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High Pressure Ammonia decomposition on Ru-K/CaO catalysts

Salvador Sayas, Natalia Morlanés, Sai P. Katikaneni, Aadesh Harale, Bandar Solami, Jorge Gascon

Potassium-promoted Ruthenium supported on CaO is a very efficient catalyst for ammonia decomposition, surpassing the performance of other Ru supported solids. At an optimum Ru loading of 3% wt., catalysts with a K/Ru atomic ratio of 0.9 showed the best catalytic performance in a wide range of operating conditions, \( P = 1-40 \) bar, \( T = 250-550 \) °C and WHSV = 9000-30000 mL g \(^{-1}\) h \(^{-1}\). Although NH\(_3\) conversion levels decrease considerably upon increasing reaction pressure \( (X_{\text{NH}_3} \approx 0.8) \), high pressure ammonia decomposition offers the possibility of CO\(_2\)-free compressed hydrogen and hydrogen productivities and TOFs 40 times bigger than when applying atmospheric pressure. Extensive characterization by CO chemisorption and HR-TEM demonstrates that potassium promotion increases metal dispersion by decreasing Ru particle size. Electronic effects derived from the close proximity between K and Ru result in a decrease in the reaction apparent activation energy, as shown by a detailed kinetic analysis.

Introduction

The use of hydrocarbons as energy carriers has facilitated human development over the last century. However, the derived environmental consequences and scarcity issues are a strong driving force to look for cleaner and more sustainable alternatives \(^{1-3}\). Among the different possibilities, the use of hydrogen offers great advantages \(^{4-7}\) especially if its production \(^{8-11}\) is accompanied by CO\(_2\) capture or if it is directly produced from water. Hydrogen storage, however, is still an issue for which several alternatives are being proposed: metal hydrides, such as NaAlH\(_4\), LiAlH\(_4\), AlH\(_3\), or methanol \(^{15-16}\) are among the most studied, but there is also a growing interest in the use of ammonia. NH\(_3\) offers several advantages: high volumetric (108 kgH\(_2\)/m\(^3\) NH\(_3\) at 20°C and 8.6 bar), and gravimetric energy density (17.8 wt. %), easiness to store and transport, and the fact that NH\(_3\) production is a very well established technology (176 million metric tons global production in 2014 \(^{17-21}\)), they all point to ammonia as a very promising energy carrier readily compatible with the current distribution network. Moreover, ammonia decomposition is economically more viable than reforming processes, including methanol reforming \(^{22-23}\) and hydrogen and N\(_2\) are the only decomposition products, in contrast to the co-production of CO, CO\(_2\), CH\(_4\) from other liquid H\(_2\) carriers \(^{24-25}\). Last but not least, this reaction can be carried out at lower temperatures (450°C or below) than reforming processes (above 800°C) \(^{17,26-27}\).

Ammonia decomposition proceeds through a stepwise dehydrogenation followed by recombination of two N and two H adatoms to form N\(_2\) and H\(_2\) followed by desorption, and it is thought that NH cleavage is the rate limiting step. Ru is at the top of the volcano-type relationship observed for the classical ammonia decomposition rate vs. nitrogen binding enthalpy plot \(^{28-30}\). Consequently, the best ammonia decomposition catalysts known to date are based on Ru. K promoted catalysts supported on either MgO or on carbon nanotubes (CNT) are among the most active for this reaction \(^{31-37}\). The nature of the support has been shown to strongly influence catalytic performance in Ru based catalysts. Widely reported is the use of basic supports like MgO, La\(_2\)O\(_3\), \(^{33,38-39}\) neutral, such as CNT \(^{40-41}\) and acidic, like Al\(_2\)O\(_3\), \(^{31-32,35,42}\). In general, the use of basic and neutral results in better catalytic properties. \(^{43}\) In addition, the use of alkali promoters has been shown to further decrease nanoparticle size and the associative desorption of nitrogen, decreasing the activation energy of the reaction. \(^{44-45}\)

As it can be derived from the previous paragraphs, ammonia decomposition is a relatively well-known process. However, for most potential applications of ammonia derived H\(_2\) (i.e. fuel cells), hydrogen should be supplied at elevated pressures, or separated from nitrogen or stored at high pressure. Therefore, in order to avoid additional compression costs \(^{46-48}\) and derived emissions (estimates are about 6.0 kWh/kg for compression of H\(_2\) to 70 MPa, which leads to approximately 1.3 kg of CO\(_2\)/kg of hydrogen) \(^{49}\), high pressure ammonia decomposition would be preferred, in spite of the obvious thermodynamic limitations. \(^{50-51}\) Surprisingly, to the best of our knowledge, this is among the first publication on this topic.

