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Isotopic transient analysis of ammonia synthesis over Ba or Cs-promoted Ru/carbon catalysts

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The effects of Cs or Ba promoters on the global and intrinsic turnover frequency of ammonia synthesis over ruthenium supported on carbon (9.1 wt% Ru) were examined at 3 atm and stoichiometric conditions by steady state and isotopic transient measurements at 573 K. Although the global turnover frequency based on total surface Ru atoms was nearly independent of promoter, Cs was more effective than Ba at promoting the intrinsic turnover frequency determined by the isotopic switching experiment. The similarity of the global turnover frequency over the two samples resulted from the coverage of nitrogen-containing intermediates being greater on the Ba-promoted catalyst. The promoters presumably affect the global activity of ammonia synthesis by modifying both the inhibition by dihydrogen and the activation barrier for dinitrogen dissociation.

KEY WORDS: carbon ruthenium; promotion of isotopic transient analysis; ammonia synthesis; cesium; barium.

1. Introduction

The Haber–Bosch process for ammonia synthesis has been considered a major breakthrough for the chemical industry. However, the unfavorable reaction kinetics over the iron-based catalyst used in the process necessitates large amounts of energy to achieve commercial yields. Thus, new catalysts that allow for operation at milder conditions are highly desired. Ruthenium-based materials are thought to be the next generation catalysts for ammonia synthesis, but the relatively high cost of Ru compared to Fe demands a high dispersion of the Ru on a suitable support.

A carbon-supported Ru catalyst was first used industrially in British Columbia in the early 1990's [1]. It allowed for less severe operating conditions compared to those normally associated with the iron catalyst, resulting in lower capital costs and a significant reduction of energy consumption [1]. In addition to the support, another critical component of an active Ru catalyst is a basic promoter such as an alkali or alkaline earth metal oxide or hydroxide.

Basic promoters have been shown to increase the global activity of Ru catalysts [2–38, 39]. The effectiveness of promoters generally scales with basicity, with alkali metal oxides or hydroxides usually being the best. It was therefore interesting to find that alkaline-earth and lanthanide promoters such as Ba and La oxides or hydroxides can be effective promoters for Ru [2,4–8,10,14–18,20,21,23,24,26–38].

The role of alkali or alkaline earth promoters on Ru ammonia synthesis catalysts is still not well understood. One plausible explanation is that promoters reduce the surface coverage of nitrogen-containing species, freeing sites for dinitrogen dissociation [5,40]. Alternatively, others suggest that the basic promoter and/or support donates electrons to surface Ru atoms, facilitating the dissociative adsorption of dinitrogen, which is speculated to be the rate-determining step [5,6,15,24,25,36–38, 40].

Cesium has been postulated to be an electronic promoter that increases the intrinsic activity of the Ru catalyst [5,6,21,24,26,28,36,38,39]. Isotopic transient analysis, temperature-programmed reaction and X-ray photoelectron spectroscopy of Cs promoted Ru catalysts on carbon, MgO, and zeolite X all support that proposition. Conversely, barium has been claimed to be both a structural promoter [5,14,21,28] and an electronic promoter [24,26,27,36–38]. A structural promoter is one that increases the concentration of active sites by facilitating a structural reorganization of the surface. Evidently, promotion of ammonia synthesis catalysts by bases is not yet understood.

In a recently submitted paper, Siporin and Davis examined a series of promoted Ru/MgO (~2 wt% Ru) catalysts with isotopic transient analysis under 3 atm total pressure and various ratios of dihydrogen to dinitrogen [36]. The presence of Cs, Ba or La promoter increased the intrinsic turnover frequency based on the coverage of nitrogen-containing intermediates, with Cs being the most effective. Steady state, global measurements revealed that Cs–Ru/MgO was strongly inhibited by dihydrogen whereas Ba–Ru/MgO and La–Ru/MgO were weakly inhibited by the reactant.

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However, isotopic transient measurements showed that the intrinsic turnover frequency was a weak positive function of dihydrogen pressure for all of the promoters studied. In addition, the coverage of nitrogen-containing intermediates was greater on Ba and La promoted catalysts than on Cs–Ru/MgO at stoichiometric reaction conditions. Therefore, the global activity of the promoted Ru/MgO catalyst appears to be a result of both a modification in the competitive inhibition by dihydrogen and an enhancement of dinitrogen dissociation.

