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Research Note

# Ammonia decomposition over the carbon-based ruthenium catalyst promoted with barium or cesium

Wioletta Raróg-Pilecka,[a] Dariusz Szmigiel,[a] Zbigniew Kowalczyk,[a,*]
Sławomir Jodzis,[a] and Jerzy Zielinski [b]

[a] *Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland*
[b] *Institute of Physical Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*

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**Abstract**

Carbon-supported ruthenium catalysts promoted with Ba or Cs were studied in ammonia decomposition. Under the experimental conditions ($p = 1$ bar, $H_2$:$N_2$ = 3:1, 5–50% $NH_3$, 370–400 °C), the reaction rates over Cs–Ru/carbon were found to be higher than those over Ba–Ru/carbon, the difference being larger for the high dispersion samples. The effect of the ruthenium precursor (carbonyl, chloride) proved to be unessential for the activity. At 20% $NH_3$ (400 °C), TOF of $NH_3$ decomposition over Cs–Ru/carbon was about $3 \times 10^2$ times higher than for K–Fe/carbon, both based on $H_2$ chemisorption. The apparent activation energies of 134 and 158 kJ/mol were determined for Cs–Ru/carbon and Ba–Ru/carbon, respectively. The temperature-programmed desorption studies revealed that the amount of nitrogen desorbed from Ba–Ru/carbon was much smaller and the peak position was shifted to higher temperatures when compared to Cs–Ru/carbon. The promoting mechanism of both Ba and Cs is discussed.

*Keywords:* Ammonia decomposition; Nitrogen desorption; Ruthenium catalyst; Carbon support; Barium and cesium promoters

## 1. Introduction

The catalytic reaction of ammonia decomposition is performed for generation of the hydrogen–nitrogen mixture used mainly, instead of hydrogen, as a reducing atmosphere in steel and electronic industries. Since residual ammonia can easily be removed from the $H_2 + N_2$ stream, the process of $NH_3$ decomposition is also considered to be an ideal source of $CO_x$-free hydrogen for power proton exchange membrane fuel cells [1,2]. Consequently, a variety of supported metal catalysts have been studied recently in $NH_3$ decomposition with respect to fuel cell applications [1]. Generally, however, including the present studies, the interaction of ammonia with metal surfaces has been investigated for a deeper insight into the industrially important ammonia synthesis catalysts [3–7].

Two types of the catalytic systems are used, at present, in large-scale installations of ammonia synthesis: the conventional, magnetite-based catalyst (fused iron) and novel, ruthenium catalyst supported on carbon [8]. Despite intensive studies, the ruthenium catalysts seem to be poorly understood. The unpromoted Ru/C systems are known to be rather inactive in $NH_3$ synthesis [9–11] but they become very active after the addition of promoters (Ba, Cs, K) [9–15]. The Ba– and Cs–Ru/carbon systems proved to be significantly more active in the $NH_3$ synthesis than the traditional, fused iron catalyst [14].

Various kinetic studies such as nitrogen adsorption [16] and desorption [17], temperature-programmed surface reaction between hydrogen and preadsorbed nitrogen [17–19], or isotopic transient kinetic studies [20] have been carried out to determine the role of the promoters in different ruthenium catalysts for ammonia synthesis. This work presents the effect of barium and cesium in Ru/carbon on the ammonia decomposition kinetics. Since nitrogen desorption is believed to be the rate-determining step of $NH_3$ decomposition, the kinetic tests were supplemented with the $N_2$ desorption experiments.

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[*] Corresponding author.
*E-mail address:* zbyko@chemix.ch.pw.edu.pl (Z. Kowalczyk).

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## 2. Experimental

### 2.1. The Ru catalysts

Two carbons of different texture, marked throughout the text as A and B, were used as supports for the ruthenium catalysts preparation, both derived from commercial, raw active carbon RO 08 (Norit Company). Carbon A was obtained by the high-temperature treatment of the commercial RO 08 product in a helium atmosphere at 1900 °C [21]. For B, the A material was gasified partly (20% mass loss) in flowing carbon dioxide at 840 °C, followed by cooling in argon [14].