Here we demonstrate the potential and limitations of Ru-based catalysts for the high-pressure decomposition of

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ammonia. In a first step, by performing experiments at atmospheric pressure, CaO is found to the most adequate support for Ru. Successive promotion with K results in further improvements in catalytic performance. Finally, the optimized catalyst is studied at different pressures. Extensive characterization by CO chemisorption and HR-TEM demonstrates that potassium promotion increases metal dispersion by decreasing Ru particle size. Electronic effects derived from the close proximity between K and Ru result in a decrease in the reaction apparent activation energy, as shown by a detailed kinetic analysis.

**Experimental**

**Catalyst Synthesis**

Commercial Multiwall Carbon Nanotubes (MWCNT, Aldrich), Magnesium Oxide (Sigma-Aldrich), Natural Sepiolite (NS) (Aldrich) and Calcium Oxide (Sigma-Aldrich), were used as supports. Ruthenium (III) chloride rehydrated (Aldrich) was selected as the Ru precursor, and it was incorporated on the different supports by incipient wetness impregnation using acetone, in order to achieve different Ru loadings (from 1 to 7 wt. %). After drying at 60°C for 3 hours, and a subsequent thermal treatment under argon at 500°C for 3 hours, the potassium promoter was introduced by incipient wetness impregnation using KOH in ethanol, to reach the desired K loading (0 to 15 wt.%). Finally, a second thermal treatment under Ar at 500°C during 3h was performed.

**Catalyst Characterization**

Nitrogen Adsorption and desorption isotherms were recorded on a Micromeritics ASAP 2040 system at 77 K. Samples were previously evacuated at 373 K for 16 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The P/P₀ range for BET analysis was 0.067 < P/P₀ < 0.249.

X-ray Diffraction (XRD) patterns were obtained using a Bruker D8 instrument in Bragg–Brentano configuration using Cu Ka radiation. The diffractograms were scanned with a step size of 0.02° in the 2θ range of 10–90°. The crystalline phase was identified by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS). CO pulse chemisorption studies were carried out on a Micromeritics ASAP 2920 analyzer. The samples were previously reduced with a 50% H₂/50% Ar gas mixture from room temperature to 500°C, and this temperature was kept for two hours. After the reduction, the samples were cooled down to 35°C, and treated with several CO pulses (10%CO/90%Hₑ). For further calculations, a stoichiometric factor Ru/CO=1, and spherical geometry for the ruthenium metal particles were assumed.

Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) was used to analyze the composition and metal loadings of the catalysts, on a Thermo-Electron 3580 instrument. Complete digestion of the powders was achieved at 240 °C and 35 bar using an UltraWAVE apparatus (Milestone) and aqua regia in a ratio of 1 mg of catalyst: 1 mL of aqua regia.

Transmission electron microscopy (TEM) of the samples was performed with a Titan Themis-Z microscope from Thermo-Fisher Scientific operated at accelerating voltage of 300 kV and beam current of 0.5 mA. Dark-field imaging was performed by scanning TEM (STEM) coupled to a high-angle annular dark-field (HAADF) detector. Furthermore, a high throughput X-ray energy dispersive spectrometer (EDS) was also utilized in conjunction with DF-STEM imaging to acquire STEM-EDS spectrum-imaging datasets. During the acquisition of these data sets, at every image pixel, a corresponding EDS spectrum was also acquired to simultaneously generate the elemental maps of Ru, O, K, and Ca atoms. It is also pertinent to note herein that spectrum-imaging data sets were acquired in so-called frame mode, in which the electron beam was allowed to dwell at each pixel for only a few microseconds in order to keep the total frame time to 6 s or less. Both imaging and spectroscopy data sets for each sample were acquired as well as analyzed with a newly developed software package called Velox from Thermo-Fisher Scientific. The elemental maps for Ru, O, K and Ca atoms were computed using the extracted intensities of their respective Ka lines after background subtraction. The generated maps were slightly post-filtered by applying a Gaussian filter (σ = 0.5).

