Catalytic ammonia decomposition: CO_x-free hydrogen production for fuel cell applications

T.V. Choudhary, C. Sivadinarayana and D.W. Goodman *

Chemistry Department, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA
E-mail: goodman@mail.chem.tamu.edu

Received 30 October 2000; accepted 8 January 2001

Catalytic decomposition of ammonia has been investigated as a method to produce hydrogen for fuel cell applications. The absence of any undesirable by-products (unlike, e.g., CO_x, formed during reforming of hydrocarbons and alcohols) makes this process an ideal source of hydrogen for fuel cells. In this study a variety of supported metal catalysts have been studied. Supported Ru catalysts were found to be the most active, whereas supported Ni catalysts were the least active. The supports were found to play a profound role in the ammonia decomposition process. The activation energies for the ammonia decomposition process varied from 17 to 22 kcal/mol depending upon the catalyst employed. The activation energies of the supported Ir catalysts were found to be in excellent agreement with our recent studies addressing ammonia decomposition on single crystal Ir.

KEY WORDS: ammonia; hydrogen production; CO_x-free

1. Introduction

The interaction of ammonia with metal surfaces has been thoroughly investigated [1–14]. These studies have been undertaken primarily to acquire insights into the industrially important ammonia synthesis process. However, motivating our interest in catalytic ammonia decomposition is the recent interest in the generation of clean hydrogen for fuel cells. Conventional processes such as steam reforming, autothermal reforming and partial oxidation yield large amounts of CO as a by-product [15–17]. Removal of this CO into the ppm range (tolerance levels of CO for the state of art proton exchange membrane fuel cells is only a few ppm) render these methods of hydrogen generation complex, bulky and expensive. These drawbacks remain a serious technological obstacle in the practical utilization of these processes for vehicular and small-scale fuel cell applications.

Recently, extensive efforts have been undertaken in our laboratory to explore CO_x-free alternatives for production of hydrogen for fuel cell applications [18–21]. We have investigated step-wise steam reforming of methane/hydrocarbons as a method for production of CO-free hydrogen. Unfortunately, hydrocarbons as fuel sources invariably lead to the production of CO_2 associated with the hydrogen. Alkaline fuel cells (highly efficient low temperature fuel cells) are very intolerant of even very low levels of CO_2 in the hydrogen fuel stream [22].

Decomposition of ammonia is a mildly endothermic process, yielding hydrogen and nitrogen:

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad \Delta H = 11 \text{ kcal/mol.}$$

The process operated as such produces no CO or CO_2, but rather nitrogen (essentially benign to the fuel cell) as the only co-product. Regarding storage, ammonia is a liquid at 293 K and 8 atm pressure. Considerable attention has been given steam reforming of methanol as a process for the generation of hydrogen for fuel cells. However, a comparison of the economics for hydrogen production via ammonia decomposition for alkaline fuel cells as opposed to the production of hydrogen by methanol reforming for acid fuel cells shows that ammonia decomposition is a more attractive process from an economic standpoint [23,24]. Commercial ammonia is prepared at 99.5% purity (the impurity is mainly water and is harmless) [22], whereas the higher alcohol impurities present in commercial methanol can result in production of contaminants during reforming that can lead to poisoning of the catalyst. Finally, the prices of the hydrogen from methanol and ammonia are comparable on a BTU basis [22]. With these considerations, the decomposition of ammonia appears to be an excellent choice for production of hydrogen for alkaline fuel cells. Ammonia can also be used as a source of hydrogen for acid fuel cells if the unreacted ammonia in the hydrogen stream is removed prior to its admission into the fuel cell.

Unfortunately, there has been no investigation that has systematically catalogued catalytic decomposition of ammonia on various supported metal catalysts for hydrogen production. In order to address this issue we have undertaken ammonia decomposition studies on single crystal model systems [25] as well as high surface area catalysts. In this paper, ammonia decomposition studies on supported Ni, Ir and Ru catalysts are reported. Various supports have been investigated to gain information relevant to the effect of the support on the ammonia decomposition process. The results

---

* To whom correspondence should be addressed.

1011-372X/01/0400-0197$19.50/0

obtained on supported Ir catalysts have been related to those obtained on single crystal model catalysts.

