Lanthanum promotion of Ru/zeolite X catalysts for ammonia synthesis

Stacey E. Siporin, Brian C. McClaine, Shaia L. Anderson [†], and Robert J. Davis [*]
Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904-4741, USA

Received 25 January 2002; accepted 22 March 2002

A series of La-promoted Ru/zeolite X catalysts (~2 wt% Ru) was examined in the ammonia synthesis reaction at 20.7 atm total pressure. Results were compared with those reported previously for analogous Ba-promoted Ru/zeolites. Exchange of the zeolite cations with La^{3+} formed an Ru catalyst (Ru/LaX) that was superior to one exchanged with Ba^{2+} (Ru/BaX). Incorporation of La^{3+} and Ba^{2+} beyond ion-exchange capacity improved the turnover frequency on Ru/LaX and Ru/BaX, respectively. However, an La-promoted sample proved to be the most active. Interestingly, all of the La-containing catalysts exhibited a weak dependence of the rate on H_2 whereas the Ba-loaded samples were strongly inhibited by the reactant. These results suggest that an appropriate choice of promoter might overcome the well-known inhibition on Ru catalysts by H_2 without sacrificing high reactivity.

KEY WORDS: ruthenium-supported catalyst; zeolite X; lanthanum; ammonia.

1. Introduction

Supported ruthenium catalysts for the production of ammonia were discovered in the 1970s by Ozaki and co-workers [1,2] and were commercialized in the 1990s [3,4]. The main advantages of the ruthenium catalysts are less inhibition by ammonia and greater tolerance of reaction poisons than conventional iron-based catalysts. Due to the higher price of Ru compared with Fe, it is necessary to disperse Ru on a high-surface-area support in order to maximize the fraction of metal atoms participating in the reaction. Ru-based catalysts are substantially promoted by basic additives like alkali metal and alkaline earth compounds. Recent work has shown that Cs-promoted Ru/MgO [5–14], Ba-promoted Ru/MgO [9,12,15], Ba-promoted Ru/carbon [16-23], Ba-promoted Ru/BN [24], and Ba-promoted Ru/zeolite [5,6,9,25,26] are excellent catalysts for ammonia synthesis.

Ammonia synthesis over an active Ru catalyst appears to be nearly first order with respect to N_2 but can be severely inhibited by H_2. In fact, the H_2 reaction order is about -1 in many cases [5]. This contrasts with the positive H_2 reaction order found over conventional iron catalysts. Clearly, the inhibitory effect of dihydrogen suggests that Ru catalysts may be more effective with non-stoichiometric reactant mixtures, and the influence of total pressure on the rate is not straightforward. To optimize the Ru catalyst system, suitable promoters are needed not only to enhance the dissociative chemisorption of dinitrogen, but also to lower the inhibition by dihydrogen.

Aika and co-workers [27–33] explored the use of lanthanides (Sm_2O_3, La_2O_3 and CeO_2) as both supports and promoters of Ru catalysts. In particular, they found that inhibition of ammonia synthesis by dihydrogen was diminished when supported Ru was promoted by Sm_2O_3 [33]. A strong metal–support interaction of lanthanide promoters with Ru was invoked to explain the change in dihydrogen inhibition [33]. Detailed kinetic studies involving La- and Ce-promoted Ru were not presented.

In this communication, we describe the synthesis and reactivity of lanthanum-promoted Ru-zeolites as catalysts for ammonia synthesis. The effect of dihydrogen pressure on catalyst activity was explored. These novel catalysts were compared with Ba-promoted Ru/zeolite catalysts that were shown previously to be highly active for ammonia synthesis.