**Catalytic Testing**

Ammonia decomposition catalytic tests were carried out in a PID Microactivity Reference system, using a continuous fixed bed stainless steel reactor coated with alumina to avoid any activity of the reactor. Prior to the activity measurement, the catalysts (200 mg pelletized between 300 μm and 500 μm and diluted with 1g of SiC) were reduced/activated in situ with hydrogen (25 mL min⁻¹) at 500°C for 3h. The catalytic performance was evaluated at different temperatures in the range 150-550 °C, achieving 7h of total reaction time. For the experiments at atmospheric pressure, ammonia in the gas phase (30-100 mL min⁻¹, WHSV=9000-30000 mL g⁻¹cat⁻¹ h⁻¹) was flown, using a mass flow controller, over the catalytic bed. For the experiments at high pressure (10-40 bar), a liquefied feeding system was used pumping liquid ammonia with an HPLC Gilson pump (30 N mL min⁻¹, WHSV=9000 mL g⁻¹cat⁻¹ h⁻¹) through a preheater at 100 °C, in order to expand the liquid ammonia into gas before reaching the catalytic bed,
where the operating pressure was automatically controlled using a back pressure regulator. Reaction products (nitrogen, hydrogen and ammonia) were analyzed under isothermal conditions with an online gas chromatograph (3000A Micro-GC gas analyzer, Agilent) using helium (1 ml min⁻¹) as internal standard for quantitative analysis. The Micro-GC is equipped with two columns: a PLOTU precolumn/Molsieve column using argon as the carrier gas for nitrogen and hydrogen; and a PLOTU column with helium carrier gas for ammonia. Both columns equipped with thermal conductivity detectors.

Results and discussion

Catalysts Characterization

BET area and ICP results are shown in Table 1. Very small specific surface areas were observed for all the catalysts based on CaO (in the range 4-10 m² g⁻¹), independently of Ru and K loadings while moderate to very high surface areas were obtained using other support materials (see MWCNT or Natural Sepiolite). The ICP results are in good agreement with the nominal composition for all samples, corroborating the successful incorporation of the active species (Ru) and promoter (K).

Table 1. BET surface area and ICP analysis for Ru based catalysts.

| Sample                  | S_BET (m² g⁻¹) | Ru* (wt. %) | K* (wt. %) |
|-------------------------|---------------|-------------|------------|
| 5%Ru10%K/MWCNT         | 758           | 4.7         | 9.7        |
| 5%Ru10%K/MgO           | 32            | 4.8         | 9.7        |
| 5%Ru10%K/NS            | 138           | 4.9         | 9.4        |
| 1%Ru10%K/CaO           | 6             | 0.9         | 9.6        |
| 2%Ru10%K/CaO           | 7             | 1.8         | 9.7        |
| 3%Ru10%K/CaO           | 5             | 2.8         | 9.6        |
| 5%Ru10%K/CaO           | 4             | 4.7         | 9.5        |
| 7%Ru10%K/CaO           | 8             | 6.6         | 9.4        |
| 3%Ru/CaO               | 10            | 2.9         | --         |
| 3%Ru5%K/CaO            | 5             | 2.8         | 4.9        |
| 3%Ru15%K/CaO           | 5             | 2.7         | 13.8       |

*Calculated by ICP-OES measurements.

The Ru-K/CaO catalysts with different Ru and K loadings were characterized by XRD at different stages: after thermal decomposition at 500°C under Ar atmosphere, after activation under H₂ at 500°C for 3h, and after being exposed to ammonia under reaction conditions for 7 h. XRD patterns shown in Figure 1. It is important to note that the CaO support tends to carbonate upon exposure to the atmosphere. Nevertheless, this phenomenon does not alter the properties of the catalysts since does not occur during the catalytic testing under the activation or reaction conditions.