2. Experimental

2.1. Catalyst synthesis

Supported Ni, Ir and Ru catalysts were prepared by a wet impregnation method with a nominal metal loading of 10%. The supports H-ZSM-5 (Degussa), HY (Na-Y, Si/Al = 100 from Degussa), Al_2O_3 (Aldrich Chemicals), SiO_2 (Cab-O-Sil) were calcined at 823 K for 4 h prior to the impregnation procedure. The Na-Y zeolite was converted to NH_4Y via aqueous ion-exchange (ammonium hydroxide solution). The procedure was repeated six times at 353 K and the product subsequently washed with deionized water and heated at 373 K for drying. The NH_4Y was then decomposed to HY by calcination at 573 K for 6 h. After impregnation the catalysts were dried overnight at ca. 373 K and then calcined at 823 K for 4 h. Following this the catalysts were finely powdered. The 65 wt% $Ni/Al_2O_3/SiO_2$ catalyst was obtained from Aldrich chemicals and was used as obtained.

2.2. Catalyst testing

The continuous-flow-reactor system consists of a conventional fixed-bed plug-flow reactor, a quartz reactor and a furnace controlled by a temperature controller (Omega). The catalyst (usually 0.1 g) was placed in a small section of the quartz reactor which, in turn, was placed in the constant temperature zone of the furnace. Product analysis was carried out with an on-line gas chromatograph (Varian 3700) equipped with a thermal conductivity detector. Separation was via a Poropak Q column with argon (Ar) used as the carrier gas. The detector was calibrated for the gases (NH_3, N_2 and H_2) over a wide dynamic range spanning the analysis region. Prior to the reaction the catalyst was reduced with hydrogen in flowing argon ($H_2 : Ar = 1 : 1$) at a total flow rate of 20 ml/min for 0.5 h at 523 K and for 2.5 h at 773 K. Following this the catalyst was flushed with argon for 0.5 h and heated to the desired temperature in a flow of carrier gas. Pure ammonia (Matheson) at a flow rate of 50 ml/min was passed over the catalyst (usually 0.1 g). Decomposition of ammonia was carried out on individual supports (silica, alumina, HY, H-ZSM-5) and empty reactor at different temperatures; reaction conditions were maintained similar to those employed for the decomposition on supported metal catalysts. The TOF values have been corrected whenever the contribution from the support exceeded 5% of the total conversion shown by supported metal catalysts.

Since mass-transfer (mainly pore-diffusion) effects are a concern at high reaction rates the catalysts were used in a finely powdered form (few microns diameter). The Weisz criterion [26] ($\phi = (\mathrm{d}N/\mathrm{d}t)(1/C_0)(R^2/D_{\mathrm{eff}})$, where $\mathrm{d}N/\mathrm{d}t$ is the reaction rate (mol/cm^3 s), C_0 reactant concentration (mol/cm^3), R particle radius (cm) and D_{eff} effective diffusivity (cm^2/s)) was used to ensure the absence of any mass-transfer limitations. Calculation for 65% $Ni/SiO_2/Al_2O_3$ catalyst (temperature 723 K, conversion 9%, flow rate 50 cm^3/min pure ammonia, particle radius 2×10^{-3} cm) provided a value of ϕ of ca. 0.02, which is well below the regime for mass-transfer effects ($\phi > 1$). Other catalysts were also similarly found to be free from mass-transfer resistance under all conditions employed for the study. The rate of the reaction was found to be the same for constant gas-hourly space velocity (mass of catalyst and flow rate was changed). Also the activation energy for the reaction was found to be unchanged when lower partial pressures of ammonia were employed for the study, thus providing direct evidence for the absence of mass-transfer limitations.

2.3. Catalyst characterization

The dispersion of the Ni catalysts was determined by CO-pulse experiments carried out at room temperature assuming a CO/Ni ratio of 1.0. Further details of this procedure can be found in [19]. The hydrogen chemisorption results were obtained from the irreversible hydrogen uptake at room temperature (standard procedure as given in [27] was employed). Before the measurements the catalysts were heated to 523 K for 0.5 h and 673 K for 2 h under a static atmosphere of hydrogen (Matheson, Research Purity). Following this the catalysts were evacuated and cooled to room temperature. Dispersion of the $Ni/SiO_2/Al_2O_3$ catalyst was measured with CO and H_2 chemisorption for comparison of the two methods.

