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Compositional Effects in Ru, Pd, Pt, and Rh-Doped Mesoporous Tantalum Oxide Catalysts for Ammonia Synthesis

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A series of early metal-promoted Ru-, Pd-, Pt-, and Rh-doped mesoporous tantalum oxide catalysts were synthesized using a variety of dopant ratios and dopant precursors, and the effects of these parameters on the catalytic activity of NH_3 synthesis from H_2 and N_2 were explored. Previous studies on this system supported an unprecedented mechanism in which N–N cleavage occurred at the Ta sites rather than on Ru. The results of the present study showed, for all systems, that Ba is a better promoter than Cs or La and that the nitrate is a superior precursor for Ba than the isopropoxide or the hydroxide. ^{15}N-labeling studies showed that residual nitrate functions as the major ammonia source in the first hour but that it does not account for the ammonia produced after the nitrate is completely consumed. $Ru_3(CO)_{12}$ proved to be a better Ru precursor than $RuCl_3{\cdot}3H_2O$, and an almost linear increase in activity with increasing Ru loading level was observed at 350 °C (623 K). However, at 175 °C (448 K), the increase in Ru had no effect on the reaction rate. Pd functioned with comparable rates to Ru, while Pt and Rh functioned far less efficiently. The surprising activities for the Pd-doped catalysts, coupled with XPS evidence for low-valent Ta in this catalyst system, support a mechanism in which cleavage of the N–N triple bond occurs on Ta rather than the precious metal because the E_a value for N–N cleavage on Pd is 2.5 times greater than that for Ru, and the 9.3 kJ mol^{-1} E_a value measured previously for the Ru system suggests that N–N cleavage cannot occur at the Ru surface.

Introduction

The activation of dinitrogen has been one of the holy grails of inorganic chemistry for several decades,[1,2] and recent advances in organometallic[3−7] and materials chemistry[8−10] only confirm the importance of this reaction. While the synthesis of ammonia using transition metal catalysts is one of the most important catalytic processes in all of chemistry, the use of dinitrogen as a feedstock for the synthesis of fine organics under mild conditions has still remained elusive. Thus, the discovery of new and milder ways of selectively cleaving and functionalizing the N−N triple bond is one of the great challenges of modern inorganic chemistry. Over the years, various supported transition metal-based catalytic systems have been studied for ammonia synthesis. For this particular process, Ru is generally accepted to be superior to Fe or other transition metals; therefore, most current efforts have focused on the investigation of the effects of different supports and promoters.[9−17] Common supports include main group oxides such as magnesia, alumina, and silica, while

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the promoters are usually alkali metals, alkali metal oxides/hydroxides, and alkali earth metal oxides because of their strong electron-donating abilities, which are believed to modify the reactivity of the active Ru center.[13] Recently, we developed a new series of Ru-doped mesoporous Ta oxide catalysts which convert dinitrogen into ammonia over the temperature range of 22−350 °C (295−623 K).[18] This system was an extension of work we conducted on bis(toluene) Ti and bis(toluene) Nb reduced mesoporous Ti, Ta, and Nb oxides, which demonstrated that metallic phases on the surface of the mesostructure are capable of stoichiometrically cleaving the N−N triple bond of dinitrogen at room temperature[19−21] and subsequently producing ammonia, as long as ambient moisture was present. Since bis(arene) complexes constitute an exotic and expensive source of electrons in any catalytic process, we developed a new Ru-doped mesoporous Ta oxide system which uses H_2 as both a source of electrons and protons in the reduction of N_2 to NH_3. The activities of this new system at 350 °C are comparable to those for standard Ru-doped Haber catalysts but drop off substantially after the first hour. Arrhenius plots in this study provided surprising activation energies of only 9.3 kJ mol^{-1},[18] roughly 10% of that reported for the traditional Ru-based Haber systems and many times lower than the threshold Ea for N_2 cleavage on a Ru surface (0.6−1.0 eV or 58−96 kJ mol^{-1}).[22,23] XPS studies on the material during several stages of the process show strong evidence for the involvement of reduced Ta species in the support mesostructure. These data suggest a new mechanism, in which the Ru acts as an interface to transfer electron density from hydrogen to neighboring Ta sites on the oxide support, which in the reduced form are then able to cleave dinitrogen. The electrochemical involvement of the Ta oxide support in the N_2-cleavage process is not possible with traditional supports, such as magnesia and alumina, which do not possess variable oxidation states. This is particularly intriguing given that Fryzuk has found that low-valent Ta complexes readily activate dinitrogen under mild conditions.[4] To better understand this new system, the dependence of the activities on Ru precursor, Ru loading levels, precious metal dopant other than Ru (i.e., Pd, Pt, Rh), promoter metal, promoter precursor, promoter loading levels, and hydrogen activation temperature have been determined.

Experimental Section

Materials and Equipment. All chemicals were obtained from Aldrich unless otherwise stated. Catalytic experiments were conducted in a U-shaped Pyrex reactor with a sintered glass frit as the fixed bed. H_2 and N_2 (99.999%) were used in all catalytic runs and in the TGA experiments. NH_3 produced from the reaction was absorbed by a 0.01 N HCl aqueous solution and was quantitatively determined by the “indophenol blue method”.[24] XRD patterns (Cu Kα) were recorded on a Siemens D500 θ-2θ 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 and EDS studies were conducted using a H9000 HR-TEM spectrometer operated at 300 kV. Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010. Hydrogen differential thermal analysis (H_2-TDA) measurements were performed on a TGA/SDTA851 (Mettler Toledo) over the temperature range from room temperature to 450 °C at a heating rate of 2 °C min^{-1}, in a stream of 96% argon and 4% hydrogen with a flow rate of 30 cm^3 min^{-1}. Mass spectrometry experiments were conducted at the University of Alberta using an Applied Biosystems Mariner TOF mass spectrometer equipped with an electrospray source. Aqueous solutions exposed to the synthesis gas for 1 h were infused into the spectrometer at a rate of 25 μL sec^{-1}.

Synthesis. (a) Mesoporous Ta Oxide. Mesoporous tantalum oxides were synthesized following the ligand-assisted templating method developed by Antonelli and Ying.[25] The template was removed by stirring of the mixture for 24 h with 1.5 equiv *p*-toluene sulfonic acid, with respect to the original amount of amine template used, in 1:1 methanol/diethylether. This was followed by a second washing in the same solvent mixture for 24 h and three additional washings in pure methanol, followed by oven-drying at 120 °C for 8 h and heating at 300 °C at 10^{-3} Torr for 24 h. This procedure was necessary to remove the last traces of the template (BP = 180 °C) and was verified by elemental analysis and the complete absence of C−C and C−N vibrations from 1000 to 1500 cm^{-1} in the IR.

