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# NH<sub>3</sub> decomposition for H<sub>2</sub> production by thermal and plasma catalysis using bimetallic catalysts



Shengyan Meng<sup>a</sup>, Shangkun Li<sup>a</sup>, Shuaiqi Sun<sup>a</sup>, Annemie Bogaerts<sup>b</sup>, Yi Liu<sup>a,\*</sup>, Yanhui Yi<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China <sup>b</sup> Research Group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, BE-2610 Wilrijk-Antwerp, Belgium

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# ABSTRACT

Plasma catalysis has emerged as a promising approach for driving thermodynamically unfavorable chemical reactions. Nevertheless, comprehending the mechanisms involved remains a challenge, leading to uncertainty about whether the optimal catalyst in plasma catalysis aligns with that in thermal catalysis. In this research, we explore this question by studying monometallic catalysts (Fe, Co, Ni and Mo) and bimetallic catalysts (Fe-Co, Mo-Co, Fe-Ni and Mo-Ni) in both thermal catalytic and plasma catalytic NH<sub>3</sub> decomposition. Our findings reveal that the Fe-Co bimetallic catalyst exhibits the highest activity in thermal catalysis, the Fe-Ni bimetallic catalysts for the two catalytic modes in NH<sub>3</sub> decomposition. Comprehensive catalyst characterization, kinetic analysis, temperature program surface reaction experiments and plasma diagnosis are employed to discuss the key factors influencing NH<sub>3</sub> decomposition performance.

#### 1. Introduction

Non-thermal plasma (NTP), characterized by thermal nonequilibrium, provides a unique pathway to drive thermodynamically unfavorable chemical reactions at low temperatures (Bogaerts et al., 2020; Mehta et al., 2019; Neyts et al., 2015; Xu et al., 2023). Plasma catalysis, the combination of catalyst and plasma technology, exhibits catalyst-plasma synergistic effects. Plasma catalysis has been widely applied to activate and convert stable molecules (e.g., CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>) for energy and environmental applications (Cui et al., 2022; Meng et al., 2023; Wang et al., 2022; Wang et al., 2023). However, it is still uncertain whether the optimal catalyst in plasma catalysis aligns with that in thermal catalysis. Addressing this question is crucial for understanding the plasma-catalyst synergy and developing efficient catalysts for specific chemical reactions under plasma catalysis.

Hydrogen production through ammonia (NH<sub>3</sub>) decomposition has received significant attention in recent years due to its exceptional qualities as a hydrogen carrier (Adamou et al., 2023; Lucentini et al., 2021; Sun et al., 2022). Although Ru has been acknowledged as the most active catalyst, its limited availability and high cost hinder large-scale applications (Chen et al., 2021; Fang et al., 2022). As a result, extensive research has been conducted on various non-noble metals, including Fe (Lu et al., 2010; Zhang et al., 2018), Ni (Kurtoglu et al., 2018; Qiu et al., 2022), and Co (Gu et al., 2015; Li et al., 2022), as well as transition metal carbide and nitride catalysts (Guo et al., 2015; Zheng et al., 2013), for NH<sub>3</sub> decomposition. The state-of-the-art results on NH<sub>3</sub> decomposition through conventional thermal catalysis have been listed in Table S1. Despite the progress, the recombinative desorption of the adsorbed nitrogen atoms (Nad) on the non-noble metal surfaces remains challenging, which results in a lower NH<sub>3</sub> decomposition activity, unless the reaction is conducted at elevated temperature (>ca. 550 °C) (Bell and Torrente-Murciano, 2016). The thermodynamic equilibrium conversion of NH<sub>3</sub> in relation to reaction temperature at atmospheric pressure is shown in Fig. 1, calculated using thermodynamic parameters of NH<sub>3</sub>, N<sub>2</sub> and H<sub>2</sub> molecules NH<sub>3</sub> decomposition benefits from favorable thermodynamics, resulting in equilibrium conversions of 85.0 %, 93.5 %, 97.0 %, 98.5 % and 99.2 % at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C, respectively. However, the current NH<sub>3</sub> conversion achieved over non-noble metal catalysts remains significantly lower than the equilibrium conversion, especially under low temperature and high space velocity conditions, attributed mainly to kinetic blocking. In other words, there is a substantial potential to enhance the low-temperature performance of non-noble metal catalysts in NH<sub>3</sub> decomposition through a rational catalyst design approach.

\* Corresponding authors. E-mail addresses: diligenliu@dlut.edu.cn (Y. Liu), yiyanhui@dlut.edu.cn (Y. Yi).

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Fig. 1. Thermodynamic equilibrium conversion of  $NH_3$  into  $H_2$  and  $N_2$  at standard atmospheric pressure as a function of temperature. (100%  $NH_3$  feed gas).

To improve the activity of non-noble metals at low temperatures, bimetallic alloys have become a pivotal strategy (Sun et al., 2022). Combining a metal with low metal-N binding energy (Ni and Co) and another metal with high metal-N binding energy (Fe and Mo) may result in a bimetallic catalyst with a moderate metal-N binding energy similar to that of Ru, ultimately enhancing non-noble metals' performance in NH3 decomposition. Therefore, bimetallic catalysts, i.e., Fe-Ni (Silva et al., 2015; Simonsen et al., 2012), Fe-Co (Lendzion-Bielun and Arabczyk, 2013; Zhang et al., 2008), Mo-Co (Srifa et al., 2016), and Co-Re (Kirste et al., 2021) have been studied in NH<sub>3</sub> decomposition. Another strategy to improve the activity of non-noble metal catalysts in this process is through plasma catalysis. Previous papers reported a significant synergistic effect between dielectric barrier discharge (DBD) plasma and supported catalysts (Fe, Co, Ni and Cu) (Mukherjee et al., 2018; Wang et al., 2017; Wang et al., 2015; Wang et al., 2013; Yi et al., 2019).