3. Results and discussion

The results obtained from the CO-pulse experiments and hydrogen chemisorption experiments are presented in table 1. Metal dispersions have been estimated assuming an adsorption of one CO (H) per Ni (Ru, Ir) site. The dispersion for 65% $Ni/SiO_2/Al_2O_3$ obtained from the CO-pulse experiments and hydrogen chemisorption experiments are in good agreement. Among the supported Ni catalysts the highest dispersion was observed for 65% $Ni/SiO_2/Al_2O_3$ and the

Table 1
Chemisorption data for the various supported metal catalysts.

Catalyst	Surface metal atoms per gram of catalyst	Dispersion (%)
10% Ni/HY	4.2×10^{18}	0.4[a]
10% Ni/SiO_2	9.6×10^{18}	0.9[a]
10% Ni/HZSM-5	3.1×10^{19}	3.1[a]
65% $Ni/SiO_2/Al_2O_3$	[a]5.7×10^{20}, [b]6.2×10^{20}	7.7[a], 8.5[b]
10% Ir/SiO_2	1.0×10^{19}	3.2[b]
10% Ir/Al_2O_3	4.8×10^{19}	15.4[b]
10% Ru/SiO_2	6.8×10^{18}	1.2[b]
10% Ru/Al_2O_3	1.52×10^{19}	2.8[b]

[a] From CO chemisorption.
[b] From H_2 chemisorption.

least for Ni/HY. The 10% Ir/Al_2O_3 catalyst showed the highest dispersion of ca. 15%. The average particle size for each catalyst can be approximated by assuming d (nm) $= 1/D$ [28]. Calculated in this manner the average particle size of the catalyst particles ranged from ca. 5 to 250 nm.

Supported Ni catalysts are used in a number of industrial processes and are relatively inexpensive. Also previous studies have shown Ni to be active for the ammonia decomposition process [12]. Figure 1(a) shows the hydrogen formation rate per site per second (TOF) for supported Ni catalysts as a function of temperature. The rate of hydrogen formation was found to be similar for HY and SiO_2, while it was found to be much lower on ZSM-5. Even though the dispersion was highest for ZSM-5 the conversion of ammonia was found to be the lowest. This clearly illustrates that the support plays an important role in determining the activity for the ammonia decomposition process. Although the conversion on the Ni/SiO_2 catalyst was higher by a factor of ca. 2 compared to Ni/HY, the TOFs were essentially the same due to the higher dispersion of the the Ni/SiO_2 catalyst. The conversion of ammonia was ca. 70 and 42% at 923 K for Ni/SiO_2 and Ni/HZSM-5, respectively. Ammonia conversions approaching 100% were reached at 923 K when high Ni loadings (65% Ni/SiO_2/Al_2O_3) were employed (table 2). Time on stream studies for Ni/SiO_2 and Ni/SiO_2/Al_2O_3 indicated constant activity at 723 K for a period of ca. 4 h. Since there was no deviation in catalytic activity during the course of the reaction, it is surmised (as in previous studies [12]) that there is no formation of bulk nitrides under the conditions used in our investigation. Figure 1(b) shows Arrhenius plots for the various catalysts; the activation energies were calculated from the slopes of the plots. The values for the activation energies (E_a) varied from 20 kcal/mol for Ni/HZSM-5 to 22 kcal/mol for Ni/SiO_2/Al_2O_3. These values are much lower than values reported for Ni films (43 kcal/mol, [10]) and Ni wires (50 kcal/mol,[12]). Similar large differences in E_a values are also observed between supported Ru catalysts [9] and Ru films [10]. The metal–support interaction probably plays a decisive role in determining the apparent E_a for the ammonia decomposition reaction in these cases.