(b) Ru-Doped Mesoporous Ta Oxide. In a general procedure, 5 wt % ruthenium-doped tantalum oxide catalyst was prepared by impregnating mesoporous Ta oxide with $Ru_3(CO)_{12}$ (99%) in tetrahydrofuran (THF). After it was stirred overnight, the mixture was evaporated in a rotary evaporator and dried in situ at 70 °C for 4 h. The resulting yellow powder was then placed in a reaction tube and evacuated at 300 °C for 3 h. The temperature ramping time was 60 min. When ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$, 99.98%) was used as the ruthenium precursor, template-free mesoporous Ta oxide was impregnated with $RuCl_3 \cdot xH_2O$ in a methanol suspension. After the mixture was stirred overnight, the organic solvent was removed in a solvent storage flask on a Schlenk line.

(c) Mesostructured Pt-Doped (or Rh-, Pd-) Ta Oxides. These doped mesostructured oxides were synthesized by the ligand-assisted templating method[25] modified to introduce Pt (or Rh, Pd) during the initial hydrolysis/condensation step. In an Ar glovebox, 15.0 g of $Ta(OC_2H_5)_5$ was added to 2.1 g of liquid dodecylamine in a 150 mL conical flask, and the mixture was stirred for 10 min. Then, 1.3 g of platinum(IV) chloride powder was added, and it was stirred for 1 day at 50 °C to form a uniform orange mixture. This mixture was then removed from the glovebox, and 100 mL of deionized water was added. The resulting precipitate was aged in solution as described above for mesoporous Ta oxide and isolated by filtration. The as-synthesized materials were then dried under vacuum for 10 h at 100 °C and for another 10 h at 300 °C (this step sublimes out ∼80% of the amine template as measured by IR), followed by a heat treatment in a flow of H_2 for 5 h at 350 °C

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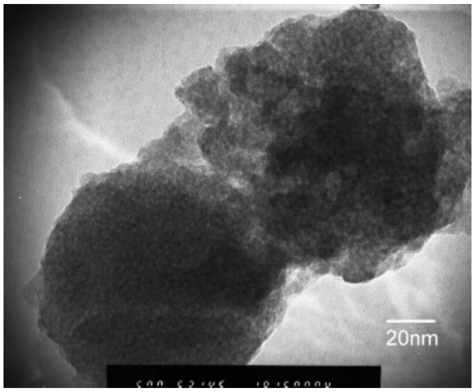

Figure 1. TEM of 5% Ru-doped mesoporous Ta oxide.

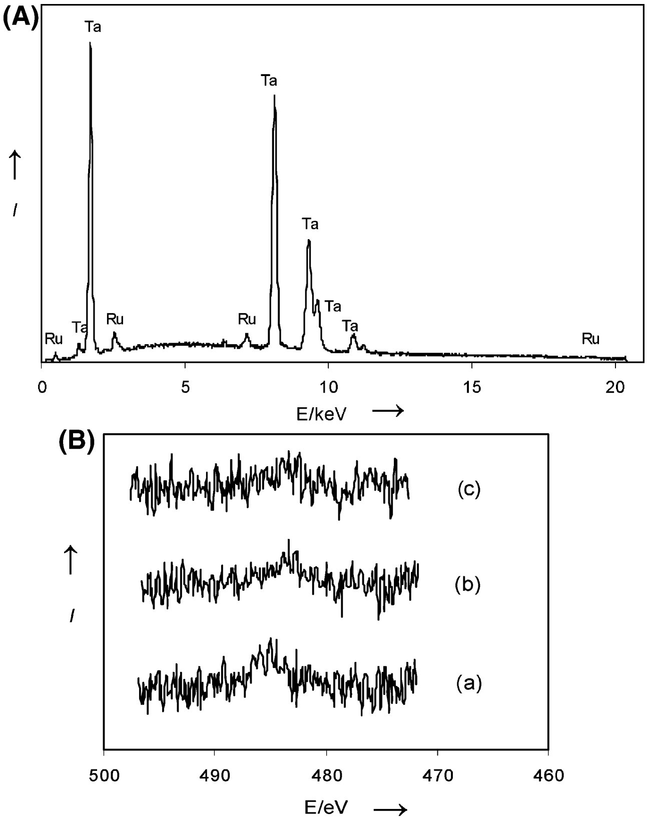

Figure 2. (A) EDS spectrum of 5% Ru-doped mesoporous Ta oxide. **(B)** XPS spectra of the Ru 3p 1/2 region for (a) parent Ba−Ru/Ta oxide catalyst, (b) after catalytic run at 175 °C, 3 h, and (c) catalyst after H_2 regeneration at 350 °C, 2 h.

to reduce the Pt and encourage metal cluster formation. Washing of the product before reduction of the precious metal salt led to significant leaching of the dopant. The materials were then subjected to acid treatment, multiple washings, and heat treatment under vacuum, exactly as described for pure mesoporous Ta oxide. Removal of the template was monitored by IR and elemental analysis to ensure complete extraction of any residual organic material. An analogous procedure was used to synthesize mesostructured Rh- ($RhCl_3 \cdot xH_2O$) or Pd-doped ($PdCl_2$) Ta oxides.

(d) $Ba(NO_3)_2$-, $CsNO_3$-, and $La(NO_3)_3$-Promoted Catalysts. Typically 0.5 g of M−Ta oxide (M = Ru, Pt, Pd, Rh) was stirred in a solution of the nitrate [$Ba(NO_3)_2$, Alfa Aesar, 99.95%, metal basis; $CsNO_3$, 99%; $La(NO_3)_3 \cdot xH_2O$, 99.9%] and solvent (H_2O/EtOH = 50:50) for 4 h. The solid was collected and subsequently dried in an oven at 120 °C overnight. The powders were then moved to a U-shaped Pyrex reactor with a sintered glass frit as the fixed bed and were further dried at 100 °C in vacuo overnight.