Ruthenium chloride ($RuCl_3 \cdot 0.5H_2O$) or ruthenium carbonyl ($Ru_3(CO)_{12}$)—the precursors of the active phase—were introduced onto the carbon surface by impregnation, using acetone and THF as solvents, respectively. Subsequently, the samples (9.1 wt% Ru) were reduced in hydrogen and passivated. The promoters (Ba, Cs) were introduced to the Ru/C systems by impregnation from aqueous solutions ($Ba(NO_3)_2$, $CsNO_3$) [14]. The activation of the samples was performed in situ, in the ammonia decomposition reactor. The characteristics of the catalysts prepared are presented in Table 1.

### 2.2. Activity studies of $NH_3$ decomposition: The $N_2$ TPD experiments

The activity measurements of $NH_3$ decomposition were carried out in a differential, quartz microreactor (4 mm internal diameter) fed with a stoichiometric hydrogen–nitrogen–ammonia mixture of controlled ammonia content (5–50%) and of constant flow rate (0.5 $dm^3$ [STP]/min) [22]. The gas mixture was prepared by adding high-purity ammonia (99.9995%, Linde Gas) to the stoichiometric, ammonia-free $H_2 + N_2$ stream (purity > 99.99995%). The $NH_3$–$H_2$–$N_2$ mixture, thus prepared, was additionally purified by passing through a guard column.

Small samples of the catalysts (typically 10–30 mg, 0.2–0.3 mm grain size) were diluted with quartz to minimize the temperature gradients inside the bed. The decrements in the $NH_3$ contents due to the reaction were monitored interferometrically. The $NH_3$ decomposition rates were calculated from the mass balance for the catalyst layer assuming that the reactor operated as a plug-flow differential reactor [22]. All the kinetic experiments were performed under atmospheric pressure, usually at 400 and 370 °C. Prior to the tests, the samples were rereduced (stabilized) in a $H_2{:}N_2 = 3{:}1$ stream at 430 °C for 24 h (Cs–Ru/C) or at 430 °C (24 h) + 470 °C (24 h) (Ru/C and Ba–Ru/C).

The temperature-programmed desorption studies of preadsorbed nitrogen ($N_2$ TPD) were performed in a glass flow setup, equipped with a gradientless microreactor [23]. Each sample was reduced in flowing hydrogen (30 ml/min) according to the temperature program applied in the ammonia decomposition studies (see above). Afterward, the sample was flushed with helium at 400 °C (30 ml/min, 30 min) to remove preadsorbed hydrogen. Then, helium was replaced with nitrogen and the reactor was cooled to room temperature with a cooling rate of 3 °C/min. Finally, the catalyst was flushed with helium (30 ml/min, 15 min) and the $N_2$ TPD experiment was started; i.e., the concentration of nitrogen desorbing to the He stream (30 ml/min) was monitored when heating the reactor with a constant heating rate of 20 °C/min.

## 3. Results and discussion

The effect of the ruthenium precursor on the activity of the Ba-, Cs-promoted Ru/carbon catalysts has been studied first. Table 2 presents the ammonia decomposition rates obtained on four different Ru samples under standard conditions (400 °C; 5.7% $NH_3$). Two of the samples were derived from ruthenium carbonyl and the other two, from ruthenium chloride, all supported on carbon A. The reaction rates over the potassium-promoted iron catalyst deposited on graphitized carbon (24 wt% Fe in Fe/C, K:Fe = 1:1,

Table 1
Characteristics of the carbon-based ruthenium catalysts

| Catalyst | $S_{BET}$ ($m^2/g$) | $S_{Hg}$ ($m^2/g$) | Ruthenium precursor | $FEO_2$[a] | Promoter/ruthenium (mol/mol) | $FEH_2$[a] |
|---|---|---|---|---|---|---|
| Ru/A | 66 | 60 | $RuCl_3 \cdot 0.5H_2O$ | 0.215 | – | – |
| Ru/A | 66 | 60 | $Ru_3(CO)_{12}$ | 0.16 | – | – |
| Cs–Ru/A | 66 | 60 | $RuCl_3 \cdot 0.5H_2O$ | 0.215 | 1.5 | 0.21 |
| Cs–Ru/A | 66 | 60 | $Ru_3(CO)_{12}$ | 0.16 | 1.4 | – |
| Ba–Ru/A | 66 | 60 | $RuCl_3 \cdot 0.5H_2O$ | 0.215 | 0.43 | – |
| Ba–Ru/A | 66 | 60 | $Ru_3(CO)_{12}$ | 0.16 | 0.40 | – |
| Ru/B | 330 | 110 | $RuCl_3 \cdot 0.5H_2O$ | 0.62 | – | – |
| Cs–Ru/B | 330 | 110 | $RuCl_3 \cdot 0.5H_2O$ | 0.62 | 2.9 | 0.48 |
| Ba–Ru/B | 330 | 110 | $RuCl_3 \cdot 0.5H_2O$ | 0.62 | 0.7 | 0.44 |