In this paper, we report that among all the investigated catalysts (Fe, Co, Ni, Mo, as well as Fe-Co, Fe-Ni, Mo-Ni and Mo-Co bimetallic catalysts), the Fe-Co bimetallic catalyst exhibits the highest activity in thermal catalysis, while the Fe-Ni bimetallic catalyst shows the best activity in plasma catalysis. Hence, the optimal catalyst for  $NH_3$  decomposition in thermal and plasma catalytic conditions is not the same. Moreover, catalyst characterization, kinetic analysis, and in-situ diagnostics were conducted to understand the reasons behind the suitability of Fe-Co and Fe-Ni catalysts for thermal catalytic and plasma catalytic NH<sub>3</sub> decomposition, respectively.

# 2. Experimental section

# 2.1. Catalyst preparation

SiO<sub>2</sub> has been widely used as an "inert" catalyst support due to its low cost and excellent durability (Zhang et al., 2022). In our previous research, various materials with different relative dielectric constants ( $\epsilon_d$ ) were explored as potential catalyst supports, and SiO<sub>2</sub> was emerged as the preferred choice (Wang et al., 2015). The monometallic catalysts (Fe, Co, Ni and Mo), bimetallic catalysts (Fe-Co, Mo-Co, Fe-Ni and Mo-Ni) with a 5:5 metal molar ratio, and the Fe-Co bimetallic catalysts with varying Fe/Co molar ratios were prepared by the incipient-wetness impregnation method, using fumed SiO<sub>2</sub> as support. The detail preparation procedure is shown in Supplementary Information.

#### 2.2. Activity test

The experimental setup for the  $NH_3$  decomposition activity test is shown in Fig. S1. The temperature of the reactor wall was continuously monitored in situ using a thermocouple, while the temperature of the catalyst bed was calibrated through FLIR equipment (Figs. S2 and S3). The exhaust gas was analyzed using an online gas chromatograph (GC) equipped with a thermal conductivity detector. During the reaction process, only  $H_2$  and  $N_2$  were produced, corresponding to a 100 % mass balance.

$$X_{NH_3} = \frac{2Y}{1 - 2Y} \times 100\%$$
(1)

$$Q = X_{NH_3(p-c)} - (X_{NH_3(p)} + X_{NH_3(c)})$$
<sup>(2)</sup>

The flow rate of NH<sub>3</sub> was precisely controlled at 120 ml/min using a mass flow controller. The NH<sub>3</sub> conversion was measured using an external standard method, and the conversion (X<sub>NH3</sub>) is defined by equation (1), where Y represents the volume fraction of N<sub>2</sub>, which was measured by GC. The accuracy of N<sub>2</sub> content is ensured by employing three different standard curve formulas (Y<sub>1</sub>  $\leq$  5 %, 5 % < Y<sub>2</sub>  $\leq$  15 %, 15 % < Y<sub>3</sub>  $\leq$  25 %). The synergistic capacity (Q) between a catalyst and a DBD plasma is defined by equation (2), where X<sub>NH3(p-c)</sub>, X<sub>NH3(p)</sub> and X<sub>NH3(c)</sub> correspond to the NH<sub>3</sub> conversion in "plasma + catalyst", "plasma alone" and "catalyst alone", respectively.

# 2.3. Catalyst characterization and plasma diagnostics

The crystalline structure of the samples was analyzed using an X-ray diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The hydrogen temperature-programmed reduction (H2-TPR) of the samples (oxidation state) was examined using a ChemBET Pulsar chemical adsorbent. X-ray photoelectron spectroscopy (XPS) was conducted using Thermo Fisher ESCALAB XI + with Al Ka X-ray source, and C 1 s binding energy value (284.8 eV) was taken as a reference to calibrate the binding energy. Metal loadings were measured using X-ray fluorescence (XRF). The morphology and particle size of the catalysts were examined with high resolution transmission electron microscopy (HRTEM) and highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM), respectively, while energy-dispersive X-ray (EDX) spectrometry was used to analyze the chemical composition of the catalysts. The specific surface area, total pore volume, and pore diameter of the samples were measured using N<sub>2</sub> physisorption. To Characterize acidity and NH<sub>3</sub> adsorption-desorption property, ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) of the samples was carried out with ChemBET Pulsar Chemical Adsorbent, while quantifying active sites for NH3 chemisorption was achieved by titration. The NH3 plasmas (in the presence and absence of catalysts) were diagnosed using optical emission spectra (OES). The detailed instrument information and specific operating parameters are shown in Supplementary Information.

# 3. Results

#### 3.1. Thermal catalytic NH<sub>3</sub> decomposition activity

Fig. 2A depicts the NH<sub>3</sub> conversion of the Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts under thermal catalysis. It is evident that the Fe-Co catalyst exhibits superior activity compared to the other catalysts. Furthermore, Fe-Co bimetallic catalysts with varying Fe/Co molar ratios (constant total loading of 10 wt%) were evaluated under the same conditions (Fig. 2B). Notably, the optimal Fe/Co molar ratio is approximately 1/1 (i.e., 5Fe-5Co). With the use of the 5Fe-5Co catalyst, NH<sub>3</sub> was nearly completely decomposed (>99.5 %) at 585 °C. As shown in Fig. 2C, the 5Fe-5Co catalyst was continuously tested for 100 h, with the temperature alternating between 560 and 585 °C, and NH<sub>3</sub> conversion fluctuating between 73 % and 99.6 %, respectively.



**Fig. 2.** Results of thermal catalytic  $NH_3$  decomposition. (A) Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts; (B) Fe-Co bimetallic catalysts with varying Fe/Co molar ratios; (C) Stability performance of 5Fe-5Co catalyst. (0.5 g catalyst, 120 ml/min  $NH_3$ , 14400  $h^{-1}$  space velocity, 3 mm discharge gap, 10 kHz discharge frequency).

establish Fe-Co bimetallic catalyst as the optimal choice for thermal catalytic  $NH_3$  decomposition, offering excellent catalytic stability.

