong enough reductant and an electrophile in the same system, while also preventing the electrophile from quenching the reductant before it can attack the more inert dinitrogen molecule. Recent work in our group showed that electroactive mesoporous Ti and Nb oxides,[11–13] form metallic oxide-based molecular sieves when treated with bis(toluene) Ti[14] or bis(toluene) Nb.[15] These materials form ammonia instantly on exposure to dinitrogen and incipient moisture. The source of the N in the ammonia was confirmed by labelling studies with $[^{15}N]$-N_2. Further studies on mesoporous Ta oxide treated with bis(toluene) Ti[16] established that both dinitrogen cleavage and protonation by water were fast steps in this reaction, suggesting that the only impediment to making this process catalytic was the re-reduction of the active site and that N_2 cleavage on the reduced mesoporous oxide surface proceeds with a low activation barrier. Since it is not practical to use bis(toluene) Ti as a reductant, we began to investigate other ways of making this process catalytic. Because mesoporous Ta oxide is more thermally stable than its Nb and Ti counterparts and reduced Ta species have been implicated in both molecular-based[17] and photocatalytic[18] nitrogen activation, we chose this metal as our catalyst support. Since Ru has been used effectively in a wide variety of Haber systems[19–22] we focused our studies on a series of Ru-doped mesoporous Ta oxides. The entire catalytic process in this case takes place on the Ru clusters in these systems, with the electrochemically inert main-group oxide support and promoter thought to modify the dispersion and electronic properties of the metal grains. In a mesoporous Ta oxide-based system there is the added possibility that dinitrogen cleavage could take place at a reduced Ta center, with the precious metal dopant functioning as a hydrogenation catalyst to regenerate the low valent Ta sites. Hydrogen in this case would continuously form reduced Ta sites while also supplying a source of protons, thus avoiding the use of bis(toluene) Ti as a reductant and water as the electrophile. Because hydrogen is a strong enough reductant to reduce Ta(V) to Ta(II) under the right conditions, such a catalyst could have several oxidation states of Ta involved and that this would further influence the behavior of the system as compared to Ru supported on main-group oxides, which do not possess variable oxidation states.

In order to make meaningful comparisons between our Ru-doped mesoporous Ta oxide catalyst and previously studied Haber systems, we followed a procedure directly analogous to that used to prepare and activate both Ru–MCM-41[21] and Ru–MgO catalysts,[20] employing $Ru_3(CO)_{12}$ as a Ru source and barium nitrate as the promoter (see ESI†). ESI 1(a) shows the X-ray powder diffraction pattern (XRD) of a sample of mesoporous Ta oxide synthesized with dodecylamine according to the method of Antonelli and Ying.[11] This material possessed a BET (Brunnaur, Emmett, Teller) surface area of 541 $m^2\ g^{-1}$ (ESI†) and an HK (Horvath Kowazoe) pore size of 23 Å. ESI 1(b) shows the XRD pattern for this same material after impregnation with 5 wt% Ru and $Ba(NO_3)_2$ at a molar ratio of Ba : Ru = 1 : 1. The diminished intensity suggests a loss of long range order, however the BET surface area of this material was 370 $m^2\ g^{-1}$ and the HK pore size was 23 Å, indicating a retention of the overall mesoporous structure. When pure water was used for the impregnation of the Ba salt, the surface area was only 250 $m^2\ g^{-1}$, possibly because damage to the pore structure caused by the higher capillary pressure of water as compared to organic solvents such as methanol. The TEM micrograph of the sample from 1a doped with 5 wt% Ru (ESI 3), clearly shows the disordered wormhole pore structure and 50–100 nm size of the individual grains. Higher magnification did not reveal any evidence of Ru nanoparticles, but this was not unexpected as the XRD region for metallic Ru showed no sign of distinguishable reflections. The energy dispersive X-ray (EDS) spectrum (ESI 4) of this sample does, however, provide evidence for Ru incorporation in the material as do Ru(0) emissions in the Ru 3p region of the XPS at various stages of

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preparation (ESI 5). These data are consistent with the presence of Ru nanoclusters smaller than the detection threshold of XRD or TEM.