(e) $Ba(OH)_2$- and Barium Isopropoxide-Promoted Catalysts. Barium hydroxide ($Ba(OH)_2$, tech. ~95%) was impregnated into template-free mesoporous M/Ta (M = Ru, Pt, Pd, Rh) oxide in methanol in an argon glove box (to avoid carbonate formation). After the mixture was stirred for 4 h, the solvent was removed in an air-free solvent storage flask on a Schlenk line at 100 °C. The barium isopropoxide ($Ba[OCH(CH_3)_2]_2$, Alfa Aesar, 20% w/v in isopropanol) analog was prepared by impregnation in isopropanol. The solvent was removed, and the solid was dried as described above for the hydroxide promoters.

Results and Discussion

Characterization. Since heterogeneous catalysts for ammonia synthesis typically exhibit complicated multicomponent behavior in which the support, metal dopant, and promoter all play an important role, we undertook a series of compositional studies to establish important trends which may shed more light on the reaction mechanism. In these studies, XRD, nitrogen adsorption, and TEM (where appropriate) were used to confirm the retention of the mesostructure in the catalysts after doping. The TEM image in Figure 1 clearly shows the disordered ~20 Å wormhole pore structure and the 50−100 nm size of the individual mesoporous particles in the 5% Ru catalyst. The retention of the mesostructure after Ru doping was also confirmed by the retention of the reflection at $d = 32$ Å in the XRD of all samples studied. Extensive TEM studies at higher magnification did not reveal individual Ru metal grains located within the pores. This was expected because XRD did not show any reflections for Ru metal, indicating that the metal particles were below the 6 nm threshold for XRD detection. However, energy dispersive X-ray spectroscopy (EDS) (Figure 2A) provided firm evidence for the presence of Ru in the materials. Quantitative values were obtained by comparison of the peak intensities to a sample of known Ru concentration. A broad low-intensity emission at 485.2 eV in the X-ray photoelectron spectroscopy (XPS) (Figure 2B, trace a) assigned as the Ru 3p $^1/_2$ emission establishes that the Ru was slightly oxidized during the synthesis of the parent catalyst. After hydrogen activation and catalysis (traces b and c), the Ru is reduced to the metallic state (483.5 eV). These materials also survive the Ba doping and subsequent heat treatment stages of catalyst preparation. Figure 3 shows the nitrogen adsorption−desorption isotherms of the mesoporous Ta oxide starting material, the Ba−Ru/Ta catalyst before H_2 reduction, and this same catalyst after H_2 reduction. BET surface areas are summarized in Table 1. Hydrogen heat treatment at 350 °C for 4 h results in a decrease in specific BET surface area from 541 to 242 $m^2\ g^{-1}$ and a corresponding decrease in the cumulative Horvath−Kawazoe (HK) volume from 0.282 to 0.092 $cm^3\ g^{-1}$, with the pore size remaining at 23.3 Å. The nitrogen adsorption−desorption isotherms show characteristics of both type I (for microporous) and type IV (for mesoporous) because of a broader pore-size distribution and the pore size on the cusp between the microporous ($d < 20$ Å) and mesoporous ($20 < d < 500$ Å) regimes.[26] This behavior is typical of the C_{12}-templated mesoporous Nb, Ta, and Ti oxides studied in our

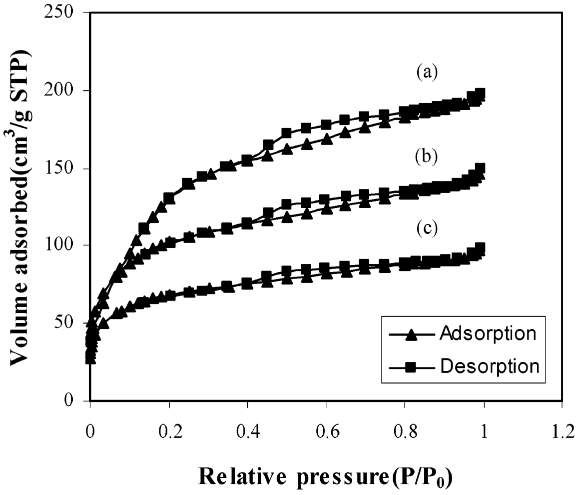

Figure 3. Nitrogen adsorption−desorption isotherms: (a) pure mesoporous Ta oxide; (b) catalyst Ba−Ru/Ta (Ru = 5 wt %, molar ratio Ba/Ru = 1) before H_2 activation; and (c) catalyst from trace b after H_2 activation at 350 °C for 4 h, followed by catalytic run at 175 °C.

Table 1. Surface Areas of Catalyst and after Subsequent Steps in the Catalytic Process

no.	catalyst processing conditions	BET surface area (m^2 g^{-1})
1	mesoporous Ta oxide starting material	541
2	5% $Ru_3(CO)_{12}$-doped Ta oxide after decomposition in vacuo at 300 °C, 3 h	470
3	parent catalyst Ba−Ru/Ta, Ru = 5 wt %, Ba/Ru = 1	370
4	parent catalyst after H_2 reduction at 350 °C, 4 h	242
5	material from 4 after vacuum treatment at 300 °C, 2 h	237
6	material from 5 after catalytic run at 175 °C, 3 h	229
7	material from 6 after H_2 regeneration at 350 °C, 2 h	220

group. The HK pore-size distribution shows a major peak at 23.3 Å, demonstrating that the doping process has not compromised the narrow pore-size distribution of the parent mesostructure.

Effect of Reduction Temperature. Before catalytic runs with N_2 and H_2, the catalysts were first reduced and activated with H_2 at elevated temperature. This step ensures that all nitrate present in the promoter decomposes to the oxide, the active form of the promoter. Catalysts can be used without this step; however, this leads to some ambiguity of the results over the first hour, when nitrate decomposition may occur parallel to ammonia formation (see below). Thus, the rate of ammonia synthesis was measured over Ru/Ta oxide catalysts promoted with $Ba(NO_3)_2$ and $CsNO_3$, and the effect of the reduction temperature was studied. The Ru precursor used for these studies was $Ru_3(CO)_{12}$ because this precursor proved to be the most effective in our previous studies and has also been used successfully in mesoporous silica-based Haber systems. Figure 4 shows the H_2-TDA results of $Ba(NO_3)_2$-promoted Ru catalysts. There is a strong exothermic peak between 190 and 250 °C that can be attributed to the reduction of promoter precursors and liberation of gaseous nitrogen species from surface nitrate. The reduction of nitrate in the presence of Ru has been shown to occur between 200 and 250 °C.[12,27] A higher promoter/Ru molar ratio moves the exothermal peak toward a higher reduction temperature with a stronger peak. No exothermal peak was observed below 450 °C in the absence of Ru, which provides evidence for the role of Ru in lowering the activation barrier for nitrate reduction in this system.