2. Experimental methods

2.1. Catalyst preparation

The preparation method for catalyst synthesis was similar to that used previously [6,26]. The starting material, NaX (UOP, Lot No. 07483-36), was exchanged three times with an aqueous solution of 1 M KNO_3 (Aldrich, 99%) for 24 h at room temperature. The resulting KX was washed with deionized distilled water and dried at 353 K overnight in air. Next, the ruthenium (~2 wt%) was added to the zeolite by ion exchange with an aqueous solution of $Ru(NH_3)_6Cl_3$ (Alfa Aesar) for 24 h. The catalyst was then washed with deionized distilled water until no chloride was present in the filtrate (confirmed with a silver nitrate test) and then dried in air

---

[*] To whom correspondence should be addressed.
[†] Current address: Chemical Engineering Department, Hampton University, Hampton, VA 23668, USA.

at 353 K overnight. The resulting Ru^{+3}/KX samples were then reduced. The sample was first dehydrated in vacuum at a rate of 0.5 K min^{-1} to 723 K and held at 723 K for 2 h (final pressure $<10^{-5}$ Torr). After cooling, the sample was then heated in 20 ml min^{-1} H_2 (palladium purified) at 1 K min^{-1} to 723 K, held at that temperature for 1 h, and cooled under vacuum (final pressure $<10^{-5}$ Torr). The reduced Ru/KX sample was then rehydrated slowly in a humidifier overnight. Next, the sample was ion exchanged three times with a 1 M aqueous solution of lanthanum acetate (Aldrich, 99%) for 24 h at room temperature. After washing with deionized distilled water, the Ru/LaX catalyst was dried in a 353 K oven overnight. In some cases, excess lanthanum was added past the ion-exchange limit by incipient wetness impregnation of a 0.25 M aqueous solution of $La(NO_3)_3$. These over-exchanged samples are designated as 10 La–Ru/LaX and 20 La–Ru/LaX to indicate the nominal loading of the La in the zeolite unit cell. For comparison, barium Ru–zeolite catalysts were included in this study. Details regarding their preparation and catalytic activity can be found in refs. [5,6,9,25,26].

2.2. Chemisorption of dihydrogen

A Coulter Omnisorp (100CX) was used to determine the fraction of Ru exposed on each of the catalysts. Before dihydrogen adsorption, the samples were heated under vacuum at 2 K min^{-1} to 673 K (final pressure $<10^{-6}$ Torr), and then reduced in flowing dihydrogen (BOC, 99.999% that was further purified with an OMI-2 purifier) for 30 min, evacuated again and then cooled under vacuum. The chemisorption was measured at room temperature. After chemisorption, the sample was evacuated at room temperature to remove weakly-held hydrogen and a subsequent backsorption isotherm was recorded.

2.3. Ammonia synthesis reactor

The system used for evaluation of the catalysts was a fixed-bed, single-pass, tubular reactor operating at 20.7 atm total pressure [5,6]. Approximately 1 g of catalyst (−40/+60 mesh) was loaded into the reactor. The reactant gases consisted of dinitrogen (BOC, 99.999%), dihydrogen (BOC, 99.999%) and sometimes helium (BOC, 99.999%). The appropriate gas composition was first passed over a bed of activated MnO_2/SiO_2 and molecular sieves to remove trace amounts of dioxygen and water before exposure to the catalyst. The products were analyzed by an online gas chromatograph with a thermal conductivity detector (TCD). The TCD peak areas were calibrated by equilibrating the ammonia synthesis reaction at 1 atm. A more detailed explanation of the calibration procedure is given in refs. [5,6].

Each of the catalysts was evaluated at 648, 673, 698 and 723 K. The ratio of dinitrogen to dihydrogen was changed from 1 : 3 to 3 : 1 (total flow rate of 400 ml min^{-1}) in order to find the orders of reaction for dinitrogen and dihydrogen. Varying the total flow rate of reactants from 100 to 400 ml min^{-1} tested the ammonia inhibition. Turnover frequencies were based on the production of ammonia per surface Ru atom counted by irreversible chemisorption of H_2.