ESI 2 shows a plot of the natural log of incremental activity *versus* time for ammonia production by the catalyst under a stream of 1 : 3 $N_2 + H_2$ at 350 °C. The catalyst has a high initial activity of 163×10^{-6} mol g^{-1} h^{-1} in the first hour, but then the rate drops off dramatically in the second hour and continues at a rate of 1–2 $\times 10^{-6}$ mol g^{-1} h^{-1}. This initial rate is over 100 times greater than those reported in our mesoporous Ta oxide Schrauzer type photocatalysts,[18] and compares favorably to the values reported for alumina, silica, or magnesia supported Ru-doped MCM-41 catalysts, which fall in the range of 300×10^{-6} mol g^{-1} h^{-1}.[21] Since Ta oxide (441.89 g mol^{-1}) possesses a greater molecular weight than silica (60.08 g mol^{-1}), magnesia (40.30 g mol^{-1}) or alumina (101.96 g mol^{-1}), these values compare even more favorably when the activities are compared on a per-mole basis. The drop off in rate after the first hour is not understood but may be related to a combination of surface deactivation and thermally-induced loss of structure, as the XRD shows a further loss of mesoscopic order (ESI 1(c)) and the BET surface area drops to 229 m^2 g^{-1}. The reason for deactivation is not yet understood. While some of the NH_3 formed in the initial hour may come from residual nitrate, previous studies show that N_2 is an intermediate in nitrate reduction to NH_3, and also that NH_3 is a stronger reducing agent than H_2 in reactions with NO_2, which is formed from nitrate as an initial reduction step.[23] $Ba(OH)_2$ also works as a promoter, although the activities are generally 40–60% lower than the nitrate. In order to verify that the catalyst is actually producing new ammonia in the second hour and the apparent activity does not come from ammonia adsorbed on the surface in the first hour, the catalyst after 1 h of initial activity at 350 °C was placed under vacuum at 10^{-3} Torr and 350 °C for 1 h before the temperature was lowered to ambient and catalysis resumed. The values obtained are 2–5 $\times 10^{-6}$ mol g^{-1} h^{-1}, virtually the same as those obtained without the vacuum step. Pure H_2 or pure N_2 alone do not produce any ammonia under these conditions. This firmly establishes that these catalysts are producing new ammonia from N_2 and H_2 and rules out ammonia formation from any residual sources.

The catalyst demonstrates only slightly lower activities in the second hour at ambient temperature than it does at 350 °C also in the second hour. This low degree of temperature dependence is somewhat surprising, as standard Ru-based Haber catalysts show a strong relationship between temperature and activity. Fig. 1 shows the Arrhenius plot over the range 295 K to 623 K and the activities are listed in Table 1 (ESI†). Samples were first reduced by H_2 only at 350 °C for 4 h and then left under vacuum for 2 h at 300 °C to remove any adsorbed surface species. The catalyst was then cooled to the reaction temperature and treated with a flow of $N_2 + H_2$ for 1 h. The activation energy (E_a) calculated from this plot is 9.3 kJ mol^{-1}, roughly 10% of that calculated by the same methods for Ru-doped catalysts on other supports (E_a for Ru–Ba–MCM-41 is 90 kJ·mol^{-1}; Ru–Ba–MgO is 76 kJ·mol^{-1}). Extensive studies on these other systems have revealed that the rate-determining step is dissociation of N_2 on Ru and that the reaction order is negative in H_2. The activation barrier to N_2 dissociation on Ru has been determined through kinetic[24] and molecular beam studies[25] to be 1.0 eV (96.5 kJ mol^{-1}) and 0.6 eV (57.9 kJ mol^{-1}), respectively. Since the activation barrier measured in our system is 6–10 times lower than either of these numbers, N_2 dissociation in our system cannot be occurring on Ru under the conditions of the experiment. This value of 9.3 kJ mol^{-1} suggests that the cleavage of N_2 may be diffusion controlled in our system, inviting some comparisons with our bis(toluene) Ti reduced mesoporous Ta oxide system. These observations, coupled with the somewhat low activities across this temperature range as compared to standard Haber catalysts, suggests a different mechanism is at work involving a small number of active sites with a low activation barrier. This is consistent with our work on bis(toluene) Ti reduced mesoporous Ta oxides, which form ammonia from dinitrogen and moisture almost instantly at room temperature, suggesting a low activation barrier to this stoichiometric process.[16]

In order to further study the mechanism of ammonia formation, X-ray photoelectron spectroscopy (XPS) was conducted at various stages of the synthesis and catalysis. Fig. 2 shows the emissions from the Ta $4f_{7/2}$, $4f_{5/2}$ region. The spectrum for the catalyst before the catalytic run is shown in (a), with emissions at 26.8 eV and 28.6 eV respectively. This compares closely with the binding energies of pure mesoporous Ta(V) oxide, which fall at 26.9 eV and 28.7 eV, respectively. The spectrum in (b) shows the 7/2, 5/2 emissions from the material in (a) after a catalytic run in $N_2 + H_2$ for 3 h at 175 °C. There is a clear broadening of these emissions with binding energies as low as 25.1 eV, indicating that several reduced surface Ta species are present. For comparison, a sample of mesoporous Ta oxide reduced with 1.0 eq. of Rb naphthalene shows a 5/2 emission centered at 26.0 eV.[26] This suggests that lower oxidation states than Ta(IV) are involved in the catalytic process. The Ru 3p region for these same samples (ESI 5) shows broad emissions with a commensurate shift of the Ru peaks to lower binding energy after a catalytic run, consistent with multiple