$S_{BET}$ and $S_{Hg}$, BET and mercury porosimetry surface areas of the supports used; $FEO_2$ and $FEH_2$, dispersions of ruthenium (“fraction exposed,” defined as the number of surface Ru atoms referred to the total number of Ru atoms), as determined for the unpromoted catalysts from the oxygen chemisorption data ($FEO_2$) and, for the promoted samples, determined from hydrogen chemisorption data ($FEH_2$).

[a] O:Ru = 1.1:1 and H:Ru = 1:1 stoichiometries were assumed [15].

Table 2
Rates of ammonia decomposition over the promoted Ru/A catalysts derived from ruthenium chloride and ruthenium carbonyl; $T = 400\,^{\circ}C$, $x_{NH_3} = 5.7\%$

| No. | Catalyst | Metal precursor | $r$ ($g_{NH_3}/(g_{Me}$ h)) | TOFH$_2$ (1/s) |
|---|---|---|---|---|
| 1 | Cs–Ru/A | $RuCl_3 \cdot 0.5H_2O$ | 189 | 1.48 |
| 2 | Cs–Ru/A | $Ru_3(CO)_{12}$ | 169 | – |
| 3 | Ba–Ru/A | $RuCl_3 \cdot 0.5H_2O$ | 82.4 | 0.56 |
| 4 | Ba–Ru/A | $Ru_3(CO)_{12}$ | 72.5 | – |
| 5 | K–Fe/carbon | $Fe(NO_3)_3 \cdot 9H_2O$ | 0.3 | 0.005[a] |
| 6 | Fused iron | – | 0.05 | 0.007[b] |

[a,b] Calculated from the kinetic and hydrogen chemisorption data presented in [24] and [6], respectively.

FEH$_2$ = 0.056) [24] and over triply promoted fused iron [6] have also been included in Table 2, for comparison.

Generally, the promoted ruthenium catalysts are significantly more active than the iron ones, both when the reaction rates are referred to the metal mass ($r$) or when they are referred to the number of surface metal atoms in the promoted specimens (TOFH$_2$). The ratio of TOFH$_2$ over Cs–Ru/A (sample 1 in Table 2) and K–Fe/carbon (sample 5) exceeds considerably the factor of $10^2$. The Cs–Ru/A and Ba–Ru/A systems derived from ruthenium chloride exhibit slightly higher reaction rates ($r$) than those obtained from carbonyl, roughly in proportion to the dispersions (FEO$_2$) determined for the unpromoted Ru/A precursors (FEO$_2$ = 0.215 and FEO$_2$ = 0.16, respectively; see Table 1). Hence, a disadvantageous effect of chlorine, observed previously in the ammonia decomposition reaction performed with the unpromoted Ru/carbon catalysts [25], has been eliminated almost totally by the promoter addition. Therefore, further studies of the ruthenium/carbon catalysts, presented below, have been limited to the systems prepared from ruthenium chloride.

Fig. 1 illustrates the effect of NH$_3$ concentration in the gas phase on the ammonia decomposition rates over the unpromoted and Ba- or Cs-promoted catalysts of lower dispersion (Ru/A, FEO$_2$ = 0.215). As seen, the reaction rate increases for each catalyst, roughly linearly, when the NH$_3$ concentration increases. The introduction of the promoters (Cs, Ba) results in a significant enhancement in the catalyst activity. Over the whole range of ammonia concentrations (5–50%), cesium is a more advantageous promoter than barium (see Fig. 1). A sequence of the apparent activation energies $E_{370-400}$ determined at 50% NH$_3$ ($E_{Cs\text{–}Ru/A}$:$E_{Ba\text{–}Ru/A}$:$E_{Ru/A}$ = 134:158:191 kJ/mol) indicates clearly the differences in the ammonia decomposition rates over Cs–Ru/A, Ba–Ru/A, and Ru/A to be higher, the lower the temperature. Analogous trends of the NH$_3$ decomposition rates vs NH$_3$ content were found for the Ba- and Cs-promoted catalysts of high ruthenium dispersion (carbon B; FEO$_2$ = 0.62, not presented), the advantage of Cs vs Ba being even more pronounced than in the case of low dispersion specimens Cs– and Ba–Ru/A.