3. Results and discussion

The results from elemental analysis (Galbraith Laboratories, Knoxville, TN, USA) and dihydrogen chemisorption are shown in table 1. The unit cell compositions are based on the assumption that 384 oxygen atoms are in each unit cell and the Si/Al ratio is constant for all samples. Protons and Na cations are assumed to balance the negative framework charge when necessary. The degree of La exchange was quite high, resulting in about 28 La^{+3} ions per unit cell. Impregnation of $La(NO_3)_3$ further increased the La loading by 14 and 30 occluded La^{+3} ions per unit cell, for 10 La–Ru/LaX and 20 La–Ru/LaX respectively. The chemisorption results indicate that most of the ruthenium in these samples was exposed. However, the 10 La–Ru/LaX catalyst revealed the lowest dihydrogen adsorption capacity of the samples. Some migration of ruthenium to the outside of the pores and/or partial collapse of the zeolite framework might explain this result. However, it

Table 1
Results from elemental analysis and dihydrogen chemisorption

Catalyst	Ru (wt%)	H/Ru_{total}	H/Ru_{irrev}	Unit cell composition [a]
Ru/LaX	1.87	0.85	0.48	$Ru_{4.2}K_{9.0}La_{27.6}Al_{89.7}Si_{102.3}O_{384}$
Ru/BaX [b]	2.02	0.85	0.42	$Ru_{3.8}K_{9.6}Ba_{31.4}Al_{84.5}Si_{107.5}O_{384}$
10 La–Ru/LaX	1.59	0.44	0.25	$Ru_{4.0}K_{9.0}La_{41.6}Al_{89.7}Si_{102.3}O_{384}$
20 La–Ru/LaX	1.55	0.57	0.34	$Ru_{4.8}K_{9.0}La_{57.2}Al_{89.7}Si_{102.3}O_{384}$
20 Ba–Ru/BaX [c]	1.36	0.89	0.45	$Ru_{3.4}K_{10.7}Ba_{52.3}Al_{87.6}Si_{104.4}O_{384}$

[a] Na and H atoms are needed in order to balance the negative charge of the zeolite framework.

[b] Sample prepared in our earlier work, where it is labeled Ru/BaX-1 [5].

[c] Sample prepared in our earlier work, where it is labeled Ru/BaX-4 [5].

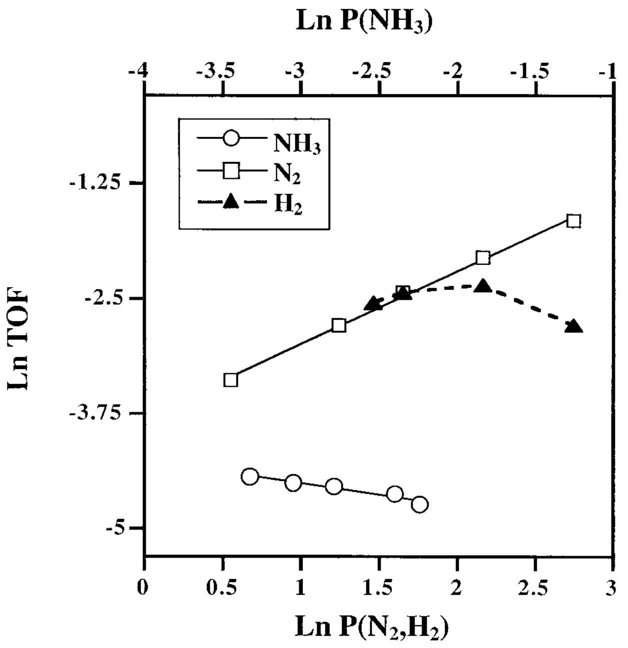

Figure 1. Dependence of the turnover frequency (s^{-1}) on the partial pressures (atm) of N_2, H_2 and NH_3 at 20.7 atm total pressure and 648 K over 10 La–Ru/LaX. The total flow rate was varied from 100 ml min^{-1} to 400 ml min^{-1} in order to determine the order in NH_3 at stoichiometric reaction conditions. Each reactant partial pressure was varied while holding the other constant at 5.2 atm.

should be noted that H_2 chemisorption can underestimate the fraction of Ru exposed when compared with results from CO and O_2 chemisorption [12].