Previous work on Ba and Cs-promoted Ru/C catalysts has revealed significant differences between them [21,39]. For example, three times more Cs is needed to get the excellent activity of a Ba-promoted catalyst [39]. Moreover, the rate over a Ba-promoted catalyst is more sensitive to total pressure and ammonia content compared to a Cs-promoted material [21]. Two explanations have been given for these differences in behavior. Either the role of the promoters is different (structural versus electronic) or the location of the promoters is different (metal versus support) [39]. The purpose of this work was to compare the intrinsic kinetics determined from isotopic transient analysis of ammonia synthesis on Cs–Ru/C and Ba–Ru/C catalysts to help elucidate the role of the basic promoters in this system.

2. Experimental methods

2.1. Catalyst preparation

A detailed description of the catalyst preparation was presented previously [21]. Briefly, a raw activated carbon (RO 08, Norit) – a precursor of the graphitized support, was heated at 2173 K (He, 400 Pa) [41] followed by partial gasification in a CO_2 stream ($CO_2 + C = 2CO$) up to about 20% mass loss. The support exhibited a turbostratic structure as shown by XRD and a well-developed texture (BET surface area = 330 $m^2\ g^{-1}$ Hg surface area = 110 $m^2\ g^{-1}$) [21].

Ruthenium chloride ($RuCl_3 \cdot 0.5H_2O$, Aldrich), was deposited onto the carbon surface by the incipient wetness impregnation from acetone solution followed by drying in air. Subsequently, the Ru/C sample (9.1 wt% Ru) was reduced in flowing dihydrogen first at 423 K for 16 h and then at 623 K for another 16 h and then passivated. The promoter precursors ($Ba(NO_3)_2$, $CsNO_3$) were deposited by impregnation from aqueous solutions. Each catalyst was crushed and sieved to give particles between 0.2 and 0.6 mm.

2.2. Catalyst characterization

The fraction of Ru exposed on each of the catalysts was determined by chemisorption of dihydrogen or dioxygen. Global turnover frequencies (TOF_{Glob}) and surface coverages of nitrogen-containing species (θ_{NH_x}) were based on surface Ru atoms counted by chemisorption. Surface Ru atoms were determined by the amount of adsorbed H atoms or O atoms assuming a H/Ru_{surf} ratio of unity or an O/Ru_{surf} ratio of 1.1, respectively.

2.3. Isotopic transient measurements during ammonia synthesis

Approximately 0.04 g of catalyst were loaded into a 4 mm inside diameter quartz tubular reactor. Quartz wool was used to hold the sample in place. Each sample was pretreated at 3 atm using a stoichiometric ratio of dihydrogen (99.999%, BOC gases; palladium purified, Matheson 837IV) and dinitrogen (99.999%, BOC gases, further purified with OMI-2 filter) at a total flow rate of 100 mL min^{-1}. After heating the catalyst to 673 K at a rate of 2 K min^{-1}, it was pretreated at that temperature for 24 h. The Cs promoted catalyst (Cs–Ru/C) was further treated at 703 K for another 24 h whereas the Ba-promoted catalyst (Ba–Ru/C) was further treated at 743 K for another 48 h before isotopic transient analysis at 573 K.

A schematic representation of the apparatus can be found in prior work [6,24] as well as a detailed description of the experimental method [36]. Briefly, a step change in isotopically labeled dinitrogen was accomplished by switching between a stream of normal dinitrogen ($^{14}N_2$/Ar) and $^{15}N_2$ (Isotec, 98+%, further purified with OMI-2 filter). The normal dinitrogen (BOC Gases, further purified with OMI-2 filter) contained 1.06% Ar in order to monitor the gas-phase holdup of the system. However, this amount of Ar was not large enough to disturb the steady state of the system. Backpressure regulators ensured that all reactant streams and vent lines were maintained at 3 atm.

A Balzers–Pfieffer Prisma 200 amu mass spectrometer monitored the concentrations of $^{14}NH_2$, $^{14}NH_3$, $^{15}NH_3$, $^{14}N_2$, $^{15}N_2$ and Ar (m/e = 16, 17, 18, 28, 30, and 40, respectively) continuously. The concentration of $^{15}NH_3$ (m/e = 18) was used to calculate the transient responses. Multiple forward switches ($^{14}N_2/Ar \rightarrow {}^{15}N_2$) and reverse switches ($^{15}N_2 \rightarrow {}^{14}N_2/Ar$) were recorded at each condition. Operating the catalyst at thermodynamic equilibrium allowed the mass spectrometer to be calibrated for ammonia in each run.