Figure 1. XRD patterns of the Ru-K/CaO samples. A) Calcined samples, B) reduced samples and C) after catalytic testing. The XRD patterns recorded after thermal treatment under Ar, Figure 1A, show CaO, K₂O and RuO₂ phases. As expected, the most intense reflections are assigned to the CaO (JCPDS 00-37-1497) with 2θ angles 32.2°, 37.4°, 53.9°, 64.2°, 67.4°. K₂O with a small diffraction peak (JCPDS 00-47-
1701) at a 2θ angle of 45.3°, is formed under Ar thermal treatment after the incorporation of the promoter by impregnation. Additionally, diffraction peaks corresponding to RuO$_2$ are also detected, due to the incorporation of Ru by impregnation (JCPDS 00-43-1027) with 2θ angles 31.7 and 44.1°; increasing the intensity of these reflections when increasing the Ru loading. After H$_2$ treatment, Figure 1B, apart from the reflections assigned to CaO and K$_2$O, full reduction of Ru is observed: see disappearance of RuO$_2$ associated diffraction and the appearance of metallic Ru (JCPDS 00-06-0663) at 2θ angles of 38.4° and 44°. In the samples with different loading of K, a well-defined Ru pattern was also observed (figure 1B). After the catalytic test, CaO, K$_2$O and Ru are still visible in the XRD patterns (Figure 1C). Ruthenium dispersion and particle size were evaluated by CO pulse chemisorption in the samples after the activation under H$_2$ treatment. Table 2 summarizes the obtained results for metal dispersion, active metal surface area (AMSA), Ru particle size and number of surface active sites.

It is interesting to observe that, in spite of the low surface area of the support, metal dispersion and particle size remain constant for Ru loadings up to a 3 wt%. Addition of enhancing dispersion; most probably by inhibiting Ru sintering as previously observed.$^{52-54}$

**Table 2.** Ruthenium dispersions, active metal surface areas and particle sizes for Ru-based catalysts.

| Sample       | Dispersion (%) | AMSA ($\text{m}^2\text{g}^{-1}$) | $d_p$ (nm) | $N_{\text{AS}} \times 10^3$ (mol g$^{-1}$) |
|--------------|----------------|----------------------------------|------------|---------------------------------|
| 1%Ru10%K/CaO | 16.2           | 87                               | 6          | 1.6                             |
| 2%Ru10%K/CaO | 15.2           | 81                               | 6          | 3.0                             |
| 3%Ru10%K/CaO | 15.5           | 83                               | 6          | 4.6                             |
| 5%Ru10%K/CaO | 8.5            | 45                               | 11         | 4.2                             |
| 7%Ru10%K/CaO | 5.2            | 28                               | 17         | 3.6                             |
| 3%Ru/CaO     | 9.8            | 52                               | 9          | 2.9                             |
| 3%Ru5%K/CaO  | 11.2           | 60                               | 8          | 3.3                             |
| 3%Ru15%K/CaO | 14.8           | 79                               | 6          | 4.4                             |

$^a$Metal Dispersion (%): weight of exposed metal atoms/weight of total metal atoms.

$^b$Active metal surface area (AMSA).

$^c$Active particle size; (spherical geometry): $d_p$ (nm) = $6/(\text{AMSA} \cdot \rho_{\text{Ru}})$, where $\rho_{\text{Ru}} = 12.2$ g cm$^{-3}$.

$^d$Number of surface active sites: $N_{\text{AS}}$ (mol g$^{-1}$) = Ru loading (wt.) $\times$ Dispersion/Ru mass (g mol$^{-1}$).
Comparison of the obtained results reveal 3%Ru10%K/CaO as the composition with the highest active surface area. The local structures of the Ru-K/CaO catalysts were evaluated using high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX). Representative TEM images are shown in Figure 2 for 3%Ru-10%K/CaO and 3%Ru/CaO catalysts after activation treatment under H₂ at 500°C for 3 h. In the TEM images of the sample without K (3%Ru/CaO), Ru nanoparticles are dispersed on the CaO support with a quite broad particle size distribution in the range of 2.5 to 22.5 nm. The mean particle size, 9 nm, is in agreement with that calculated by CO chemisorption (Table 2 and Table S4). Elemental mapping shows that Ru dispersion is not completely regular in these samples, with Ru localized preferably in certain regions. In the TEM images for the sample containing K (3%Ru10%K/CaO), significant differences are observed compared to the sample without potassium. Ru nanoparticles are better dispersed, with a narrower particle size distribution, from 2 to 15 nm, and a smaller mean particle size, 7 nm, that matches with the particle size calculated by CO chemisorption (6 nm). Mapping shows that K, although is dispersed through all the catalyst nanoparticles, is better dispersed, with a narrower distribution, in these samples.