# 3.2. Plasma catalytic NH<sub>3</sub> decomposition activity

In Fig. 3A, the Fe-Ni catalyst exhibits the highest activity, achieving approximately 60 % NH<sub>3</sub> conversion, compared to other catalysts under plasma catalysis conditions, even at a relatively low temperature of 460 °C (570 °C without plasma). Detailed reaction conditions and NH<sub>3</sub> conversion for both "plasma alone" and "catalyst alone" are shown in Table S2. The synergistic capacity of the catalysts in plasma catalytic NH<sub>3</sub> decomposition was calculated using equation (2) (Fig. 3B). It is evident that Fe-Ni bimetallic catalysts (i.e., 5Fe-5Ni) exhibit the strongest plasma-catalyst synergistic capacity. These results indicate that the Fe-Ni bimetallic catalyst in plasma catalytic NH<sub>3</sub> decomposition for H<sub>2</sub> production.

#### 3.3. Physicochemical properties of the catalysts

In plasma catalytic NH<sub>3</sub> decomposition, the phase states of the fresh

and spent catalysts (Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni) are shown in Figs. S4-S7. The phase states of the fresh catalysts were dominated by Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO and MoO<sub>3</sub>. However, they transformed into the crystalline phases of Ni, Fe<sub>2</sub>N, Mo<sub>2</sub>N and Co<sub>5.47</sub>N, respectively, upon NH3 decomposition. For the fresh Mo-Ni and Mo-Co bimetallic catalysts, " $MoO_3 + NiO$ " and " $MoO_3 + Co_3O_4$ " mixed crystals formed, transforming into "Mo<sub>2</sub>N + Ni" and "Mo<sub>2</sub>N + Co<sub>5.47</sub>N", respectively, after the NH<sub>3</sub> decomposition. Interestingly, in the fresh Fe-Co and Fe-Ni bimetallic catalysts, spinel structures of CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> emerged, later converting into FeCo alloys and Fe<sub>3</sub>NiN after the NH<sub>3</sub> decomposition. The XRD profiles of the bimetallic Fe-Co catalysts with varied Fe/ Co ratios under thermal catalysis are shown in Fig. S8. The Fe-Co bimetallic catalysts transformed from the initial CoFe<sub>2</sub>O<sub>4</sub> spinel phase to FeCo alloy phase after undergoing NH3 decomposition reaction. It should be mentioned that the final crystalline phase remains constant regardless of thermal or plasma catalysis NH3 decomposition, indicating uniformity in the catalytically active phase.

The H<sub>2</sub>-TPR profiles of 10Fe, 10Co and Fe-Co bimetallic catalysts with varying Fe/Co ratio are depicted in Fig. 4. Clearly, the H<sub>2</sub>-TPR profile of 10Fe catalyst shows four peaks at 412  $^{\circ}$ C, 550  $^{\circ}$ C, 677  $^{\circ}$ C and



**Fig. 3.** Results of plasma catalytic NH<sub>3</sub> decomposition over Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts. (A) NH<sub>3</sub> conversion; (B) Synergistic capacity. (0.5 g catalyst, 120 ml/min NH<sub>3</sub>, 14400 h<sup>-1</sup> space velocity, 3 mm discharge gap, 10 kHz discharge frequency).



Fig. 4. H2-TPR results. (A) Fe-Co bimetallic catalysts with varying Fe/Co molar ratios; (B) The fitting peaks of H2 consumption for 10Fe, 5Fe-5Co and 10Co catalysts.

748 °C, attributed to the reduction of Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> → FeO, FeO → Fe and reduction of FeO species with strong interaction with the support, respectively. Likewise, the 10Co catalyst primarily shows three peaks at 340 °C, 391 °C and 445 °C, associated with the reduction of Co<sub>3</sub>O<sub>4</sub> → CoO, CoO → Co and reduction of CoO species with strong interaction with the support, respectively. The H<sub>2</sub>-TPR profile of the 5Fe-5Co catalyst displays four peaks at 379 °C, 489 °C, 580 °C and 730 °C, corresponding to the reduction of CoFe<sub>2</sub>O<sub>4</sub> → Co-Fe<sub>3</sub>O<sub>4</sub>, Co-Fe<sub>3</sub>O<sub>4</sub> → Co-FeO, Co-FeO → Co-Fe, and the reduction of Co-FeO species with strong interaction with the support, respectively. Comparative analysis of 10Fe, 5Fe-5Co and 10Co samples (Fig. 4B) indicates that the addition of Co lowers the reduction temperature of iron oxide. Furthermore, the H<sub>2</sub>-TPR profile of 5Fe-5Co sample provides evidence for the formation of CoFe<sub>2</sub>O<sub>4</sub> spinel phase, consistent with XRD results (Fig. S8).

The XPS profile the 10Fe, 10Co and Fe-Co bimetallic samples with varying Fe/Co ratio is shown in Fig. 5. The Fe 2p core level XPS profile of the 10Fe and Fe-Co bimetallic samples reveals that the intensity of both  $Fe2p_{3/2}$  (710.5 eV) and  $Fe2p_{1/2}$  (724.5 eV) elevates with increasing Fe content (Fig. 5A). Furthermore, the signal of Fe<sup>III</sup> has been observed, suggesting the existence of Fe<sub>2</sub>O<sub>3</sub> or CoFe<sub>2</sub>O<sub>4</sub> phase, which is consistent with XRD and H<sub>2</sub>-TPR results. In Fig. 5B, the Co 2p core level XPS profile of the 10 Co and Fe-Co bimetallic samples with varying Fe/Co ratio is presented, in which the intensities of both Co2p3/2 (779.7 eV) and  $Co2p_{1/2}$  (795.8 eV) increase with higher Co content. It is worth mentioning that the main peaks of  $Co2p_{3/2}$  (779.7 eV) and  $Co2p_{1/2}$ (795.8 eV) for Co<sup>II</sup> species are usually indistinguishable from those of Co<sup>III</sup> species, respectively, making them inadequate for distinguishing between Co<sup>II</sup> and Co<sup>III</sup> species. However, the satellite peaks cannot be clearly identified, due to the low ratio of signal to noise. Therefore, regarding the 5Fe-5Co catalyst, XPS spectra show the presence of Fe<sup>III</sup>, as well as Co<sup>II</sup> or Co<sup>III</sup>, while XRD and H<sub>2</sub>-TPR results confirm the existence of CoFe<sub>2</sub>O<sub>4</sub> spinel phase.