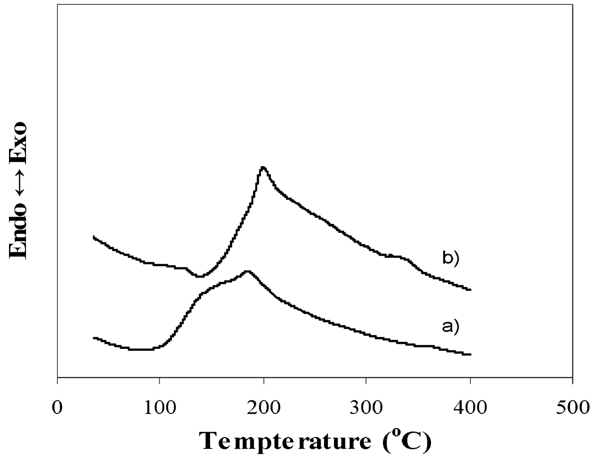

Figure 4. H_2-DTA of Ru/Ta oxide catalysts promoted with $Ba(NO_3)_2$: (a) Ba/Ru = 1 and (b) Ba/Ru = 3.

In previous studies, much of the initial high activity of the catalysts occurred only if this H_2-only activation step was not conducted and the entire process was performed in the presence of both N_2 and H_2. Thus, if the catalyst is first reduced in H_2 for 1−4 h and then a catalytic run is started, the activities are generally 50−100 times lower. This suggests that nitrate may be involved in the generation of ammonia; however, studies have shown that nitrate reduction proceeds through an N_2 intermediate, making these two pathways indistinguishable as long as N_2 is present in excess. To further investigate the possible role of nitrate during this high-activity phase of the process, a labeling study was conducted using ^{15}N-labeled $Ba(NO_3)_2$, with unlabeled N_2 as a feedstock. Mass spectrometry (MS) analysis of the ammonia produced over the first hour confirmed that 92% is generated from the ^{15}N-labeled nitrate source. If ammonia production from nitrate went through an N_2 intermediate as previous work suggests, then more ^{14}N ammonia would be detected during this first hour because the amount of nitrogen passing through the system (1 mL s^{-1}) during this time greatly exceeds that contained within the surface nitrate. After nitrate is fully decomposed, the MS showed that all ammonia formed originates from N_2, ruling out ammonia formation from any residual nitrate during this second, lower activity phase. Further kinetic studies demonstrated that after nitrate reduction the catalyst only produces new ammonia when exposed to *both* N_2 and H_2; however, the catalyst activity drops off significantly at H_2/N_2 ratios of less than 1:1 but functions at nearly the same rate at H_2/N_2 ratios as high as 5:1. For example, at a 4:1 H_2/N_2 ratio at 623 K and 2% Ru loading, the rate was 2.1 μmol h^{-1} g, but at an H_2/N_2 ratio of 1:4 for the same catalyst, the rate was 0.8 μmol h^{-1} g. For these studies, the flow rates were held constant as compared to the total flow rate of the 1:1 control experiment.

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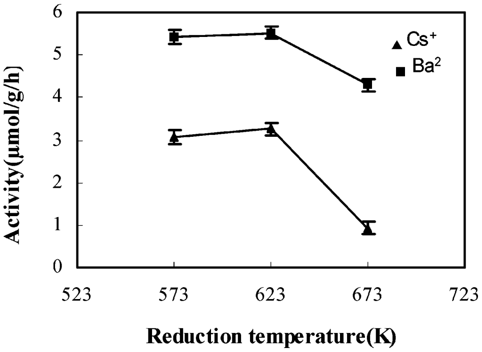

Figure 5. Activity of ammonia synthesis for 5 wt % Ru−Cs/Ta and Ru−Ba/Ta oxides (promoter/Ru = 1 mol/mol) as a function of the reduction temperature. The rate was measured at 623 K.

The reaction thus depends more on H_2 concentration than on N_2 concentration, which is quite different from standard Ru-based catalysts, which have a negative order in H_2 because of blocking of the Ru sites by H_2 binding. This suggests that reduction of the active Ta sites is the rate determining step, and this is consistent with the low activities and the observation from bis(toluene) Ti reduced materials that reduction of N_2 on a reduced Ta oxide surface is instantaneous. These and other kinetic effects will be the subject of a more detailed study later, but they underscore the unique mechanism of our system. The low activity at higher temperatures where standard Ru-based Haber catalysts operate further supports this mechanism where electron density is transferred from the Ru grains to neighboring Ta sites, effectively crippling the ability of the Ru grains to mediate the cleavage of N_2 and shifting this role to the reduced Ta sites. This is not observed in Ru catalysts supported on other metals, such as Mg or Si, because these metals do not have variable oxidation states like Ta.

Figure 5 shows that the activity of Ru-doped mesoporous Ta oxide catalysts is steady for reduction temperatures between 250 (523 K) and 350 °C(623 K) but that it decreases substantially for both promoters when the reduction temperature is increased to 400 °C (673 K). While these rates are clearly lower than those for standard Haber catalysts, the much greater molar mass of the Ta oxide support relative to silica and magnesia,[18] makes these values more favorable. The BET surface area of Cs- or Ba-promoted catalysts remain about 200−220 $m^2\ g^{-1}$ after 4 h of hydrogen reduction at 350 °C (Table 1). In contrast, the surface area drops to 120−150 $m^2\ g^{-1}$ if hydrogen treatment is performed at 400 °C. While loss of surface area may explain the drop in activity of the catalyst after heat treatment, it may also be caused by sintering of Ru metal particles because of the structural loss of the support and increased diffusion of Ru particles at higher temperatures, although we could not confirm this by XRD. Conversely, the loss of activity may be related to a migration of promoter oxides from the Ru metal surface or an evaporation of promoter oxides from the catalyst, as has been observed previously.[17] The decrease in activity at higher temperature is more extensive for the $CsNO_3$-promoted catalyst than for the $Ba(NO_3)_2$-promoted analogue, possibly, because the former metal oxide tends to vaporize more easily than the latter metal oxide at high temperature. Although catalysts with lower H_2 reduction temperature at 300 °C have somewhat higher surface areas at the range of 240−260 $m^2\ g^{-1}$, the lower activities are more likely related to the lower decomposition percentage of the promoter precursors.