Each catalyst was evaluated at 573 K, 3 atm, a total flow rate of 40 mL min^{-1}, and $N_2{:}H_2 = 1{:}3$. In addition, the effect of interparticle readsorption of ammonia was determined by varying the total flow rate between 20 and 60 mL min^{-1} for Cs–Ru/C at 573 K. To avoid overestimation of the residence time of nitrogen-containing species, all intrinsic parameters were determined at conditions that were far from equilibrium (>98%).

Table 1
Properties of carbon-supported Ru catalysts [21]

Catalyst	Ru wt%	Promoter wt%	Mol promoter: Mol Ru	H/Ru_{tot}	O/Ru_{tot}
Ru/C	9.1	–	–	–	0.62
Cs–Ru/C	5.98	22.8	2.9	0.48	–
Ba–Ru/C	7.52	7.2	0.7	0.44	–

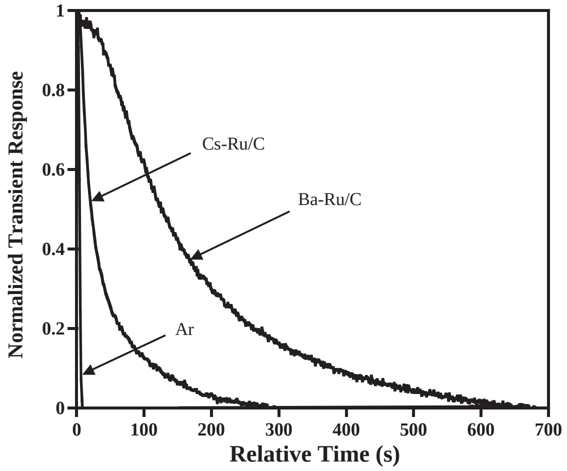

Figure 1. Normalized transients of $^{15}NH_3$ and Ar at 573 K and 40 mL min^{-1} for Cs and Ba-promoted Ru/C.

3. Results

Table 1 summarizes the properties of the catalysts [21]. The procedures used for dihydrogen and dioxygen chemisorption are provided elsewhere [42].

A typical set of isotopic transients for ammonia following a switch between $^{14}N_2/Ar$ and $^{15}N_2$ can be found in figure 1. In addition, this figure shows the Ar transient. The average residence time of surface intermediates leading to ammonia (τ_{cat}) is calculated by integrating the area between the normalized transients,

$$\tau_{cat} = \int_0^\infty [F_{cat^{14}NH_3}(t) - F_{blank_{NH_3}}(t)]dt \tag{1}$$

$$\tau_{cat} = \int_0^\infty [1 - F_{cat^{15}NH_3}(t) - F_{blank_{NH_3}}(t)]dt \tag{2}$$

where, $F_{cat^{15}NH_3}$ and $F_{blank^{14}NH_3}$, are the normalized transient responses for $^{15}NH_3$ and the blank transient that was collected following a step change from $NH_3/N_2/H_2$ to N_2/H_2 under similar conditions without catalyst present, respectively. Both the $^{14}NH_3$ transient response in an empty reactor and the Ar transient response were significantly quicker than the $^{15}NH_3$ transient response in the presence of catalyst. The number of surface intermediates per gram of catalyst, N_{NH_3}, was calculated using the following steady-state mass balance:

$$N_{NH_3} = \tau_{cat} R_{NH_3} \tag{3}$$

where R_{NH_3} is the steady-state rate of ammonia synthesis per gram of catalyst. The coverage of nitrogen-containing species on the surface of the catalyst can then be calculated by dividing N_{NH_3} by the number of surface Ru atoms per gram of catalyst determined by chemisorption. Finally, the intrinsic turnover frequency is defined as

$$\mathrm{TOF}_{intr} = 1/\tau_{cat} \tag{4}$$

This relationship assumes that ammonia synthesis can be described by the expression

$$\text{rate} = k\theta_{NH_x} \tag{5}$$

where θ_{NH_x} is the coverage of nitrogen-containing species ($x = 0$–3) and k is a pseudo-first order rate constant [43].