The XRF results of the Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts are shown in Tables S3 and S4, while Tables S5 and S6 present the XRF results for Fe-Co bimetallic catalysts with varying Fe/Co ratios. These results indicate that the actual loading is approximately 10 wt% (ranging from 9.6 to 10.1 wt%), which closely aligns with the calculated loading.

HRTEM images of the fresh catalysts are presented in Fig. S9 and the particle size distributions are shown in Fig. S10. The Co catalyst exhibits the smallest particle size, ranging from 3 to 8 nm, while the Fe and Mo catalysts show particle sizes ranging from 10 to 16 nm and 8 to 20 nm, respectively. The Fe-Co and Fe-Ni catalysts fall within 4 to 20 nm, whereas the Mo-Co and Mo-Ni catalysts show relatively larger particles (10 to 100 nm and 5 to 500 nm, respectively).

The distribution of elements in the spent bimetallic catalysts particles was investigated using HAADF-STEM and EDX spectrometry. Fig. 6 illustrates that in the Fe-Co and Fe-Ni bimetallic catalysts, the corresponding metals are found at the same location in the scanning mapping images, indicating their combination. The line scanning results (Figs. S11 and S12) reveal synchronous variations in the content of the corresponding metals along the scanning line. These results provide additional evidence for the formation of FeCo alloys and Fe<sub>3</sub>NiN, which aligns with the XRD results (Figs. S7 and S8). Furthermore, the HAADF-STEM mapping images of Mo-Co and Mo-Ni catalysts are shown in Figs. S13 and S14.

The BET surface area, pore volume and average pore diameter were calculated for all the samples using  $N_2$  adsorption–desorption isotherms (Tables S7 and S8). The BET surface area and pore volume showed a slight decrease for the catalysts after loading with metals, which could be attributed to the impregnation of the precursor in the support pores. As for the BET surface area, pore volume and average pore diameter, no significant differences were observed among the prepared catalysts.

The  $NH_3$ -TPD was employed to characterize the  $NH_3$  adsorption–desorption properties of the catalysts, as it is closely related to the



Fig. 5. XPS profile of Fe, Co and Fe-Co bimetallic catalysts. (A) Fe 2p XPS results; (B) Co 2p XPS results.



Fig. 6. HAADF-STEM mapping images. (A) Fe-Co bimetallic catalysts (5Fe-5Co), (B) Fe-Ni bimetallic catalysts (5Fe-5Ni).

catalytic performance, given  $NH_3$ 's role as the reactant. Furthermore, in  $NH_3$  decomposition reaction, the process is typically initiated by the chemisorption of  $NH_3$  molecules on the catalysts surface. Consequently,  $NH_3$ -TPD provides indirect insights into the active sites rather than an accurate measurement.

Fig. 7A illustrates the NH<sub>3</sub>-TPD profiles of the spent Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts. The Fe and Ni monometallic catalysts exhibit weak chemisorption sites for NH<sub>3</sub> (desorbing at low temperatures, i.e., < 300 °C), along with moderate chemisorption sites (300–400 °C) and strong chemisorption sites (desorbing at high temperatures, i.e., > 400 °C). However, the Co catalyst shows some weak

sites and a small part of moderate sites, while the Mo catalysts only display weak chemisorption sites. Among the bimetallic catalysts (Fe-Co, Mo-Co, Fe-Ni and Mo-Ni), the Fe-Ni and Fe-Co catalysts reveal abundant moderate sites, while the Mo-Ni catalysts exhibit numerous weak sites and a very small number of strong sites. Only weak sites are detected in Mo-Co catalysts. These results indicate that Fe-Co and Fe-Ni bimetallic catalysts exhibit a large number of moderate sites for NH<sub>3</sub> chemisorption, which could be attributed by the formation of FeCo alloy and Fe<sub>3</sub>NiN phase. Furthermore, the number of the NH<sub>3</sub> chemisorption sites was measured indirectly through titration following the NH<sub>3</sub>-TPD experiment, and the results are shown in Fig. 7B. The active sites for NH<sub>3</sub>



Fig. 7. The (A) NH<sub>3</sub>-TPD profiles and (B) NH<sub>3</sub> chemisorption active site numbers of the spent Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts.

chemisorption over the Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts are measured at 15.22, 13.54, 11.50, 26.28, 13.83, 17.45, 15.65 and 18.76  $\mu$ mol/g, respectively.

#### 4. Discussion

Figs. 2 and 3 exhibit the superior performance of the Fe-Co bimetallic catalyst in thermal catalytic NH3 decomposition, while the Fe-Ni bimetallic catalyst is the optimal catalyst in plasma catalysis. The N<sub>2</sub>physisorption results (Tables S7 and S8) indicate a similar porosity among the prepared catalysts, including BET surface area, pore volume and pore diameter, suggesting that these factors do not determine the catalytic activity. In light of the diameters of the mesopores in the catalysts (>12 nm), which significantly exceed the size of NH<sub>3</sub> molecules (0.326 nm), N<sub>2</sub> molecules (0.364 nm) and H<sub>2</sub> molecules (0.289 nm), it is plausible that mass transfer, specifically diffusion, may not serve as the limiting factor. Essential insights are provided by XRD, H<sub>2</sub>-TPR, XPS, HRTEM and HAADF-STEM analyses. Integrating the above activity and characterization results, the high activity of the Fe-Co catalyst in thermal catalytic NH3 decomposition is probably attributed to the FeCo alloy phase, while the exceptional performance of the Fe-Ni catalyst in plasma catalytic NH<sub>3</sub> decomposition may be caused by the Fe<sub>3</sub>NiN phase.