Effect of Different Promoters. The effect of alkali and alkaline earth metal promoters on Ru-based Haber systems has been an area of much study. Electronegativities of these promoters have been used as a rough criterion to evaluate their mechanism of promotion, which often correlates well with the rate of ammonia production; however, this is not always the case.[9,10,16] Alkali metals are effective electron donors; however, these metals are quite sensitive to oxygen-containing compounds such as water and dioxygen and, consequently, are converted into oxides or hydroxides. Because of this concern, oxide promoters might be more practical than the metal analogs although the promotion effects are somewhat lower.[17] Although the most widely accepted mechanism for ammonia synthesis over Ru-based catalysts is one in which electron density from the promoter is first donated to the Ru metal grains and then transferred to the dinitrogen antibonding orbital to weaken the robust N−N triple bond, this is still a matter of contention because the detailed role of the promoter has never fully elucidated.[10] Some disagreements have arisen from conflicting experimental observations; however these may be attributed to some extent to the different support materials and promoters used in the various catalytic systems in question.[13,14,17] Previous studies by a number of groups have shown that alkali metal Cs and alkali earth metal Ba promoters are the two best choices for Ru-based Haber systems. The supports employed in these studies include active carbon (AC), oxides (MgO, Al_2O_3), zeolite (X, Y), and MCM41 mesoporous silica. One anomaly is that rare earth metal La promoters are the most effective for Al_2O_3 systems. This has fully been explained by a SMSI (strong-metal support interaction) effect, which is related to coverage by the promoter of the precious metal surface when this surface is reduced to a lower valency.[28] SMSI was used to explain the strong suppression of the ability of a surface to chemisorb H_2 (and CO) and has been observed for catalytic metals (e.g., group VIII noble metals) on titania with H_2 activation at ordinary temperature. Other documented SMSI materials include oxides of niobium, manganese, and lanthanum. For the sake of completeness, all three of these promoters were selected and tested in our Ru-doped mesoporous Ta oxide catalyst system. The activities of these catalysts are compared in Table 2. These results clearly show that Ba is the best promoter for our Ru/Ta oxide system. $La(NO_3)_3$-promoted catalysts did not show any activity in our system below 250 °C but are active above this threshold. This could be attributed to the SMSI effect of La, as observed in the alumina systems. The rationalization of why the Ba promoter should work best in a system that clearly may involve a different mechanism than the standard Haber catalysts (insofar as the variable oxidation

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Table 2. Promoter Effect on the Rate of Ammonia Synthesis over 5 wt % Ru/Ta Oxide

promoter element (M)	promoter precursor	M/Ru (mole ratio)	BET surface area[a] (m^2 g^{-1})	activity (μmol g^{-1}) over 3 h		
				298 K	448 K	623 K
none			319	0.22	0.28	0.55
Cs	$CsNO_3$	1	213	1.44	1.72	6.37
Ba	$Ba(NO_3)_2$	1	220	1.78	4.35	11.56
La	$La(NO_3)_3$	1	208	0	0	8.19

[a] BET surface areas were measured after catalysts were activated by H_2 at 623 K for 4 h and a catalytic run at 623 K for 3 h.

states of the Ta oxide support may be involved) requires some knowledge of the role of the support in the traditional systems. The presence of a K promoter in Fe-based Haber systems not only greatly enhances the reactivity of previously inactive Fe surfaces (e.g., Fe(110), Fe(210)), but also lowers the energy of adsorption of ammonia on the Fe metal.[29] Therefore, as the concentration of NH_3 on the surface decreases, more active sites remain available for dissociative adsorption of N_2. Studies on thermal desorption spectroscopy of NH_3 by Benndorf and Madey suggested a similar mechanism for catalysis on Na-doped Ru (001).[30] Aika and co-workers have proposed that rate enhancement by alkali or alkali earth metal promoters in Ru-based systems result from electronic promotion. Electron density is donated from the promoter to the Ru, lowering its ionization potential, which allows the electrons at the Ru surface to be readily donated into the N_2 antibonding orbital, thus reducing the activation energy for dissociative adsorption of N_2.[31] When this observation is related to our system, it stands to reason that the effectiveness of electron transfer from Ru to Ta should rely in part on the potential at the surface of the Ru particles. Thus, the decrease of the binding energy of electrons at the Ru surface should lead to a more effective transfer of electrons to the Ta centers in the generation of low-valent sites, as long as a suitable electron pathway exists between the Ru and the Ta. This would mean that promoters which decrease the binding energy of Ru surface electrons would be more effective in the generation of reduced Ta sites than those promoters which increase the binding energy of surface electrons and would lead to an increase in the reaction rate if reduced Ta is indeed involved, which all E_a data from our system imply.[18] This is also consistent with a high dependency of the rate on H_2 concentration because increased surface coverage of Ru by H_2 would lead to a more highly reducing surface better able to transfer electrons to the Ta.

The role of the Ba in our system may not be this simple; however, various other groups have conducted studies that suggest that electron density is not transferred from alkali promoters to the Ru metal[32] and the electrostatic interaction is limited to the vicinity of the alkali[33] or that efficient electron transfer occurs to oxygen rather than ruthenium.[34] This is supported by the observation that the addition of promoters to the catalytic systems in question generally does not cause a significant change in the activation energies. However, when $Ba(NO_3)_2$ is used as promoter for Ru/MgO catalyst, a large decrease in apparent activation energy for ammonia production is observed.[10] This unusual change is apparently not caused entirely by the effect of Ba because this drop in activation energy does not occur in the Ba−Ru/zeolite X system; the apparent activation energy of Ba−Ru/zeolite X catalyst is actually similar to the values for alkali-exchanged zeolite X. Therefore, the combined interaction of promoter, the support, and the Ru metal is possibly responsible for the change in activation energy. Also, according to Aika's mechanism, Ba should never be superior to Cs as an electronic promoter. However, Ba functions as a better promoter than Cs in almost all studied Ru catalyst systems.[35] With many competing factors potentially at play and evidence for involvement of low-valent Ta in the process, it is not yet possible to delineate the exact reason why Ba functions as the best promoter in our system. The simplest explanation is that it facilitates electron transfer between the Ru and the Ta by modifying the Fermi level of the Ru, but this neglects possible direct interactions between Ba and Ta, Ba and O, or other factors mentioned above. Clearly more experimental work needs to be done on both the mechanism and structure of the active site before more definite conclusions can be drawn.