Figure 1 shows a representative plot of the ammonia synthesis rate as a function of N_2, H_2 and NH_3 pressure. The positive order in N_2 and weak negative order in NH_3 are apparent from the figure. The striking result of this work is the dependence of the rate on H_2 pressure. The results illustrated in figure 1 indicate a very weak dependence of the rate on H_2. The order in H_2 is essentially zero at low H_2 pressures and slightly negative at high pressures. Table 2 summarizes the apparent orders of reaction measured over the La-promoted catalysts and analogous Ba-promoted catalysts. The very weak dependence of the rate on H_2 pressure was observed over all of the La-promoted catalysts and contrasts sharply with the -1 order in H_2 seen over Ba-promoted catalysts. Strong inhibition of ammonia synthesis by dihydrogen was also found on a highly active Cs-promoted Ru/MgO catalyst (order ~ -1) [5]. The order with respect to N_2 also appears to be slightly lower on the La-promoted catalysts compared with the Ba-promoted catalysts. However, the magnitude of the change is much less than that observed with H_2.

Table 2
Effect of La promoter on the orders of reaction at 20.7 atm[a]

Catalyst	Temperature (K)	α (N_2)	β (H_2)[d]	γ (NH_3)
Ru/LaX	673	0.68	−0.16	−0.19
Ru/LaX	648	0.69	−0.46	−0.07
10 La–Ru/LaX	648	0.79	−0.19	−0.25
20 La–Ru/LaX	648	0.81	−0.24	−0.09
Ru/BaX[b]	673	0.74	−0.92	−0.05
20 Ba–Ru/BaX[c]	623	0.93	−0.96	−0.15

[a] Where the reaction rate expression is $r = kP_{N_2}^{\alpha}P_{H_2}^{\beta}P_{NH_3}^{\gamma}$.
[b] Sample prepared in our earlier work, where it is labeled Ru/BaX-1 [5].
[c] Sample prepared in our earlier work, where it is labeled Ru/BaX-4 [5].
[d] Results presented here are for a linear correlation of the data. In some cases the R^2 value was rather low, indicating a poor fit. Figure 1 shows why.

Table 3
Effect of La and Ba promoters on the TOF and E_a of ammonia synthesis at 20.7 atm and stoichiometric feed

Catalyst	TOF c.f.[c] (10^{-4} s^{-1})	TOF c.p.[d] (10^{-4} s^{-1})	E_a[e] (kJ mol^{-1})
Ru/LaX	48	93	105
10 La–Ru/LaX	250	1850	102
20 La–Ru/LaX	196	940	99
Ru/BaX[a]	28.5	27.5	173
20 Ba–Ru/BaX[b]	197	252	151

[a] Sample prepared in our previous work where it is labeled Ru/BaX-1 [5].
[b] Sample prepared in our previous work where it is labeled Ru/BaX-4 [5].
[c] Turnover frequency measured at constant flow rate (400 cm^3 min^{-1}) and 673 K.
[d] Turnover frequency measured at constant ammonia pressure (P_{NH_3} = 0.001 atm) and 673 K.
[e] Apparent activation energy calculated at constant ammonia pressure (P_{NH_3} = 0.001 atm).

Addition of occluded La improved the catalytic activity of Ru/LaX by almost an order of magnitude. Table 3 summarizes the observed turnover frequencies measured at 673 K in conditions of constant flow (measured) and constant ammonia pressure (calculated). The Ru/LaX catalyst was substantially more active than Ru/BaX, illustrating the important role that the charge-balancing cation plays in the catalyst. More importantly, addition of La beyond ion-exchange capacity resulted in a catalyst (10 La–Ru/LaX) that was even more active than the highly promoted 20 Ba–Ru/BaX catalyst (this catalyst was the most active of our Ba-promoted Ru/BaX catalysts). Addition of more occluded La to form 20 La–Ru/LaX did not improve the catalyst but actually decreased its activity slightly. Apparently there is an optimal loading of about 10 occluded La atoms per unit cell. The temperature dependence of the observed rate is summarized in the Arrhenius-type plot given in figure 2. The apparent activation energies for La-promoted catalysts were about 100 kJ/mol, which is consistent with other Ru-based catalysts [5,11,27] but is substantially lower than that associated with Ba-promoted zeolites.