# 4.1. Kinetic analysis

To elucidate the superior activity of Fe-Co and Fe-Ni catalysts in thermal and plasma catalytic NH<sub>3</sub> decomposition, respectively, we conducted tests on above catalysts at a tenfold higher space velocity using both thermal and plasma catalysis. The elevated space velocity condition ensures NH<sub>3</sub> conversion remains below 20 %, thereby eliminating the influence of surface coverage and gas phase composition on the reaction kinetics. The reason for choosing different temperature ranges (420–600 °C for thermal and 360–460 °C for plasma) is to ensure similar conversion degrees under thermal and plasma catalysis conditions. Consequently, the rate of NH<sub>3</sub> decomposition could be utilized to

calculate the apparent activation energy (Ea) of the  $NH_3$  decomposition reaction through the Arrhenius equation.

Fig. 8A illustrates the Arrhenius plots of the Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts in thermal catalytic NH<sub>3</sub> decomposition, while Fig. 8B shows the Arrhenius plots of the Fe-Co bimetallic catalysts with varying Fe/Co ratio. Notably, the 5Fe-5Co catalyst exhibits the lowest Ea (Table 1) for thermal catalytic NH<sub>3</sub> decomposition. In plasma catalytic NH<sub>3</sub> decomposition, the Arrhenius plots of the Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts are shown in Fig. 8C, where the Fe-Ni catalyst exhibits the lowest Ea (Table 1). Based on the NH<sub>3</sub> decomposition rate (at 460 °C) and the number of active sites derived from the NH<sub>3</sub>-TPD results (Fig. 7), we calculated the turnover frequency (TOF) of the catalysts. Table 1 indicates that the Fe-Co catalyst exhibits the highest TOF for thermal catalytic NH<sub>3</sub> decomposition, and the TOFs of the catalysts follow the order Fe-Co > Ni > Co > Fe-Ni > Mo-Co > Mo-Ni > Fe, with the sequence of Ni > Co > Fe aligning with the literature results summarized in the most recent review (Mukherjee

#### Table 1

Apparent activation energy and turnover frequency of  $NH_3$  decomposition over the various catalysts under thermal and plasma catalysis.

Catalysts	Apparent activation energy (kJ/ mol)		Turnover frequency (TOF; $s^{-1}$ ) <sup>a</sup>	
	Thermal catalysis	Plasma catalysis	Thermal catalysis	Plasma catalysis
Fe	93.5	60.8	1.16	2.73
Со	70.8	61.5	2.46	4.61
Ni	66.5	60.5	2.54	3.21
Mo	90.9	65.2	0.97	1.27
Fe-Co	62.9	51.6	2.77	3.75
Mo-Co	79.6	53.6	1.37	2.75
Fe-Ni	69.1	48.5	1.56	5.95
Mo-Ni	76.0	52.6	1.33	2.01

<sup>a</sup>The TOF value was calculated based on the reaction results at 460  $^{\circ}$ C, and the TOF of plasma catalysis has deducted the corresponding NH<sub>3</sub> conversion from plasma alone.



**Fig. 8.** (A-C) Arrhenius plots. (A) Thermal catalytic NH<sub>3</sub> decomposition by Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts; (B) Thermal catalytic NH<sub>3</sub> decomposition by Fe-Co bimetallic catalysts with varying Fe/Co molar ratios; (C) Plasma catalytic NH<sub>3</sub> decomposition over Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts (0.5 g catalyst, 1200 ml/min NH<sub>3</sub>, 144000  $h^{-1}$  space velocity, NH<sub>3</sub> conversion was maintained below 10 %). The apparent activation energy is provided within brackets. (D) The variation of reaction rates with NH<sub>3</sub> partial pressure over Fe-Ni and Fe-Co catalysts (350 °C, Ar as the balance gas).

et al., 2018). The reaction rates of NH<sub>3</sub> decomposition were calculated as a function of its partial pressure, as shown in Fig. 8D. In thermal catalysis, the NH<sub>3</sub> decomposition rate exhibited a linear relationship with its partial pressure, consistent with a first-order reaction. This observation confirms that NH<sub>3</sub> decomposition is indeed a first-order reaction under conventional thermal catalysis. However, under plasma catalysis conditions, the NH<sub>3</sub> consumption rate showed a non-linear relationship with its partial pressure, indicating that the reaction order may fall between first-order and second-order kinetics, suggesting a different reaction mechanism or rate limiting step in plasma-catalytic NH<sub>3</sub> decomposition.

This result strongly suggests that under plasma catalysis, the reaction mechanism and the steps controlling the reaction rate are different from those under thermal catalysis. Plasma catalysis likely allows for a more favorable set of conditions that enable alternative reaction pathways.

The Fe-Ni catalyst exhibits the highest TOF for plasma catalytic NH<sub>3</sub> decomposition, and Table 1 presents the kinetic data revealing two crucial phenomena. (i) The Ea of NH<sub>3</sub> decomposition under plasma catalysis is lower that than for thermal catalysis, suggesting that plasma reduces the Ea during NH<sub>3</sub> decomposition. (ii) The specific catalyst's TOF for NH<sub>3</sub> decomposition under plasma catalysis is significantly higher compared to thermal catalysis, indicating that the plasma enhances the rate of the catalytic cycling. In the case of Fe-Ni, a change in Ea of 20.6 kJ/mol according to the Arrhenius equation should result in a rate change of 30-fold. However, we only observed an approximately 4fold increase in TOF and conversion. The main reason may be the difference in reaction mechanism and rate-limiting step (section 4.4). In thermal catalysis, the rate-limiting step is well-established as the recombination and desorption of adsorbed nitrogen species (N\*). Plasma catalysis, however, involves a more intricate mechanism, and the exact nature of its rate-limiting step remains an ongoing area of research.