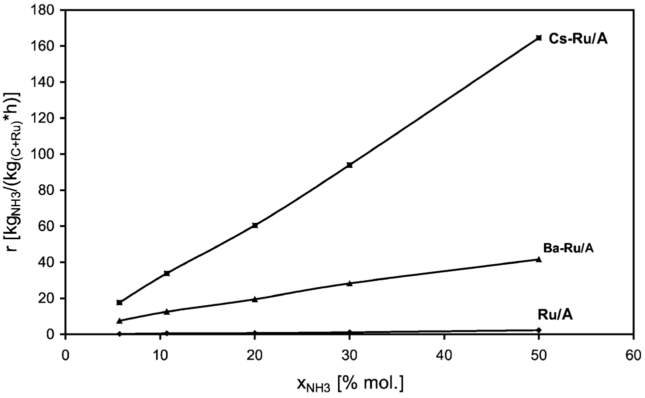

Fig. 1. Dependence of the ammonia decomposition rate on $x_{NH_3}$ over the Ru/A catalysts of lower dispersion (FEO$_2$ = 0.215); $T = 400\,^{\circ}C$.

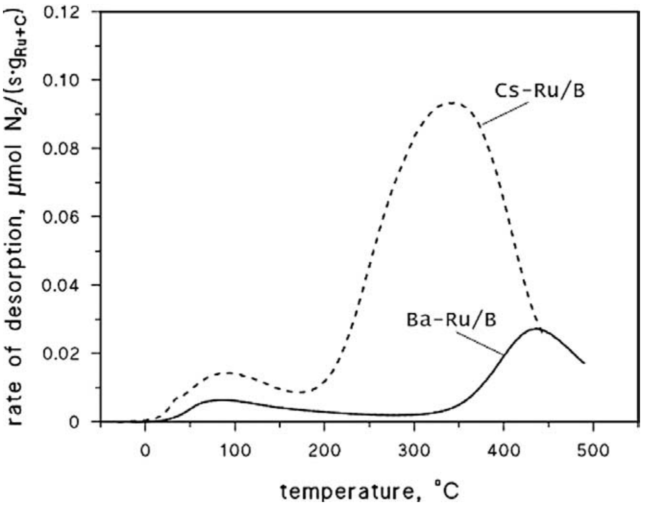

Fig. 2. The N$_2$ TPD profiles for the Ba–Ru/B and Cs–Ru/B catalysts.

Fig. 2 shows the results of nitrogen desorption studies performed with the promoted catalysts of high dispersion (Cs–Ru/B and Ba–Ru/B); the relationships for the low dispersion samples (Cs–Ru/A and Ba–Ru/A, not presented) were very similar. At first look, the N$_2$ TPD results correspond well to those of ammonia decomposition: the significantly lower NH$_3$ decomposition rates over Ba–Ru/B vs Cs–Ru/B are accompanied by the much higher temperatures of N$_2$ desorption for the former (Fig. 2). However, there are some doubts. The amount of nitrogen desorbed from Cs–Ru/B ($\Theta_{N_{ads}} = 0.24$ when normalized to H$_2$ chemisorption) is four times larger than that for Ba–Ru/B ($\Theta_{N_{ads}} = 0.06$), thus indicating the saturation coverages to be different. It is possible, however, that despite identical preadsorption procedures for both Ba- and Cs-doped specimens, the saturation of the Ba–Ru/B sample with N$_{ads}$ might not be achieved. In such a case, the N$_2$ TPD peak size measured for Ba–Ru/B would be underestimated and its position would be shifted to higher temperatures when compared to the saturation state. According to Fastrup [16], the rates of nitrogen adsorption on Ba–Ru/MgAl$_2$O$_4$ are by several orders of magnitude lower than those on Cs–Ru/MgAl$_2$O$_4$, thus showing the N$_{ads}$ saturation coverage to be hardly attainable when barium is present in the system instead of cesium.