Figure 2(a) shows the hydrogen formation rates for supported Ir catalysts. Although the conversion on the alumina support was slightly higher, the catalytic activity on a TOF basis is higher for the silica support (taking into account the Ir dispersion in table 1). Conversions approaching 100% were reached for both catalysts at 973 K. The slopes of the Arrhenius plots (figure 2(b)) yield E_a values of 17.2 and 19.5 kcal/mol for Ir/SiO_2 and Ir/Al_2O_3, respectively. We have recently investigated ammonia decomposition (static system, 0.5–1.5 Torr, 698–798 K) on Ir(100) [25]. The E_a values

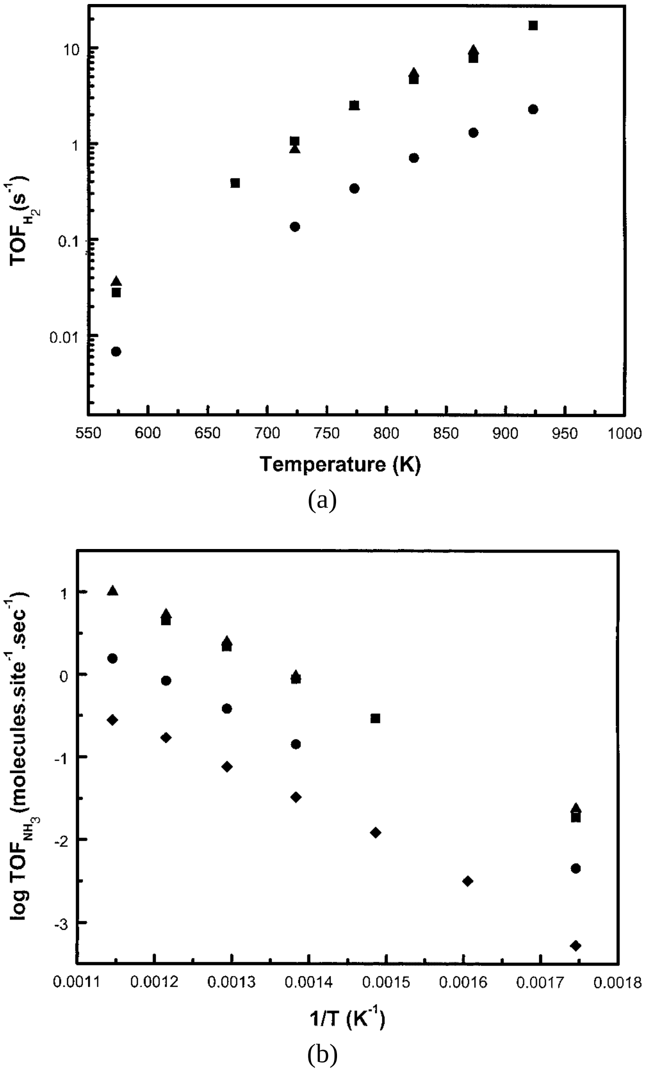

Figure 1. (a) Comparison of hydrogen formation rates (molecules/site s) as a function of temperature for (▲) Ni/HY, (■) Ni/SiO_2 and (●) Ni/HZSM-5. (b) Arrhenius plots for (▲) Ni/HY (■), Ni/SiO_2, (●) Ni/HZSM-5 and (◆) Ni/SiO_2/Al_2O_3.

Table 2

Conversion and hydrogen formation rates for silica-containing catalysts.

Temp. (K)	10% Ni/SiO_2		65% Ni/SiO_2/Al_2O_3		10% Ir/SiO_2		10% Ru/SiO_2	
	Conv. (%)	Rate (H_2) (mmol/min g_{cat})	Conv. (%)	Rate (H_2) (mmol/min g_{cat})	Conv. (%)	Rate (H_2) (mmol/min g_{cat})	Conv. (%)	Rate (H_2) (mmol/min g_{cat})
673	1.4	0.44	3.5	1.1	3.9	1.2	14.3	4.5
723	4.2	1.3	9.3	2.9	8.1	2.6	36.4	11.4
773	10.5	3.3	21.7	6.8	18.2	5.7	64.0	20.0
823	21.6	6.8	48.7	15.2	30.4	9.5	–	–
873	36.4	11.4	79.5	24.9	56.0	17.6	97	30.3
923	70.0	21.1	97.0	30.3	–	–	99	30.9
973	–	–	–	–	98	30.6	–	–