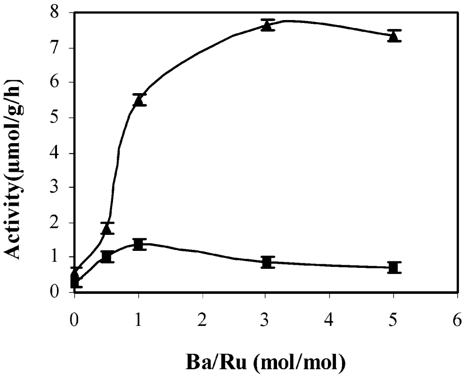

Figure 6. Activity of ammonia synthesis on 5 wt % Ba−Ru/Ta as a function of Ba/Ru mol ratio: (▲) rate was measured at 448 K on the catalyst reduced at 623 K and (■) rate was measured at 623 K on the catalyst reduced at 623 K.

Effect of Promoter/Ru ratio. Since $Ba(NO_3)_2$ was found to be the best promoter in our system, the amount of $Ba(NO_3)_2$ was systematically varied, and the activity was measured. The results are shown in Figure 6. In the case of 5 wt % Ru/Ta oxide catalyst, a Ba/Ru ratio of 1:1 gave the maximum activity at lower temperature, while 3:1 proved to be the best at higher temperature. The surface of activated mesoporous Ta oxide, with the BET surface area of 242 m^2 g^{-1}, can accommodate 7.13 mmol g^{-1} of Ba^{2+} ions or 7.07

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mmol g^{-1} of Ru when Ba^{2+} ions or Ru are closely packed on the surface.[25] The surface quantities of Ba^{2+} and Ru with promoter/Ru = 1 and 5.0 wt % Ru loading are about 0.4 and 0.4 mmol g^{-1}, respectively, and cover only about 5.6 and 5.7 % of the surface of Ta oxide, respectively. According to Aika's mechanism, in the case of an acidic support like Ta oxide, a small amount of an alkaline promoter will be consumed to neutralize the support and so a higher promoter/Ru is preferred. Jacobsen and co-workers, by using atomic-resolution in situ TEM, observed that Ba atoms distributed as single atoms close to the crystal edges (B_5 sites) and bound to oxygen are responsible for the electronic promotion of the catalyst.[36] Since very few such active sites are present in the catalyst, the majority of Ba atoms from the relatively large, optimal Ba/Ru ratio (0.3−2.0)[37−39] are used as reservoirs to maintain a constant coverage of mobile Ba atoms in the vicinity of all B_5-type sites in the catalyst.

While Ru is the active agent for the standard Haber process at high temperature, with all bond breaking and forming processes occurring on the metal surface, Arrhenius plots on our system provide an E_a of 9.3 kJ mol^{-1}, which is a fraction of the minimum 58−96 kJ/mol required to break an N−N triple bond on a pristine Ru surface.[22,23] XPS data also provide evidence for low-valent Ta on the surface during reaction conditions, and our previous work shows that reduced mesoporous Ta oxide cleave N_2 instantaneously at room temperature. The activity of the catalyst at elevated temperature shows a strong dependence on the Ru/Ba ratio and a maximum activity at 3:1, similar to traditional Haber catalysts. However, the plot at lower temperature shows far less of a dramatic dependence on this ratio and a maximum at 1:1. Two mechanisms may be at work in varying proportions depending on temperature. At higher temperature, the majority of N_2 cleavage occurs at the Ru surface, while at lower temperature, where traditional Haber catalysts are generally inactive, the second mechanism involving reduced Ta predominates. However, for this to be true, an inflection at higher T in the Arrhenius plot reflecting the greater activation barrier of N_2 cleavage at Ru would be observed, but this was not the case because the plot remained linear. Another explanation for the different dependency of activity on Ba/Ru ratio observed at different temperatures is that, because of the much higher molecular weight of Ta_2O_5 than other supports, only 4.5 mmol Ta atoms present in 1 g of Ta oxide. Excessive promoter could thus block the active Ta sites, and for this reason, a somewhat lower ratio (Ba/Ru = 1) is preferable at lower (448 K) temperature. Catalysts with an even higher ratio of 5:1 were also tested at 350 °C and relatively low activity was found. In this case, XPS studies showed that only about 85% $Ba(NO_3)_2$ was decomposed to BaO under our activation conditions.

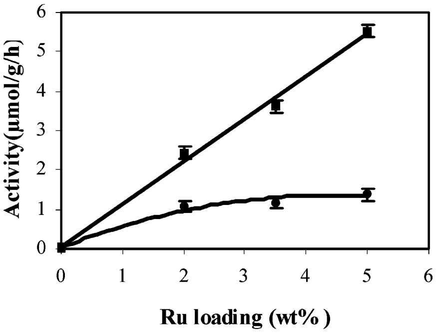

Figure 7. Activity of ammonia synthesis at 448 (▲) and 623 K (■) as a function of Ru loading.

Effect of Absolute Ru Loading. Ru/Ta oxides prepared from $Ru_3(CO)_{12}$ using different Ru loading were prepared and doped with $Ba(NO_3)_2$ at a Ba/Ru ratio of 1. The rates of ammonia synthesis from these catalysts at 175 (448 K) and 350 °C (623 K) are shown in Figure 7. The rate increases linearly with Ru loading at 350 °C, but it increases only slightly before leveling off at 175 °C. This pattern of greater dependency on catalyst loading levels at higher temperature is consistent with the trends relating activity and the Ba/Ru ratio shown in Figure 6. Aika and co-workers have observed a linear relationship up to 5 wt % of Ru loading over their Ru/MgO systems,[14] which is not unexpected since with the entire catalytic reactions take place on the Ru clusters in these systems. However, in our Ru/Ta oxide catalysts, the Ru could also function as an interface to funnel electrons from H_2 to the Ta reducible sites at lower temperature. The fact that activity does not increase with Ru loading at 175 °C is in accord with a new mechanism, at least at this temperature, in which the number of reduced Ta active sites might be more important than Ru and the rate of reaction depends more strongly on electron transfer between the Ru and the Ta. This is in accord with the low activation energies (9.3 kJ mol^{-1}) measured previously, which suggest a small number of highly active sites. Since six electrons are required per N_2, several Ta centers must be involved. This can occur in several steps at Ta sites spread through the mesostructure or in one step at an active site involving several low-valent Ta sites. In the latter case, the binding of N_2 might be compared to binding to the FeS core in nitrogenase. Once the electrons are transferred to the Ta, the reaction proceeds rapidly, consistent with the almost instantaneous cleavage of N_2 and subsequent formation of NH_3 in bis(toluene) Ti reduced mesoporous Ta oxide. Thus, the limiting factor in this mechanism would be the transfer of electrons to the Ta and the low activities coupled with low activation barrier can be explained by the presence of only limited effective electron-transfer pathways in the material. Increasing the temperature does not substantially improve electron transport across the amorphous surface, but it allows the second mechanism to become more important. This hypothesis also suggests that improving electron transport across the surface should lead to more reduced Ta sites and higher activities and is supported by the fact that Ba is the best promoter and is known to influence the energy of the electrons at the Ru surface and thus their facility for mobility across the surface.