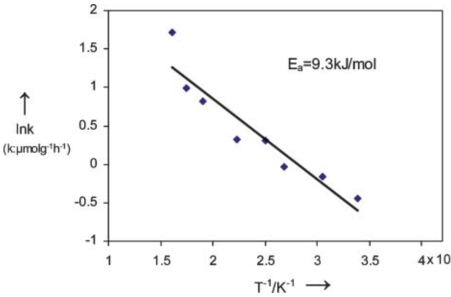


Fig. 1 Arrhenius plot for the catalyst Ba–Ru/Ta oxide.

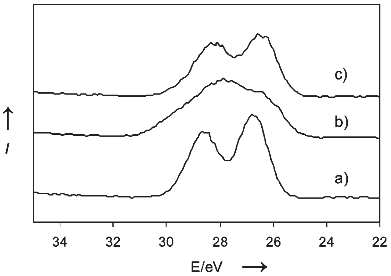
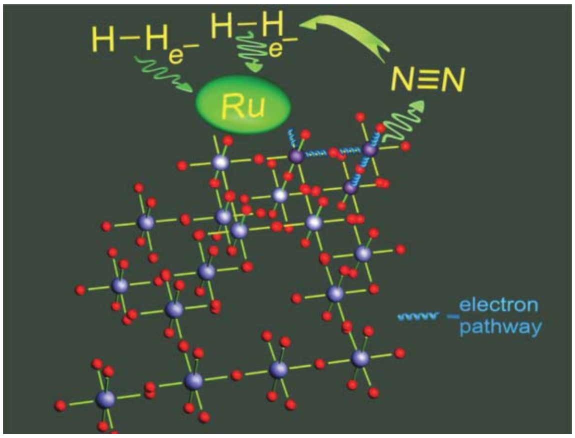


Fig. 2 XPS spectra of the Ta 4f region for: (a) parent catalyst Ba–Ru/Ta oxide, (b) after catalytic run at 175 °C, 3 h, (c) catalyst after H_2 regeneration at 350 °C, 2 h.

reduced Ru species on the surface. Since pure mesoporous Ta oxide does not react with H_2 under these conditions, the Ru dopant must act as an interface and lower the activation barrier to the reduction of the Ta species. Reduced Ta has been previously implicated[16,17] in stoichiometric N_2 activation by organometallic complexes, suggesting that these Ru-doped mesoporous Ta oxide catalysts may function *via* a different mechanism than standard Ru-based Haber systems. The latter catalysts are somewhat structure sensitive and reaction orders in hydrogen are negative in the Ru systems, suggesting that surface coverage by hydrogen can block adsorption of dinitrogen and retard the rate. It is clear from the XPS that hydrogen must at some stage provide electrons to the Ta sites and that some overspill from the Ru particles is thus involved. Scheme 1 shows a representation of a possible mechanism in which electrons from H_2 are funneled through the Ru particles to the mesoporous Ta network, where they reduce certain sites (dark) to a form capable of attacking N_2. This mechanism would likely depend on the work function, Fermi level and degree of Ohmic contact at the metal–metal oxide interface as well as the presence of conduction pathways across the surface. Work by our group has shown that reduced mesoporous transition metal oxides can be semiconducting or metallic depending on the composition, suggesting that electron transfer across the mesoporous Ta oxide framework is indeed possible.[12–16] Furthermore, catalytic activities of Pt, Pd, and Rh-doped mesoporous Ta oxides are of the same order of magnitude as the Ru system. While Ru is capable of dissociating both N_2 and H_2, these other metals dissociate H_2 but the barrier for N_2 dissociation is prohibitive. For example, calculations show that N_2 dissociation on Pd is 2.5 eV, giving a minimum activation energy of 241 kJ mol^{-1} for any mechanism depending on this step.[27] A 10% Pd on mesoporous Ta oxide also shows XPS evidence for reduced Ta during catalysis, and functions with $Ba(OH)_2$ as a promoter. These observations further support the general mechanism proposed for our mesoporous Ta oxide supported N_2 reduction catalysts in which nitrogen cleavage occurs on the reduced Ta center and not the precious metal surface as in traditional Ru-Haber systems. The role of the Ba promoter in our system is not yet clear.