#### 4.2. Strength of metal-N binding

To elucidate the reasons for the lowest Ea and the highest TOF in thermal catalytic  $NH_3$  decomposition over Fe-Co catalysts, it is meaningful to clarify the mechanism of thermal catalytic  $NH_3$  decomposition. In thermal catalysis,  $NH_3$  molecules first adsorb on the catalyst surface, gradually dehydrogenate to form adsorbed  $NH_{2ad}$ ,  $NH_{ad}$ ,  $H_{ad}$  and  $N_{ad}$  species (Wang et al., 2015), and finally desorb from the catalyst surface through recombinative desorption (Langmuir-Hinshelwood mechanism) to produce  $H_2$  and  $N_2$ .

We designed temperature program surface reaction (TPSR) experiments for further investigation. Initially, the fresh catalysts (metal oxide) were reduced to metals (or alloys) at 600 °C through H<sub>2</sub> treatment, followed by purging with Ar flow at 450 °C. Subsequently, continuous NH<sub>3</sub> feed was supplied for thermal catalytic NH<sub>3</sub> decomposition (450 °C) over the samples for 1 h. Afterward, the above samples were cooled to 250 °C and maintained at this temperature for 1 h under Ar atmosphere, resulting in abundant adsorbed N<sub>ad</sub>, H<sub>ad</sub>, NH<sub>ad</sub>, NH<sub>2ad</sub> and NH<sub>3ad</sub> species on the surface of the catalysts. Finally, using a mass spectrometer (MS), we examined the desorption of N<sub>2</sub> and H<sub>2</sub> (in Ar atmosphere) with a temperature program ranging from 250 °C to around 780 °C at a heating rate of 10 °C/min.

The MS signal in Fig. 9 exhibits the N<sub>2</sub> generation resulting from recombinative desorption reaction of adsorbed NH<sub>2ad</sub>, NH<sub>ad</sub> and N<sub>ad</sub> species on the catalysts surface, and the accompanying signal of H<sub>2</sub> formation is exhibited in Fig. S15. A comparison of the initial N<sub>2</sub> formation and desorption temperatures (indicated by arrows) between Mo and Fe catalysts (490 °C and 450 °C, respectively) and the surfaces of Co and Ni catalysts (335 °C and 390 °C, respectively) indicates varying M–N binding energies. Specifically, Mo and Fe catalysts display relatively strong M–N binding energies, whereas Co and Ni catalysts are relatively weak. This discrepancy leads to the easier recombinative desorption of adsorbed NH<sub>2ad</sub>, NH<sub>ad</sub> and N<sub>ad</sub> on the Co and Ni catalysts surfaces, which may be the essential reason for the higher Ea and lower



Fig. 9. MS signal of N<sub>2</sub> formation during TPSR experiments.

TOF observed on the surfaces of Mo and Fe catalysts during thermal catalysis (Table 1).

Bimetallic catalysts (Fe-Co, Mo-Co, Fe-Ni and Mo-Ni) generally exhibit lower initial temperatures of N<sub>2</sub> formation compared to monometallic catalysts, with the exception of Co. Specifically, the initial N<sub>2</sub> desorption temperatures on Fe, Fe-Co and Co catalysts are 450 °C, 360 °C and 335 °C, respectively. This suggests that combining one metal with weak metal-N binding energy (e.g., Co and Ni) and another metal with strong metal-N binding energy (e.g., Fe and Mo) results in bimetallic catalysts with moderate metal-N binding energy. Furthermore, the dominant N<sub>2</sub> desorption peak temperatures on Mo-Ni, Fe-Ni and Mo-Co catalysts are somewhat higher than on Fe-Co catalyst, indicating that the recombinative desorption of adsorbed NH<sub>2ad</sub>, NH<sub>ad</sub> and N<sub>ad</sub> on Fe-Co catalysts is easier than on Mo-Ni, Fe-Ni and Mo-Co catalysts.

The NH<sub>3</sub> decomposition activity is not only closely related to the metal-N binding strength, but also to the adsorption strength of NH<sub>3</sub> molecules on the active sites. Generally, strong chemisorption of NH<sub>3</sub> indicates an outstanding capability of the catalysts in activating NH<sub>3</sub> and transforming it into adsorbed NH<sub>2ad</sub>, NH<sub>ad</sub> and N<sub>ad</sub> species. As shown in Fig. 7A, the initial temperature of NH<sub>3</sub> desorption from the catalysts follows the sequence Mo < Mo-Co < Mo-Ni < Co < Fe-Ni < Fe-Co < Fe < Ni (see arrows), which suggests that the Ni, Fe, Fe-Co and Fe-Ni catalysts exhibit a relatively strong capability in adsorbing NH<sub>3</sub>. In contrast, the Mo, Mo-Co, Mo-Ni and Co catalysts show a relative weak capability in adsorbing NH<sub>3</sub> molecules.

NH<sub>3</sub> desorption competes with NH<sub>3</sub> adsorption and subsequent recombinative desorption of NH<sub>2ad</sub>, NH<sub>ad</sub> and N<sub>ad</sub>·NH<sub>3</sub> molecules with a weak chemisorption on the catalyst surface usually do not result in NH<sub>3</sub> decomposition, as they can easily desorb before further dehydrogenation and recombinative desorption can take place. In addition, it is reported that the recombinative desorption of N is the rate-limiting step in thermal catalytic NH<sub>3</sub> decomposition on a non-noble metal surface (Hansgen et al., 2010, Mukherjee et al., 2018, Schueth et al., 2012). The metal-N binding is too strong for N to recombine and desorb from the catalyst surface. The trade-off effect significantly influences the adsorption and desorption of N, and the trade-off between these two factors leads to an optimized catalyst (Xie et al., 2019). Therefore, only a catalyst with both a strong capability in activating NH<sub>3</sub> (strong chemisorption of NH<sub>3</sub>) and a weak metal-N binding strength can exhibit excellent activity in thermal catalytic NH<sub>3</sub> decomposition. In brief, the

Fe-Co catalyst has both a strong capability in activating  $NH_3$  and a weak metal-N binding strength, attributed to the formation of an FeCo alloy phase. Consequently, the Fe-Co catalyst exhibits a better activity than the other seven catalysts in thermal catalytic  $NH_3$  decomposition, as it is highly favorable for all of the adsorption, surface reaction, and desorption steps of  $NH_3$  decomposition.