The calculation of TOF_{intr} does not require knowledge of the coverage of nitrogen-containing species or the number of active sites. It is solely the inverse of the area underneath the isotopic transient of ammonia. Therefore, TOF_{intr} is a better measure of the turnover of the surface. In contrast, TOF_{Glob} is calculated from the steady-state rate of ammonia synthesis divided by the number of sites that are titrated by chemisorption.

It is possible that ammonia can readsorb on catalytically active and inactive sites before leaving the reactor, which will cause an overestimation of τ_{cat} and θ_{NH_x}. However, the global rate of ammonia synthesis, R_{NH_3}, is unaffected by the overestimation. In our previous work, we showed that for a Cs-promoted Ru/MgO catalyst as well as a La-promoted Ru/MgO catalyst the effect of ammonia readsorption was negligible [6,36]. However, ammonia readsorption on a Ba-promoted zeolite X supported Ru catalyst was severe [24]. Therefore, the influence of ammonia readsorption was re-examined in this study. The total flow rate was varied between 20 and 60 mL min^{-1} over the Cs–Ru/C at 573 K, 3 atm, and stoichiometric conditions. The results are summarized in table 2 and in figure 2. Increasing the total flow rate by a factor of three changed τ_{cat} by approximately 20%. The effect of ammonia readsorption on the observed residence time of surface intermediates was negligible. Therefore, it is assumed that τ_{cat} is a good measure of the residence time of nitrogen-containing species on all catalyst samples studied here.

The global turnover frequency, TOF_{Glob}, determined at 3 atm, 573 K and stoichiometric conditions is reported for each catalyst in table 2. This turnover frequency was based on the ammonia partial pressure at the reactor outlet and the number of Ru sites on the catalyst titrated by chemisorption. Comparison of the global turnover frequencies (at a total flow rate of 40 mL min^{-1}) revealed that promotion of Ru/C by Ba or Cs increased the activity by a factor of 80. The global activity of Ba–Ru/C and Cs–Ru/C was similar at these experimental conditions.

Table 2
Isotopic transient results at 573 K, 3 atm, and N_2:H_2 = 1:3

Catalyst	Total flow rate (ml min^{-1})	P_{NH_3} (atm)	TOF_{Glob} (10^{-4} s^{-1})	τ_{cat} (s)	θ_{NH_x}[c]	TOF^{b}_{intr} (10^{-4} s^{-1})
Ru/C	40	0.000045	0.2[a]	–	–	–
Ba–Ru/C	40	0.00211	15[c]	109 ± 12.0	0.16	90
Cs–Ru/C	40	0.00164	13[c]	27 ± 3.7	0.04	370
Cs–Ru/C	20	0.00363	15[c]	21 ± 2.2	0.03	480
Cs–Ru/C	60	0.00136	16[c]	25 ± 2.7	0.04	400

[a] Based on total oxygen chemisorption.
[b] $TOF_{intr} = 1/\tau_{cat}$.
[c] Based on total hydrogen chemisorption.

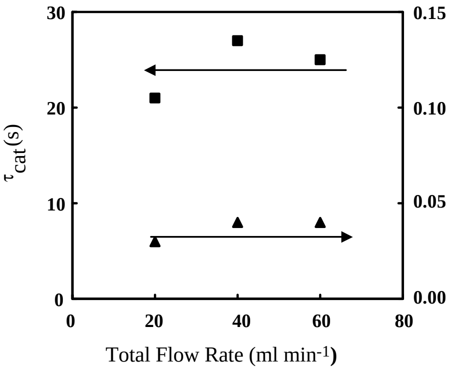

Figure 2. Effect of total flow rate on the intrinsic kinetic parameters over Cs–Ru/C.

In contrast, the kinetic parameters determined by isotopic transient analysis were dependent on the promoter. The intrinsic turnover frequency over Cs–Ru/C was a factor of four greater than Ba–Ru/C. Conversely, the surface coverage of nitrogen-containing species, θ_{NH_x}, was a factor of 4 greater on the Ba promoted catalyst compared to the Cs-promoted sample. The surface coverage on both samples was very low. Interestingly, only a small fraction of Ru atoms is believed to be involved in the rate-limiting step for ammonia synthesis (dinitrogen dissociation) [44]. Because of the very low activity of unpromoted Ru/C, quantitative measurements of the intrinsic turnover frequency could not be evaluated.