The results reported in this study for La-promoted Ru/zeolites compared with Ba-promoted Ru/zeolites are reminiscent of those reported earlier by Kadowaki and Aika [33]. For example, Kadowaki and Aika use the N_2 isotopic exchange reaction (IER) and the

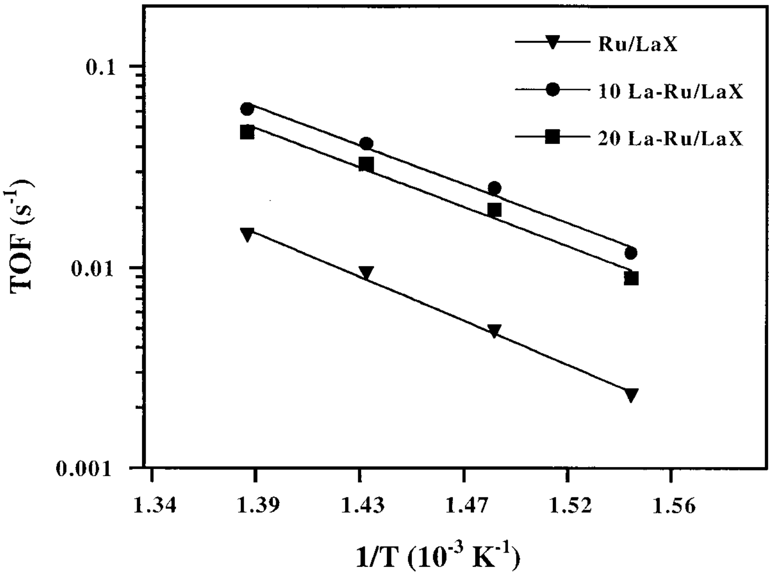

Figure 2. Effect of excess lanthanum loading on the turnover frequency for ammonia synthesis at 20.7 atm ($N_2:H_2 = 1:3$, constant flow rate of 400 $cm^3\ min^{-1}$) over Ru zeolites.

ammonia synthesis reaction to probe Ru catalysts promoted with Sm_2O_3 and CsOH [33]. They found that the ammonia synthesis rate on CsOH-promoted Ru was retarded by the presence of H_2 (presumably due to competitive adsorption with N_2) since it was lower than the N_2 isotopic exchange rate. The opposite result was found over an Sm_2O_3-promoted catalyst. Kadowaki and Aika speculate that lanthanide oxides interact strongly with supported Ru and weaken the adsorption of hydrogen atoms.

Fleish *et al.* [34] used XPS to study the metal–support interaction of Pd with La_2O_3. They found that the Pd $3d_{5/2}$ binding energy of Pd/La_2O_3 was shifted below that of Pd metal, indicating significant charge redistribution in the supported sample due to interaction with lanthana. Ongoing work in our lab is pursuing the positive role of lanthanide cations on supported Ru catalysts for ammonia synthesis.

4. Conclusions

Zeolite-supported ruthenium catalysts containing La are more active in ammonia synthesis than analogous samples containing occluded Ba. However, inhibition of the reaction by dihydrogen is greatly reduced by the presence of lanthanum.

Acknowledgments

This work was supported by NSF grant CTS9729812. S.L.A. acknowledges support of a separate NSF grant (CTS0000485) that was subcontracted by Hampton University to the University of Virginia.