Catalytic activity

In a preliminary stage, the catalytic performance of potassium-promoted Ru catalyst on different supports was evaluated. Table 3 shows ammonia conversion levels and hydrogen production rates at 400°C for Ru-K catalysts on the different supports. Ru-K supported on CaO and NS were found to be more efficient catalysts compared to other supports reported for this process, such as MWCNT or MgO, with Ru-K/CaO showing the highest ammonia conversion (54%) and hydrogen productivity (574.3 mol H₂ mol Ru⁻¹ h⁻¹) at 400°C. It is worth highlighting that these results are not correlated with the measured surface areas of the different catalysts. Considering that both Ru loadings and Ru:K ratios are similar for all catalysts, this suggests that the chemical nature of the support has an important influence on catalytic performance. For instance, the use of basic supports resulted in better catalytic performance, in line with this fact, CaO is more basic support with a larger number and strength of basic sites.²⁵⁻⁵⁶

Table 3. Ammonia conversion and hydrogen productivity of Ru-based catalysts on different supports at 400°C. (P=1 atm; NH₃ flow rate 30 ml min⁻¹; WHSV= 9000 mL h⁻¹ g⁻¹)

| Catalyst                | Xₐ (%)  | H₂ production (mol H₂ mol Ru⁻¹ h⁻¹) |
|-------------------------|---------|-----------------------------------|
| 5%Ru10%K/MWCNT          | 30.8    | 322.7                             |
| 5%Ru10%K/MgO            | 39.4    | 407.8                             |
| 5%Ru10%K/NS             | 46.6    | 474.4                             |
| 5%Ru10%K/CaO            | 53.7    | 574.3                             |

In view of these results, the optimal metal and promoter loadings were subsequently investigated using CaO as support. Figure 3 depicts ammonia conversion versus reaction temperature, while the insets compare the activity at 400°C for different Ru and K loadings. Conversions not affected by heat or mass transport limitation (Figure S1-S3).
Figure 3. Ammonia conversion versus temperature of RuK/CaO catalysts; effect of Ru and K loadings. P=1 atm; T=250-550°C; NH$_3$ flow rate 30 Nml min$^{-1}$; W$_{cat}$ = 200 mg; WHSV: 9000 mL g$^{-1}$ h$^{-1}$.

First, samples with Ru loadings in the range 1-7 wt.% and constant K loading (10 wt.%) were evaluated. The positive effect of Ru is clearly observed up to a 3 wt. % loading. After that, activity decreases significantly. Secondly, samples with the optimum Ru loading (3 wt. %) and K in the range 0-15 wt. % were also analyzed. For K, also an optimum in promotion is observed, in this case a 10 wt. %. For CaO supported samples, catalytic performance is very well in line with the obtained characterization results, especially in terms of Ru dispersion, active metal surface area and TEM characterization, according to the beneficial effect of K preventing Ru agglomeration under activation and reaction conditions.$^{52-54}$ The best catalytic results are obtained for Ru nanoparticles of 6-7 nm. Ammonia decomposition on Ru has been shown to be a highly structure-sensitive reaction, with terrace sites being the main active sites$^{57}$ and with particles below 6 nm being hardly active. Our experimental results further confirm this earlier observation.

Once catalyst composition was optimized, we studied the high-pressure (10-40 bar) decomposition performance of the 3%Ru10%K/CaO sample. Figure 4A displays the impact of operating pressure on catalytic performance. Ammonia conversion is greatly decreased when the pressure increases from 1 to 40 bar. While still high conversion, around 80%, is observed at 550 °C and 40 bars. This is further analysed in Figure 4B. Interestingly, although a drastic decrease is observed in the conversion level, hydrogen productivity increases with pressure (Figure 4C), already anticipating a positive reaction order for NH$_3$ (vide infra) (Figure 4C & 4D).

Figure 4. Effect of pressure on catalytic performance of RuK/CaO catalysis in ammonia decomposition reaction. Ammonia conversion (%), hydrogen productivity (mol H$_2$ g$_{cat}$ h$^{-1}$), ammonia decomposition rate (mol NH$_3$ g$_{cat}$ h$^{-1}$) and TOF (s$^{-1}$) versus temperature. The reaction
rates of ammonia conversion and hydrogen production were calculated from the ammonia conversion values assuming a differential reactor and taking into account the operating pressure. P=1-40 atm; T=250-550°C; NH₃ flow rate 30 Nml min⁻¹; WHSV= 9000 mL h⁻¹g⁻¹.
Finally, turnover frequencies (TOF) were calculated (Figure 4D and 5) considering the number of active surface sites evaluated by CO chemisorption studies (see above in section 3.1, Table 2). Rates far from equilibrium were considered to compare the TOF calculated for both samples. The promotion effect of potassium on the catalytic activity of the Ru catalysts is clearly observed in Figure 5.