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Table 3. Effect of Ru and Ba Precursor Compound

Ru precursor compound (5 wt %)	Ba precursor compound	Ba/Ru (mole ratio)	BET surface area[a] (m^2/g)	activity (μmol g^{-1} h^{-1})	
				448 K	623 K
$Ru_3(CO)_{12}$	$Ba(NO_3)_2$	1	219	1.38	5.52
	$Ba(OH)_2$	1	252	0.42	0.75
	$Ba[OCH(CH_3)_2]_2$	1	232	0	0.13
$RuCl_3.xH_2O$	$Ba(NO_3)_2$	1	225	0.34	1.87
	$Ba(OH)_2$	1	249	0.16	0.51
	$Ba[OCH(CH_3)_2]_2$	1	241	0	0.08

[a] BET surface areas were measured after catalysts were activated by H_2 at 623 K for 4 (barium nitrate precursor) or 2 h (other barium precursors), followed by a catalytic run at 623 K for 3 h.

Table 4. Reaction Data for Pd/Ta Catalysts[a]

catalyst	promoter precursor	synthesis gas	BET surface area (m^2 g^{-1})	activity (μmol g^{-1}) over 3 h		
				298 K	448 K	623 K
10% Pd	$Ba(OH)_2$	He	279	0.00	0.00	0.00
10% Pd	$Ba(OH)_2$	1:1 $N_2 + H_2$	243	0.302	0.73	1.61
10% Pd	$Ba(NO_3)_2$	He	271	0.00	0.00	0.00
10% Pd	$Ba(NO_3)_2$	1:1 $N_2 + H_2$	222	0.67	1.10	2.21
10% Rh	$Ba(NO_3)_2$	1:1 $N_2 + H_2$	238	0.02	0.04	0.06
10% Pt	Ba(NO3)2	1:1 N2 + H2	229	0.01	0.08	0.18

[a] Reaction data and BET surface areas were measured after catalysts were activated by H_2 at 623 K for 4 h and then heated under vacuum at 623 K for 3 h. All materials prepared using a Pd/Ba ratio of 1:1.

Effect of Ba and Ru precursor. Promoter precursor effects of $Ba(OH)_2$ and Ba(isopropoxide) were examined and compared with that of $Ba(NO_3)_2$. The activities were measured in each case after hydrogen reduction was complete and all ammonia formed during this initial period (arising from nitrate or residual N_2 in the system) ruled out. The results of this study are shown in Table 3. All the Ba salts are effective, with $Ba(NO_3)_2$ giving the best results at both 175 (448 K) and 350 °C (623 K). $RuCl_3{\cdot}3H_2O$ was also used as an alternative of Ru precursor. These catalysts were prepared by impregnating $RuCl_3{\cdot}3H_2O$ with mesoporous Ta oxide in methanol and were further promoted by $Ba(OH)_2$ and Ba(isopropoxide). The activities of thus prepared catalysts were compared with that of the standard catalyst, and the results are also shown in Table 3. The trend follows exactly that using $Ru_3(CO)_{12}$ as the precursor. A possible explanation for the observation that $Ba(OH)_2$ is a poorer promoter than $Ba(NO_3)_2$ may be the result of the lower basicity of BaO originating from the hydroxide rather than $Ba(NO_3)_2$. However, the fact that the hydroxide works at all is further evidence that the ammonia formed in this system cannot arise from residual nitrate. The reason that Ba isopropoxide did not exert a promotion effect may be because it did not decompose completely to BaO under our operating conditions. Table 3 shows that $RuCl_3{\cdot}3H_2O$ is not as effective a precursor as $Ru_3(CO)_{12}$. This is not surprising because of results from standard Haber systems, and it has been related to three major effects. Ru exists as Ru^{3+} in the parent catalyst, which has to be reduced before nitrate promoters decompose. $Ba(NO_3)_2$ is not reduced with H_2 below 450 °C in the absence of Ru. On the other hand, because of the nature of the precursor and the method of decomposition used, there is already some Ru metal existing in parent $Ru_3(CO)_{12}$ catalyst before H_2 treatment, so that Ru-catalyzed nitrate decomposition in this case should be more facile. Another major reason that $RuCl_3{\cdot}3H_2O$ is a less effective precursor is that chloride ions are known to poison the catalyst. Aika and co-workers found that much higher activities can be obtained after removal of chloride at very higher temperatures, for example 1000 °C.[40] Magnesia was also found to be one of the best oxide supports for ammonia synthesis, especially when $Ru_3(CO)_{12}$ was used as precursor.[14] The high activities might be contributed from high Ru dispersion, the chloride-free system, and the basicity of MgO. Finally, water vapor from $RuCl_3{\cdot}3H_2O$ could also be another poison and thus decrease the catalyst activity when used as a source of Ru.[12]