#### 4.3. Interaction between plasma and catalysts

As shown in Fig. 3, all catalysts exhibit synergy with plasma in  $NH_3$  decomposition, which can be attributed to the capacity of plasma to reduce Ea and enhance TOF values (Table 1). However, the extent of synergistic capacity, the Ea and TOF vary among the catalysts, with the Fe-Ni catalyst showing the strongest synergistic capacity, the lowest Ea and the highest TOF.

To understand why Fe-Ni performs as the most effective catalyst in plasma catalytic NH<sub>3</sub> decomposition, it is essential to comprehend the mechanism of plasma catalytic NH3 decomposition. As previously reported (Huang et al., 2023), in plasma catalytic NH<sub>3</sub> decomposition, the NH<sub>3</sub> molecules are initially activated by energetic electrons, leading to excited NH3\*, NH2 and NH species. These highly reactive species rapidly adsorb on the catalysts surface and dehydrogenate into adsorbed NH<sub>2ad</sub>, NH<sub>ad</sub>, H<sub>ad</sub> and N<sub>ad</sub> species (the adsorption step is enhanced by plasma). After that, the gas phase active species (NH<sub>3</sub>\*, NH<sub>2</sub> and NH) react with the adsorbed NH<sub>2ad</sub>, NH<sub>ad</sub>, H<sub>ad</sub> and N<sub>ad</sub> species through a Eley-Rideal (E-R) mechanism. Finally, the produced intermediates (e.g. N<sub>2</sub>H<sub>2</sub>) can easily decompose into adsorbed N2 and H2. In summary, the plasma accelerates the rate-limiting step (recombinative desorption of Nad) through an additional reaction path (E-R mechanism) resulting from the interaction between the plasma and the catalyst. As a result, the interaction between the excited species (NH<sub>3</sub>\*, NH<sub>2</sub> and NH) and the catalyst surface plays a critical role in determining the activity of plasma catalytic NH<sub>3</sub> decomposition. Thus, we designed the following experiments to compare the interaction between catalysts and plasma.

In-situ optical emission spectroscopy (OES) was employed to diagnose the NH<sub>3</sub> plasma in the absence and presence of the catalyst. To ensure that the OES results were not affected by NH<sub>3</sub> conversion (i.e., gas composition, which can lead to different OES intensity), a lens was installed in the DBD reactor near the inlet of the feed gas (Fig. S1). The distance between the head of the lens and the upper edge of plasma area was precisely fixed precisely at 4 cm. In the absence of a catalyst, molecular bands of NH<sub>3</sub>\* (564–567 nm),  $\bullet$ NH<sub>2</sub> (610–670 nm and 720–780 nm) and  $\bullet$ NH (336 nm) were observed (Fig. S1 6) (Watson et al., 1986; Yi et al., 2019), which demonstrates that ground state NH<sub>3</sub> molecules were excited and dissociated in the plasma. However, in the presence of the catalysts, the OES intensity was dramatically reduced (Fig. S1 7). This reduction was attributed not only to the shielding effect by the packed solid catalysts, but also to the adsorption of the excited species on the catalyst surface.

Fig. 10 clearly illustrates that the intensity at 564 nm (i.e., the 564–567 nm band associated with the NH<sub>3</sub> Schuster's band) decreases in the order Ni > Mo > Mo-Ni > Fe-Co > Fe > Mo-Co > Co > Fe-Ni. The effect is somewhat more pronounced for the 5Fe-5Ni catalyst, indicating that more excited species (NH<sub>3</sub>\*, and the same applies to •NH<sub>2</sub> and •NH) adsorbed on the surface of the latter catalyst compared to the other catalysts. Indeed, a similar trend was observed for the intensities originating from the •NH<sub>2</sub> and •NH species.

Interestingly, the synergistic capacity of the catalysts follows exactly the opposite order: Ni < Mo < Mo-Ni < Fe-Co < Fe < Mo-Co < Co < Fe-Ni, as indicated in Fig. 10A as well, with the most significant difference observed for the Fe-Ni catalyst. In addition, the TOF enhancement induced by plasma (i.e., TOF of plasma catalysis minus TOF of thermal catalysis) also exhibits the opposite order of the OES intensity, except for the Ni catalyst (which may be caused by the smallest number of active sites), as shown in Fig. 10B. This implies that the synergistic capacity of the catalyst is directly related to the capability of the catalyst in adsorbing reactive plasma species (either excited species or radicals). In conclusion, the stronger the capability in adsorbing reactive plasma species, the higher the synergistic capacity of the catalyst and the higher the TOF of NH<sub>3</sub> decomposition on the catalysts.