Figure 5. Calculated turnover frequencies (TOF) for K promoted and unpromoted Ru/CaO catalysts. P=1 atm; T=150-500°C; NH₃ flow rate 30 ml min⁻¹; WHSV= 9000 mL h⁻¹g⁻¹

Kinetic Analysis

Kinetic studies at atmospheric pressure were performed for the optimized 3%Ru-10%K/CaO, as well as for the unpromoted catalyst in order to elucidate the effect of potassium from a kinetic point of view. Reaction orders for NH₃ and H₂ were calculated from differential experiments varying the NH₃ and H₂ partial pressures and the temperature (Details of the kinetic study in the S.I. and Figures S4-S6). The results are summarized in Table 4. The apparent activation energy was calculated from the Arrhenius plots for both catalysts. Incorporation of K results in a decrease in the activation energy from 96 to 75 kJ mol⁻¹. Promotion with alkali metals is well known to decrease the hydrogenation ability of Ru via electronic promotion.27

Table 4. Kinetic parameters of the Ru-K/CaO catalysts for the ammonia decomposition reaction at 350 °C and P₀=1 atm

| Sample          | E_a (kJ mol⁻¹) | a   | b   |
|-----------------|---------------|-----|-----|
| 3%Ru /CaO       | 96            | 0.8 | -1.9|
| 3%Ru10%K/CaO    | 75            | 0.5 | -1.2|

Inhibition of ammonia decomposition rate by the hydrogen produced is observed. The negative orders observed for hydrogen for both catalysts, can be explained considering that chemisorbed hydrogen blocks surface sites that are necessary for ammonia decomposition, or reacts chemically and hydrogenate NH₃ intermediates generated during the ammonia decomposition.58 As shown in Table 4, potassium promotion results in a decrease of both the reaction order on NH₃ (from 0.8 to 0.5) and the negative reaction order on H₂ (from -1.9 to -1.2), highlighting the positive electronic promotion of the alkali metal.

For Ru-based catalysts, it is generally agreed that the limiting reaction step is the dissociation of ammonia and the observed negative order on hydrogen is related to the re-hydrogenation of partially dehydrogenated species (NH₂ intermediates, x= 1.2). The kinetic data clearly show the ability of K to decrease hydrogenation capability of Ru. In this way, inhibition of ammonia decomposition by hydrogen becomes less important and this is translated in an enhancement of the catalytic activity.

The observed kinetics for Ru-K/CaO catalysts at atmospheric pressure, are well described using the power law given by eq.1.

\[
(-r_{\text{NH₃}}) = k \times P_{\text{NH₃}}^a P_{\text{H₂}}^b
\]  

(eq. 1)

In order to develop a reliable kinetic model able to predict the catalytic performance under relevant operating conditions for the industrial application of this process, where almost complete NH₃ conversion is achieved, such as the usually high temperatures needed or the high pressures used in this work, the overall approach to thermodynamic equilibrium needs to be considered in order to contemplate the effect of the reverse reaction that suppress the decomposition rate. Under these operating conditions, to attain the large conversions, the reaction rate is better described by eq. 2, including a term that accounts the influence of the reverse reaction with the approach to the equilibrium.35, 61-62 This term becomes increasingly significant at temperature above 400°C or when ammonia conversion is close to the equilibrium conversion. And will definitively be important at the high pressures used here, above the atmospheric.

\[
(-r_{\text{NH₃}}) = k \times P_{\text{NH₃}}^a P_{\text{H₂}}^b \left(1 - \frac{1}{X_{\text{eq}} \left( \frac{P_{\text{NH₃}}}{P_{\text{NH₃}}^{\text{eq}}} \right)} \right)
\]  

(eq. 2)

The kinetic model (eq.2) considers that the rate is inhibited by hydrogen product and also by the reverse reaction, non-negligible at temperatures below 500 °C.61 Considering the inhibition of the decomposition rate by the hydrogen produced, and taking into account that the gas composition is very different along the reactor with the increasing conversion level, an integral reactor must be considered for the kinetic analysis in this case, to account the increasing hydrogen concentrations at the different conversion levels along the catalytic bed.61 The integration of the eq. 3...
allows the calculation of the ammonia conversion in a plug-flow reactor, where the ammonia conversion rate ($-\frac{dX_{NH3}}{dt}$) is given by the expression in eq. 2, and can be compared with the experimental values. See details of the kinetic study in an integral reactor in the S.I.

\[ W/F = \int_{0}^{\infty} \frac{dx_{NH3}}{(-r_{NH3})} \]  

(eq. 3)

\[ y = 0.9837x \]

\[ R^2 = 0.9846 \]

Figure 6. Experimental vs. modeled ammonia conversion using the proposed power-law model (eq.2) for ammonia decomposition over 3%Ru-10%K/CaO catalyst. Red: ammonia conversion at high pressure. Black: conversion at atmospheric pressure.