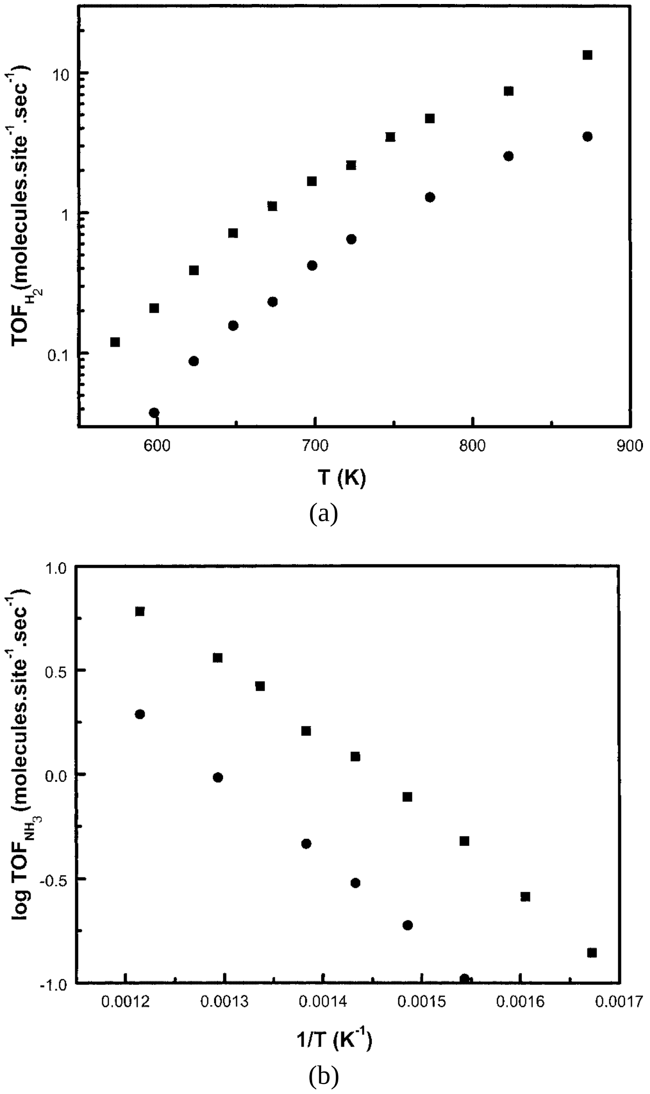

Figure 2. (a) Comparison of hydrogen formation rates (molecules/site s) as a function of temperature and (b) Arrhenius plots for (■) Ir/SiO_2 and (●) Ir/Al_2O_3.

(ca. 20 kcal/mol) obtained from these studies are in excellent agreement with the corresponding values obtained on the high surface area supported Ir catalysts in this work. Previous studies on Ir wires report values ranging from ca. 19 [8] to 31.2 kcal/mol [11]. It is noteworthy that Ir differs from Ni and Ru in that the apparent E_a values are similar for Ir metal and supported Ir catalysts (unlike Ni and Ru where the E_a values are much lower for the supported catalysts).

Similar to supported Ir catalysts the TOF values for Ru/SiO_2 are greater than that of Ru/Al_2O_3 (figure 3(a)). Even though the dispersion of Ru is greater on the alumina support, a larger ammonia conversion was obtained for the silica support. The influence of the support for the catalytic decomposition of ammonia has also been observed in a previous study by Vannice and co-workers [9]; 1.6% Ru/Al_2O_3 was found to have an order of magnitude greater TOF value than 4.8% Ru/C. Interestingly the E_a values (figure 3(b)), unlike the catalytic activity, are essentially the same for both Ru/Al_2O_3 and Ru/SiO_2 (19.0 and 19.5 kcal/mol). The E_a value for Ru/Al_2O_3 is in good agreement with a recent kinetic study on an identical catalyst (21 kcal/mol) [9].