After several hours of catalytic activity, the materials were regenerated by treatment with H_2 at 350 °C for 2 h. The BET surface area drops slightly to 220 $m^2\ g^{-1}$ and the main reflection in the XRD diminishes further in intensity as shown in ESI 1(d). The binding energy in the Ru 3p region remains relatively constant to that after regeneration, but the Ta 5/2, 7/2 emissions sharpen considerably (Fig. 2, trace c), indicating a change in oxidation state and diminution in the number of surface Ta species in the lowest oxidation states (*ca.* 25 eV). The activities of the catalyst after regeneration drop to around 2×10^{-6} mol $h^{-1}\ g^{-1}$. These data are consistent with a loss of active sites from some surface deactivation process, and demonstrate that hydrogen treatment does not completely regenerate the catalyst. This also suggests that the active sites may be related to the emissions at *ca.* 25 eV, which correspond to small amounts of Ta in oxidation states between IV and II.



Scheme 1 Possible mechanism for ammonia formation on Ru-doped mesoporous Ta oxide materials showing reduced Ta sites in dark blue.

In summary, mesoporous Ta oxide doped with Ru and Ba is an active catalyst for the conversion of N_2 and H_2 into ammonia. Initial activities are high, but drop and stabilize after the first hour and continue for several hours, even at room temperature. The Arrhenius plot and XPS data suggest a different mechanism than standard Ru-doped Haber catalysts, where the precious metal acts as an electrode interface to reduce surface Ta sites, which are then able to attack N_2. Further kinetic studies and use of different metal dopants and promoters are required to better understand the nature of the active site and improve activity and longevity of the catalyst.

Notes and references

1 K. Hoshino, *Chem. Eur. J.*, 2001, **7**, 2727.
2 M. D. Fryzuk and S. A. Johnson, *Coord. Chem. Rev.*, 2000, **200**, 379.
3 M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115.
4 T. A. Bazhenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69.
5 J. Kim and D. C. Rees, *Nature*, 1992, **360**, 553.
6 J. B. Howard and D. C. Rees, *Chem. Rev.*, 1996, **96**, 2965.
7 C. E. Laplaza and C. C. Cummins, *Science*, 1995, **268**, 861.
8 M. D. Fryzuk, J. B. Love, S. J. Rettig and V. G. Young, *Science*, 1997, **275**, 1445.
9 D. V. Yandulov and R. R. Schrock, *Science*, 2003, **301**, 76.
10 J. A. Pool, E. Lobkovsky and P. J. Chirlik, *Nature*, 2004, **427**, 527.
11 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 426.
12 M. Vettraino, M. Trudeau and D. M. Antonelli, *Adv. Mater.*, 2000, **12**, 337.
13 X. He and D. M. Antonelli, *Angew. Chem., Int. Ed.*, 2002, **41**, 214.
14 M. Vettraino, X. He, M. Trudeau, R. Schurko and D. M. Antonelli, *J. Am. Chem. Soc.*, 2002, **124**, 9567.
15 M. Vettraino, X. He, M. Trudeau, J. E. Drake and D. M. Antonelli, *Adv. Funct. Mater.*, 2002, **3**, 174.
16 A. Lezau, B. Skadtchenko, M. Trudeau and D. M. Antonelli, *Dalton Trans.*, 2003, 4115.
17 S. A. Johnson, S. J. Rettig and M. D. Fryzuk, *J. Am. Chem. Soc.*, 2001, **123**, 3960.
18 C. Yue, M. L. Trudeau and D. M. Antonelli, *Can. J. Chem.*, 2005, **83**, 308.
19 S. Murata and K.-I. Aika, *J. Catal.*, 1992, **136**, 110.
20 H. Bielawa, O. Hinrichsen, A. Birkner and M. Muhler, *Angew. Chem., Int. Ed.*, 2001, **40**, 1061.
21 C. T. Fishel, R. J. Davis and J. M. Garces, *J. Catal.*, 1996, **163**, 148.
22 F. Rosowski, A. Hornung, O. Hinrichson, D. Herein, M. Muhler and G. Ertl, *Appl. Catal.*, 1997, **151**, 443.
23 A. Ueda and M. Haruta, *Gold Bull.*, 1999, **32**, 1, 3.
24 S. Dahl, P. A. Taylor, E. Törnqvist and I. Chorkendorff, *J. Catal.*, 2000, **192**, 381.
25 R. C. Egeberg, J. H. Larsen and I. Chorkendorff, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2007.
26 B. O. Skadtchenko, M. Trudeau, R. W. Schurko, A. Y. H. Lo and D. M. Antonelli, *Chem. Mater.*, 2005, **17**, 1467.
27 T. Bligaard, K. Honkala, A. Logadottir, S. Dahl, C. J. H. Jacobsen and J. K. Nørskov, *J. Phys. Chem. B*, 2003, **107**, 9325.