4. Discussion

Ammonia synthesis catalysts should be studied under working conditions (i.e. elevated temperatures and pressures) because the reaction is highly structure sensitive [44] and the surface structure can be dependent on reaction conditions. Therefore, every hydrogen atom that adsorbs on Ru is not necessarily an active site and chemisorption will therefore over count the number of active sites. The isotopic transient technique is very powerful because it allows for characterization of a catalyst surface under working conditions. Ammonia synthesis catalyzed by both Fe [45] and Ru [6,24,36,46] has been studied previously with isotopic transient analysis. Recently, Shannon and Goodwin reviewed the theory behind this technique [43].

Three times the amount (wt%) of Cs compared to Ba gave a catalyst with a similar global turnover frequency at 3 atm. This is consistent with previous results obtained on a similar set of catalysts tested at 89 atm and in a different laboratory [39].

Results presented in table 2 illustrate that the Cs-promoted catalyst is four times more intrinsically active (TOF_{intr}) than Ba–Ru/C, which seems to suggest that activity parallels promoter basicity and that promotion is electronic in nature. We reported the same conclusion in a previous paper that compared an unpromoted Ru/SiO_2 to a Cs-promoted Ru/MgO catalyst [36].

Since the coverage of nitrogen-containing species was four times greater over Ba–Ru/C than Cs–Ru/C, there appears to be a trade-off between NH_x coverage and intrinsic activity of the promoted samples. A similar trade-off was observed earlier for Ba, La, and Cs promoted Ru on MgO [36]. The intrinsic turnover frequency of Ba–Ru/MgO and La–Ru/MgO was less than half that of Cs–Ru/MgO, but the θ_{NH_x} was greater by a factor of 2 or 3 on the former catalysts. In addition, the effect of dihydrogen pressure the intrinsic and global kinetics over magnesium supported catalysts was tested by varying the dihydrogen partial pressure at constant flow rate and total pressure. When based on the global turnover frequency, the cesium promoted catalyst was strongly inhibited by dihydrogen, with an order of reaction ($\alpha_{H_2} = -0.87$). However, promotion by Ba or La decreased the inhibition by H_2 to $\alpha_{H_2} = -0.39$ and -0.07, respectively. Conversely, the order of reaction with respect to H_2 is *slightly positive* when based on TOF_{intr} regardless of the promoter. The observed inhibition by H_2 on the global rate measurements is entirely the result of a lower coverage of NH_x intermediates at higher H_2 pressures.

For the current set of materials, promoted Ru/C catalysts are known to exhibit different dependencies on total pressure and ammonia content [21]. The ammonia synthesis reaction is generally considered to be first-order in N_2 and weakly inhibited by ammonia. However, the inhibition of the rate by H_2 is a strong function of the promoter. The small influence of total pressure on the rate of Cs–Ru/C suggests that the order in dihydrogen is nearly −1. The stronger influence of total pressure on the rate over Ba–Ru/C likely indicates weaker inhibition by dihydrogen. Thus, the results reported in this communication are entirely consistent with those found previously for Ba, La or Cs-promoted Ru/MgO. Although Cs appears to be a better promoter of the intrinsic ammonia synthesis rate, a change in global dihydrogen inhibition with Ba promotion compensates for its weaker promotional effect on intrinsic activity.

It should be mentioned that the intrinsic activity of Cs-promoted Ru/C was about $0.04\ s^{-1}$ at 573 K (table 2) whereas a Cs-promoted Ru/MgO had an activity of $0.08\ s^{-1}$ at the higher temperature of 623 K and identical partial pressures [36]. Evidently, the carbon-supported catalyst in this work is intrinsically more active than the magnesia supported catalyst in Ref. [36].

5. Conclusions

Whereas the intrinsic turnover frequency was four times greater over Cs–Ru/C compared to Ba–Ru/C, the surface coverage of nitrogen-containing intermediates was four times greater over the Ba-promoted sample. Thus, the global activity of the promoted catalysts was similar. Promotion of Ru by these bases can be explained in terms of stronger dihydrogen inhibition and lower activation barrier for dinitrogen dissociation over the most basic catalysts containing Cs.

Acknowledgments

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