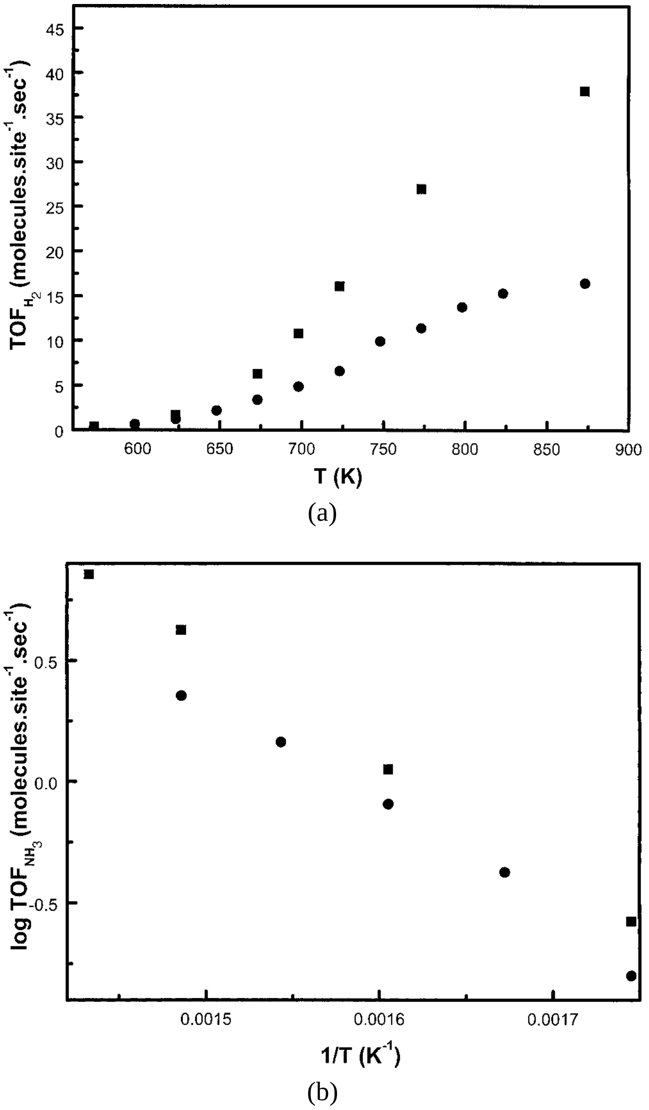

Figure 3. (a) Comparison of hydrogen formation rates (molecules/site s) as a function of temperature and (b) Arrhenius plots for (■) Ru/SiO_2 and (●) Ru/Al_2O_3.

Figure 4 provides a comparison of catalytic activity (TOF) for hydrogen production via ammonia decomposition over Ni, Ir and Ru supported on silica. Ru is clearly the most active catalyst for the process, whereas Ni is the least. The ammonia conversion (disregarding the metal dispersion) at various temperatures shows the same trend: Ru > Ir > Ni for the same nominal metal loading (table 2); high loading 65 wt% $Ni/SiO_2/Al_2O_3$ is shown for comparison. Previous studies involving ammonia decomposition over wire catalysts have shown that Ir was far more active than Rh, Pd and Pt [11]. Also Ir wire [11] was found to be more active than Ni wire [12] for the ammonia decomposition process. This in good agreement with our high surface area supported catalyst studies. All the catalysts studied showed stable conversions over several hours. It is known that no bulk nitrides exist for Ru and Ir [29] and as such no decline in cat-

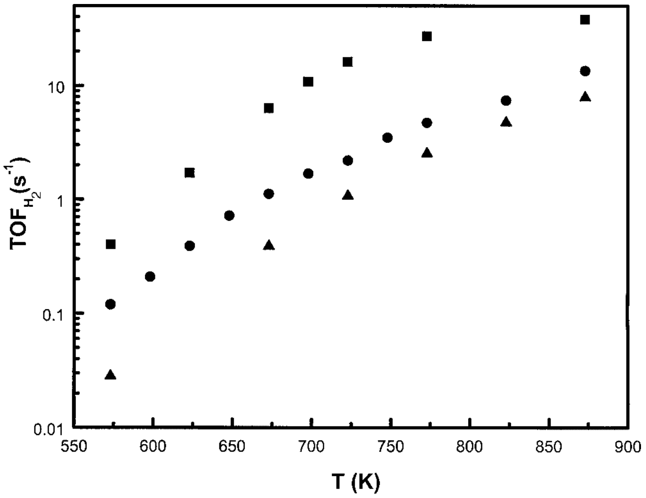

Figure 4. Comparison of hydrogen formation rates (molecules/site s) as a function of temperature for (▲) Ni/SiO_2, (●) Ir/SiO_2 and (■) Ru/SiO_2.

alytic activity is expected. Also our recent studies on Ir(100) [25] did not show the presence of surface nitride species (via Auger electron spectroscopy). Nitrogen desorption is generally assumed to be the rate-limiting step in ammonia decomposition [2,10]. The catalytic activity for various metals, therefore, is likely related to the E_a for desorption of nitrogen from the metal surfaces. With this assumption it can be speculated that nitrogen formed from ammonia decomposition is least strongly bound on Ru and most strongly bound on Ni. Investigations are currently underway to probe this question.