References

[1] A. Ozaki, K.-I. Aika, A. Furata and A. Okagami, US Patent 3,770,658 (1973).
[2] K.-I. Aika, H. Hori and A. Ozaki, J. Catal. 27 (1972) 424.
[3] Chementator, Chem. Eng. 3 (1993) 19.
[4] T.A. Czuppon, S.A. Knez, R.V. Schneider III and G. Worobets, Ammonia Plant Safety and Related Facilities 34 (1994) 236.
[5] T. Becue, R.J. Davis and J.M. Garces, J. Catal. 179 (1998) 129.
[6] B.C. McClaine, T. Becue, C. Lock and R.J. Davis, J. Mol. Catal. A: Chemistry 163 (2000) 105.
[7] K. Aika, M. Kumasaka, T. Oma, O. Kato, H. Matsuda, N. Watanabe, K. Yamazaki, A. Ozaki and T. Onishi, Appl. Catal. 28 (1986) 57.
[8] K. Aika, A. Ohya, A. Ozaki, Y. Inoue and I. Yasumori, J. Catal. 92 (1985) 305.
[9] C.T. Fishel, R.J. Davis and J.M. Garces, J. Catal. 163 (1996) 148.
[10] Y. Izumi, M. Hoshikawa and K.-I. Aika, Bull. Chem. Soc. Jpn. 67 (1994) 3191.
[11] K.-I. Aika, T. Takano and S.J. Murata, Catal. 136 (1992) 126.
[12] D. Szmigiel, H. Bielawa, M. Kurtz, O. Hinrichsen, M. Muhler, W. Raróg, S. Jodzis, Z. Kowalczyk, L. Znak and J.J. Zieliński, Catal. 205 (2002) 205.
[13] O. Hinrichsen, F. Rosowski, A. Hornung, M. Muhler and G. Ertl, J. Catal. 165 (1997) 33.
[14] O. Hinrichsen, F. Rosowski, M. Muhler and G. Ertl, Chem. Eng. Sci. 51 (1996) 1683.
[15] H. Bielawa, O. Hinrichsen, A. Birkner and M. Muhler, Angew. Chem. Int. Ed. 40(6) (2001) 1061.
[16] K.-I. Aika, T. Kawahara, S. Murata and T. Onishi, Bull. Chem. Soc. Jpn. 63 (1990) 1221.
[17] Z. Zhong and K.-I. Aika, Inorg. Chim. Acta 280 (1998) 183.
[18] Z. Zhong and K.-I. Aika, Chem. Commun. (1997) 1223.
[19] I. Rossetti, N. Pernicone and L. Forni, App. Catal. A: General 208 (2001) 271.
[20] Z. Zhong and K.-I. Aika, J. Catal. 173 (1998) 535.
[21] L. Forni, D. Molinari, I. Rossetti and N. Pernicone, Appl. Catal. A: General 185 (1999) 269.
[22] C. Liang, Z. Wei, Q. Xin and C. Li, Appl. Catal. A: General 208 (2001) 193.
[23] Z. Kowalczyk, S. Jodzis, W. Raróg, J. Zieliński and J. Pielaszek, Appl. Catal. A: General 173 (1998) 153.

[24] C.J.H. Jacobsen, J. Catal. 200 (2001) 1.
[25] C.T. Fishel, R.J. Davis and J.M. Garces, Chem. Commun. (1996) 649.
[26] B.C. McClaine, S.E. Siporin and R.J. Davis, J. Phys. Chem. B. 105(31) (2001) 7525.
[27] Y. Niwa and K.-I. Aika, Res. Chem. Intermed. 24(5) (1998) 593.
[28] Y. Niwa and K.-I. Aika, J. Catal. 162 (1996) 138.
[29] S. Murata and K.-I. Aika, J. Catal. 136 (1992) 118.
[30] S. Murata, K.-I. Aika and T. Onishi, Chem. Lett. (1990) 1067.
[31] Y. Niwa and K.-I. Aika, Chem. Lett. (1996) 3.
[32] Y. Izumi, Y. Iwata and K.-I. Aika, J. Phys. Chem. 100 (1996) 9421.
[33] Y. Kadowaki and K.-I. Aika, J. Catal. 161 (1996) 178.
[34] T.H. Fleisch, R.F. Hicks and A.T. Bell, J. Catal. 87 (1984) 398.