In summary, in NH<sub>3</sub> plasma, a portion of ground state NH<sub>3</sub> is preactivated into highly reactive species (NH3\*, NH2 and NH). Compared to ground state NH<sub>3</sub>, these reactive species possess a weaker N-H bond energy and a longer N-H bond, providing a greater possibility and energy advantage to interact with the catalysts surface, which can explain the reduced Ea and enhanced TOF (Table 1). However, the question remains why the Fe-Ni catalyst exhibits more potential in adsorbing the reactive plasma species (NH3\*, NH2 and NH) than the other seven catalysts. In the nanoparticles of the Fe-Ni catalyst, both Fe and Ni atoms were observed (Fig. 6). Typically, Fe atoms form iron nitride, showing a strong interaction with N atoms, as supported by the XRD results (Figs. S6–S8) and the high temperature of  $N_2$  desorption from the Fe catalyst surface (Fig. 9). On the other hand, Ni catalysts are generally known for being excellent catalyst in hydrogenation and/or dehydrogenation reactions, due to the strong interaction between Ni atoms and H atoms. Therefore, when the Fe-Ni catalyst is exposed to NH<sub>3</sub> plasma, the highly reactive plasma species (NH3\*, NH2 and NH) can be rapidly adsorbed by the FeNi alloy particles. In other words, in plasma-catalytic NH<sub>3</sub> decomposition, the plasma species (NH<sub>3</sub>, •NH<sub>2</sub> and •NH) can be efficiently utilized by the Fe-Ni bimetallic alloy catalysts to trigger the E-R reaction for NH<sub>3</sub> decomposition, although the sites were too weak for surface reactions in thermal-catalytic NH3 decomposition, as evidenced by the challenging desorption of N<sub>2</sub> (Fig. 9). This explains why the Fe-Ni catalyst exhibits better activity than the other catalysts in plasma-



**Fig. 10.** Correlation between the OES intensity of the NH<sub>3</sub> Schuster band (red squares, left axis) and the (A) synergistic capacities of the catalysts in plasma catalytic NH<sub>3</sub> decomposition and (B) TOF enhancement by plasma, for the various catalysts investigated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

# catalytic NH3 decomposition.

#### 4.4. Final consideration

Plasma-catalytic NH<sub>3</sub> decomposition can significantly lower the reaction temperature more than 100 °C at the same conversion, as compared to thermal catalysis, which is attributed to the fact that reactive plasma species can regulate the catalyst surface reactions via the E-R mechanism, accelerating the reaction process. The gas reactive plasma species (NH<sub>3</sub>\*, NH<sub>2</sub> and NH) could easily desorb N atoms on the catalyst surface through the E-R process (Engelmann et al., 2021; Liu et al., 2022).

The characterization results reveal that the optimal catalyst for plasma-catalytic ammonia decomposition is Fe-Ni/SiO<sub>2</sub> (the highest NH<sub>3</sub> conversion) with Fe<sub>3</sub>NiN being the active phase during the reaction. Therefore, the pure Fe<sub>3</sub>NiN catalyst was synthesized using a nitridation process of NiFe<sub>2</sub>O<sub>4</sub> sample (Supplementary Information), and its performance and TOF in the NH3 decomposition reaction was evaluated. However, the Fe<sub>3</sub>NiN catalyst shows a lower conversion and TOF value than Fe-Ni/SiO<sub>2</sub> catalyst (Figs. S18–S20). Despite that "active component" achieves full filling within the plasma zone, which appears favorable at the microscopic scale, it is crucial to consider the electrical properties of catalysts. A higher relative dielectric constant implies a stronger ability to accumulate surface electrons in the solid material, thereby weakening the net electric field and resulting in an reduced induced electric field, especially for the supports with large  $\varepsilon_d$  values (Wang et al., 2015). The relative dielectric constant of Fe<sub>3</sub>NiN and Fe-Ni/SiO<sub>2</sub> is measured to be 29.7 and 17.3, respectively. The difference in activity between Fe-Ni/SiO2 and Fe3NiN is indeed attributed to variations in exposed active sites and the relative dielectric constants. As a result, the performance of plasma catalysis is significantly influenced by both the loading of the active component and the electrical properties of the catalyst.

# 5. Conclusions

In summary, the Fe-Co bimetallic catalyst shows optimal activity in thermal catalytic NH<sub>3</sub> decomposition, while the Fe-Ni bimetallic catalyst exhibits the most favorable performance in plasma catalytic NH3 decomposition. The activities of the catalysts in thermal catalysis are significantly linked to the physicochemical properties, including particle size, metal-N binding energy, and NH<sub>3</sub> adsorption strength. Specifically, strong NH<sub>3</sub> adsorption and weak metal-N binding are found to be favorable for thermal catalytic NH<sub>3</sub> decomposition. Moreover, plasma catalysis involves not only the determination of the physicochemical properties of the catalysts (with particular attention to the influence of relative dielectric constant on discharge) but also their interaction with the reactive plasma species. Notably, a strong interaction with the plasma species is observed to reduce the apparent activation energy, enhance the turnover frequency of the reaction, and ultimately promote the plasma catalytic activity. These findings underscore the importance of comprehending the intricate interplay between catalyst properties and plasma interactions in catalyst design for plasma catalysis applications. In addition, this study emphasizes the need for tailored catalyst optimization based on the specific catalytic environment to achieve enhanced performance in plasma catalytic processes.

#### 6. Authorship contribution statement

Shengyan Meng: Conceptualization, Data curation, Formal analysis, Writing – review & editing. Shangkun Li: Data curation, Formal analysis, Software. Shuaiqi Sun: Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft. Annemie Bogaerts: Formal analysis, Resources, Data curation, Writing – review & editing, Supervision, Funding acquisition. Yi Liu: Formal analysis, Resources, Writing – review & editing, Supervision. Yanhui Yi: Conceptualization, Validation, Formal analysis, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

# CRediT authorship contribution statement

**Shengyan Meng:** Conceptualization, Data curation, Formal analysis, Writing – review & editing. **Shangkun Li:** Data curation, Formal analysis, Software. **Shuaiqi Sun:** Conceptualization, Data curation, Formal analysis, Methodology, Writing – original draft. **Annemie Bogaerts:** Formal analysis, Resources, Data curation, Writing – review & editing, Supervision, Funding acquisition. **Yi Liu:** Formal analysis, Resources, Writing – review & editing, Supervision. **Yanhui Yi:** Conceptualization, Validation, Formal analysis, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

No data was used for the research described in the article.

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# Appendix A. Supplementary data

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