4. Conclusions

Catalytic decomposition of ammonia is a viable route for the production of CO_x-free hydrogen for fuel cells. This investigation has shown that the ammonia decomposition activity over the catalysts studied decreases in the order Ru > Ir > Ni. The supports were found to play a crucial role in determining the activity of the catalysts. The ammonia decomposition activity per metal site was found to be greater for a silica support compared with alumina. The activity of the supported Ni catalysts, although lower than the supported Ir catalysts, was not significantly different, making it attractive as an economical catalyst for ammonia decomposition. Further in-depth studies addressing the role of promoters, catalyst life-time and effect of promoters are currently underway.

Acknowledgement

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences. TVC gratefully acknowledges the Link Foundation for the Link Energy Fellowship.

References

[1] W.L. Guthrie, J.D. Sokol and G.A. Somorjai, Surf. Sci. 109 (1981) 390.
[2] E. Shustorovich and A.T. Bell, Surf. Sci. Lett. 259 (1991) L791.
[3] G. Ertl and M. Huber, J. Catal. 61 (1980) 537.
[4] K. Hashimoto and N. Toukai, J. Mol. Catal. A 161 (2000) 171.
[5] D.G. Loffler and L.D. Schmidt, J. Catal. 44 (1976) 244.
[6] Z. Kowalczyk, J. Sentek, S. Jodzis, M. Muhler and O. Hinrichsen, J. Catal. 169 (1997) 407.
[7] Y.-K. Sun, Y.-Q. Yang, C.B. Mullins and W.H. Weinberg, Langmuir 7 (1991) 1689.
[8] M. Grosman and D.G. Loffler, React. Kinet. Catal. Lett. 33 (1987) 87.
[9] M.C.J. Bradford, P.E. Fanning and M.A. Vannice, J. Catal. 172 (1997) 479.
[10] S.R. Logan and C. Kemball, Trans. Faraday Soc. 56 (1960) 144.
[11] G. Papapolymerou and V. Bontozoglou, J. Mol. Catal. A 120 (1997) 165.
[12] R.W. McCabe, J. Catal. 79 (1983) 445.
[13] W. Tsai and W.H. Weinberg, J. Phys. Chem. 91 (1987) 5302.
[14] C. Egawa, T. Nishida, S. Naito and K. Tamaru, J. Chem. Soc. Faraday Trans. I 80 (1984) 1595.
[15] J.R. Rostrup-Nielsen, in: *Catalytic Steam Reforming*, Science and Engineering, Vol. 5, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1984).
[16] J.N. Armor, Appl. Catal. 176 (1999) 159.
[17] V.R. Choudhary, B.S. Uphade and A.S. Mamman, J. Catal. 172 (1997) 281.
[18] T.V. Choudhary and D.W. Goodman, Catal. Lett. 59 (1999) 93.
[19] T.V. Choudhary and D.W. Goodman, J. Catal. 192 (2000) 316.
[20] T.V. Choudhary, C. Sivadinarayana, C. Chusuei, A. Klinghoffer and D.W. Goodman, submitted.
[21] T.V. Choudhary, C. Sivadinarayana, A. Klingehoffer and D.W. Goodman, submitted.
[22] A.J. Appleby and F.R. Foulkes, *Fuel Cell Handbook* (Van Nostrand Reinhold, New York, 1989).
[23] R. Metkemeijer and P. Achard, Int. J. Hydrogen Energy 19 (1994) 535.
[24] R. Metkemeijer and P. Achard, J. Power Sources 49 (1994) 271.
[25] T.V. Choudhary, C. Sivadinarayna, K. Davis and D.W. Goodman, in preparation.
[26] P.B. Weisz, Chem. Eng. Prog. Series 55 (1959) 29.
[27] F. Delannay, ed., *Characterization of Heterogeneous Catalysts* (Dekker, New York, 1984).
[28] M. Boudart and H. Hwang, J. Catal. 39 (1975) 44.
[29] J.R. Jennings, ed., *Catalytic Ammonia Synthesis: Fundamentals and Practice* (Plenum, New York, 1991).