Pd, Pt, and Rh Catalysts. To more fully explore the effects of composition on the catalytic behavior of this system, we prepared a series of Pd, Pt, and Rh analogues to the catalysts studied above. These metals are of special interest because the very high activation energies of N_2 cleavage on the surface precludes the possibility of direct N_2 cleavage by the precious metal under the conditions in this study. For example, the E_a for N_2 dissociation on a Pd surface has been calculated as 2.6 eV (250 kJ mol^{-1}).[23] This compares to the somewhat lower E_a value for this process on a Ru surface (0.6−1.0 eV or 58−96 kJ/mol), which is still too high to allow direct N_2 cleavage in our Ru-based system, given that the activation barrier is 9.3 kJ mol^{-1}. Skeptics may still argue that at high temperature we cannot rule out some small amount of ammonia being formed on Ru through this traditional mechanism because of a Boltzman distribution of molecular energies in the system, especially since some of our data on Ru and Ba loading could suggest a second mechanism may be operative at higher temperature. So, to add further indirect verification of the involvement of N_2 cleavage on Ta in our system, we exchanged Ru for Pd, Pt, and Rh metals on which N_2 dissociation is energetically prohibitive and rarely, if ever, observed. Thus mesoporous Ta oxide catalysts doped with metallic Pd, Pt, or Rh were synthesized by solution impregnation of the metal chloride followed by H_2 reduction at elevated temperature and characterized by XRD, nitrogen adsorption, TEM, EDS, and XPS. Table 4 shows data for the 10% Pd catalysts using either $Ba(OH)_2$ or $Ba(NO_3)_2$ as a promoter at 350 (623 K) and 175 °C (448 K). The catalyst activities for ammonia production are roughly one-third those for the Ru analogues and drop off further over several hours as shown in the table. Blanks are also shown for the system using He as a feedstock to rule out residual ammonia formed from some other contaminant source. As with the Ru system, the catalyst also does not function with either pure N_2 or pure H_2. If N_2 cleavage occurred on the Pd surface, on the basis of the E_a for this process (250 kJ/mol, almost five times greater than that for Ru), the rate of N_2 cleavage would be 10^{15} times slower for a Pd/Ta catalyst. However, it is actually about 30% of the activity of the Ru catalyst. This high rate of production relative to that predicted for any process involving dissociation of N_2 on Pd, firmly establishes that N_2 cleavage must occur on the low-valent Ta sites. Figure 8 shows the

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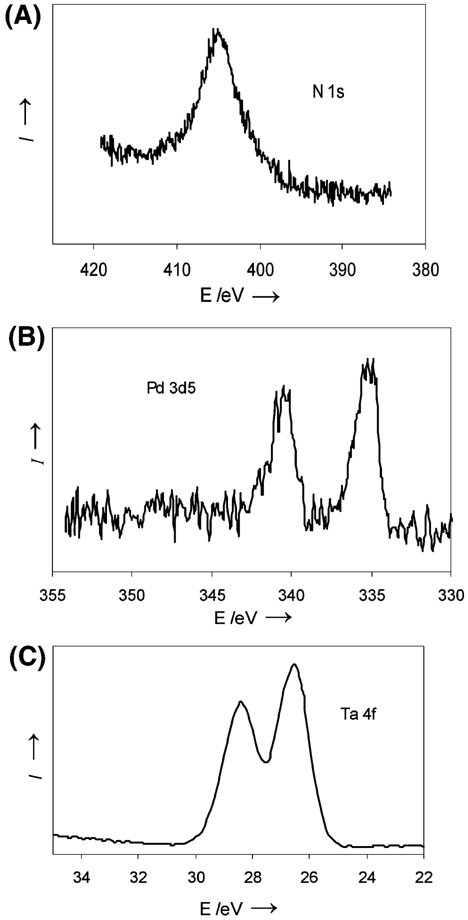

Figure 8. XPS emissions for (A) N 1s, (B) Pd 3d, and (C) Ta 4f regions in mesoporous Ta oxide doped with 10% Pd at a 1:1 Ba(OH)$_2$ ratio after heat treatment at 623 K for 4 h in pure H$_2$, 4 h vacuum at 623 K, and 3 h catalytic run with 1:1 H$_2$ and N$_2$.

XPS of the (a) N 1s, (b) Pd 3d, and (c) Ta 4f regions of the catalyst after 1 h under operating conditions at 350 °C. The N 1s region is obscured by the Ta 4p$_{3/2}$ peak; however, there is a small shoulder at 398 eV corresponding to surface bound ammonia.[20] The Pd 3d region shows emissions consistent with metallic Pd with small shoulders at higher binding energies corresponding to a fraction of a second, possibly oxidized species. The Ta 4f region shows a broad 5/2 emission with a maximum at 26.4 eV tailing off below 25.0 eV. For comparison, pure mesoporous Ta (V) oxide shows this emission at 26.9 eV, and the Ru-doped catalyst shows this emission at 26.2 eV at this stage of catalyst preparation. The binding energy of this peak, the broadness of this emission, and the tailing off to lower binding energies are evidence of reduction to oxidation states lower than Ta(IV) and confirm that low-valent Ta is indeed involved in the process. The catalysts activities using Pt and Rh as precious metals generally provided ammonia yields over 3 h of less than 0.5 μmol h^{-1} g^{-1}. Yet the fact that any measurable amount of ammonia is being formed using these metals is further evidence for N$_2$ cleavage on the Ta sites because the E_a for cleavage on these metals is also prohibitive for direct N$_2$ cleavage under the conditions of experiment.

While the activities in this new family of ammonia synthesis catalysts are low at this early stage, improvement of electron transport across the surface may lead to enhanced rates. These observations aside, the new mechanism proposed in this work supports much recent work in organometallic chemistry revolving around N$_2$ cleavage at early metal centers and may lead to the development of multicomponent organometallic systems employing early and late transition metal centers. These studies also show that mesoporous Ta oxides may be important in other areas of catalysis because of their unique combination of controlled pore size, high surface area, and variable oxidation states. Future studies are ongoing to further clarify the mechanism and improve the activities.

Conclusion

A study was conducted on the effect of composition on activity for a series of metal-doped mesoporous Ta oxide catalysts for conversion of N$_2$ and H$_2$ to ammonia. Labeling studies established that the majority of ammonia formed in the first hour originated from nitrate, but that once nitrate was consumed, new ammonia from N$_2$ and H$_2$ was formed. For the mesoporous Ta oxide catalytic system, Ru$_3$(CO)$_{12}$ and Ba(NO$_3$)$_2$ were found to be the most effective precursors of Ru catalysts. La(NO$_3$)$_3$ was a poorer promoter at mild conditions but a better promoter at higher temperature than CsNO$_3$ possibly because of the SMSI effect. Studies on Ru/Ba ratio and absolute Ru loading show different behaviors at 175 (448 K) and 350 °C (623K), suggesting that two mechanisms may be at play, although further studies are required to confirm this. Catalysts were also prepared with Pd, Pt, and Rh in place of Ru. The Pt and Rh catalysts showed poor activity, but the Pd catalyst was almost as active as the Ru catalyst. Since N$_2$ dissociation on Pd is prohibitive, this lends support to a mechanism involving cleavage at low-valent Ta. Further kinetic investigations of this new catalytic system are ongoing with an effort to better understand the controlling factors and thus be able to develop strategies to improve activity and longevity.

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