Table 3
Effect of barium, cesium, and potassium on the kinetic behavior of the Ru/A catalyst in ammonia synthesis ($r_{synt}$), ammonia decomposition ($r_{dec}$), and nitrogen desorption ($T_{onset}$, $T_{max}$—the onset temperature and temperature of desorption maximum, respectively)

| Catalyst | $r_{synt}$[a] (63 bar, 400 °C) | | $r_{dec}$[a] | $N_2$ TPD (°C) | |
|---|---|---|---|---|---|
| | at 1% $NH_3$ | at 8% $NH_3$ | (1 bar, 400 °C, 50% $NH_3$) | $T_{onset}$ | $T_{max}$ |
| K–Ru/A | 1 | 1 | 1 | 210 | 320 |
| Cs–Ru/A | 1.3 | 1.4 | 1.6 | 200 | 320 |
| Ba–Ru/A | 6.5 | 2.5 | 0.4 | 320 | 400 |

[a] The relative reaction rates, i.e., referred to those for K–Ru/A.

A direct comparison of the $N_2$ TPD and ammonia decomposition data shows, in turn, that the rates of $NH_3$ decomposition are significantly, even by orders of magnitude, higher than those of $N_2$ desorption for both Cs–Ru/B and Ba–Ru/B. The discrepancies result, most likely, from the difference in the chemical composition of active surfaces in the experiments compared [22]. In contrast to the $N_2$ desorption studies, the ruthenium surface is covered with various intermediate species ($H_{ads}$, $NH_{ads}$, $NH_{2ads}$, $NH_{3ads}$) when operated under ammonia decomposition conditions. Such species may interact with nitrogen atoms ($N_{ads}$), thus leading to the lowering of the activation energy for $N_2$ associative desorption and, consequently, to the enhancement in the $NH_3$ decomposition rate [22].

The above discussion shows that $N_2$ TPD studies are not fully informative for the ammonia decomposition itself. They allow, however, to distinguish among the promoters. Table 3 summarizes the effects of the alkali (Cs, K) and those of barium on the kinetic behavior of the Ru/carbon system in the reactions of ammonia decomposition [present work and 22], of nitrogen desorption [present work and 22] and ammonia synthesis [14], all the catalysts being derived from the same Ru/A precursor. The reported data demonstrate that the differences between potassium and cesium are small and rather quantitative. Cesium is a slightly more efficient promoter than potassium in both $NH_3$ synthesis and decomposition, with the $N_2$ desorption parameters close to those of K. In contrast, barium demonstrates a totally different kinetic behavior; i.e., Ba is more efficient in $NH_3$ synthesis than the alkali—the relative effect being dependent on the ammonia content in the gas, but is less efficient in $NH_3$ decomposition and less efficient in nitrogen desorption or adsorption, as stated above. One may conclude, therefore, that the role of the alkali (K, Cs) in Ru/C catalysts is also different from that of barium.

The promotion of ammonia synthesis by the alkali is believed to proceed via electron transfer from alkali to the active metal surface. As a result of such an interaction, the barrier for $N_2$ dissociation is lowered [26] and/or the $NH_{xads}$ species, including $N_{ads}$, are destabilized [27,28]. Recent steady-state isotopic transient analysis suggests the lowering of the $N_2$ dissociation barrier to be essential for the alkali promotion [20]. In such a case, the barrier for $N_{ads}$ association would also be lowered. Since cesium is less electronegative than potassium, both $NH_3$ synthesis and decomposition rates are expected to be higher for Cs than for K, in agreement with the results of our studies (see Table 3).

Barium is considered to act either as an electronic promoter [29,30], similarly to an alkali, or as a structural one [14,31], that modifies the local arrangement of surface Ru atoms, thus creating superactive sites, e.g., B-5 sites. The latter concept explains nicely why the kinetic behavior of Ba–Ru/carbon is different from those of K– or Cs–Ru/carbon (see Table 3). We believe, therefore, that Ba is a structural promoter, whereas Cs and K are electronic ones. Unfortunately, there is still no direct evidence for this.

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