In order to check the validity of the kinetic model based on the power-law to predict the catalytic performance at elevated pressures, the ammonia conversions were calculated at these operating conditions, assuming an integral reactor and solving the eq.3 with the reaction rate given by eq 2. In the Figure 6 the experimental conversions are compared with those predicted by the kinetic model given by eq 2, showing an excellent matching and corroborating the goodness of the kinetic model. (Further details in the S.I., with the fittings in Figures S7-S8). This excellent correspondence between the experimental and calculated values indicates the kinetic model (eq.2) is not only very robust to predict low and high conversion levels, in a wide range of reaction conditions of temperature and space velocity; but also very reliable when predicting the catalytic performance at high pressure. The study demonstrates the validity of the selected kinetic model to predict performance outside of the data used for the fitting and suggest that experiments at higher pressures are probably not per se needed to assess the high-pressure performance of ammonia decomposition catalysts. Furthermore, other kinetic models taking into account different mechanistic considerations and assuming different rate determining steps (given by equations S5-S8 in the S.I.), were explored here to fit the experimental data, as well as to predict the catalytic performance at high pressure. Fittings obtained with all the kinetic models selected are shown in the Figures S7-S8 in the S.I. Considering the parity plots that compares experimental and calculated values of ammonia conversion, it is difficult to draw conclusions related to the limiting step, since almost identical fittings are obtained with the mechanistic models that consider different rate determining step, such as those assuming the ammonia dissociation (eq. S7) or nitrogen desorption as limiting rates (eq. S5). That is the main reason why, in spite of the research over decades in this reaction, there is no agreement about the limiting step or the kinetically relevant surface species. In fact, the results in Figures S7-S8, clearly corroborate that all the species present at the catalyst surface must be considered as kinetically relevant. The fitting of the experimental data with the models that consider a few adsorbed species as the most abundant ones (such as the kinetic equations S6 and S8) provide worse matching. This aspect becomes more significant when the process is conducted at high pressure (Figure S8).

Interestingly, from the Figure 6 and Figures S7-S8 in the S.I., with the parity plots for different kinetic models, it is concluded that the power law given by the equation 2, is as good as the mechanistic models that take into account different rate limiting steps, while offering, by far, the simplest equation for a kinetic model. Furthermore, this model is the most robust to predict the catalytic performance for ammonia decomposition at high pressure (Figure S8).

Conclusions

In summary, our work further demonstrates that Ru based catalysts are very efficient for the decomposition of ammonia. Considering the relatively low Ru loadings desired and the strong structure sensitivity of this reaction, with an optimal Ru particle size in the order of 7 nm, the chemical nature of the support, specially its basicity, plays a much bigger role than other physical properties such as surface area. Considering those facts, among the studied supports, CaO has been identified as a very promising one.

The reaction proceeds with inhibition of the decomposition reaction rate by hydrogen produced, suggesting competitive adsorption of H2 and/or re-hydrogenation of NH3, intermediates occur, and pointing to the ammonia dissociation as the limiting step of the reaction rate. By promoting Ru with K, competitive adsorption of H2 is reduced and hydrogenation capability of Ru decreased, as shown by the strong decrease in the H2 negative reaction order. This effect translates into higher intrinsic catalytic activity. Last but not least, our modelling results demonstrate that kinetic analysis in the low-pressure regime using the power law-derived equation can be used to accurately predict catalytic performance at higher decomposition pressures, which, from an application perspective, are much more attractive but may be difficult to measure in many laboratories.
Conflicts of interest
There are no conflicts to declare.

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Graphical abstract

$2\text{NH}_3 \leftrightarrow \text{N}_2 + 3\text{H}_2$

$-r_{\text{NH}_3} (\text{mol} \, \text{NH}_3 \, \text{mol}^{-1} \, \text{cat}^{-1} \, \text{h}^{-1})$

$T$ (°C)

TOF (h$^{-1}$)

Ru-K/CaO catalysts

1 bar

10 bar

20 bar

40 bar