

Probing the Metal/Oxide Interface of IrCoCeO_x in N₂H₄·H₂O Decomposition: An Experimental and Computational Study

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Significance and Relevance

This work aims to disclose the complex mechanism at the metal/oxide interface in boosting the hydrogen production from hydrous hydrazine in presence of NaOH. To this end, cobalt-ceria oxides doped with Ir where used as a catalyst in this reaction. A complete characterization combined with robust computational modelling was employed to unveil the processes at the Ir/Co interfaces. Moreover, the role of NaOH was studied operando with ATR-IR. We expect these results to help designing and adapting catalytic systems with improved performances in nitrogen hydrides decomposition, positively impacting the mild-CO-free H₂ production.

Preferred and 2^{nd} choice for the topic: (1^{st}) H_2 storage and transportation, green H_2 production, hydrogen vectors (2^{nd}) Fundamental advances in understanding catalysis. Preferred presentation: Oral preferred

Introduction and Motivations

Liquid Hydrogen Carriers (LHCs) are chemical compounds easily storable and transportable with a high intrinsic hydrogen content, which can be released at mild conditions. Many LHCs exist, but the need to reduce net carbon emissions has led to a focus on nitrogen-hydrides. In particular, hydrous hydrazine (N_2H_4 · H_2O) possesses a hydrogen content as high as 8 wt.%, and its decomposition produces either molecular hydrogen and nitrogen or ammonia and nitrogen, which is the thermodynamically favoured process.¹ Great efforts have been made to improve the catalytic activity and selectivity of catalysts for this reaction. Non-noble metals (Ni, Co, Fe) present high selectivity at the cost of lower catalytic activity², whereas noble metals, such as Ir, Ru and Pt, are well known for their high catalytic activity but rather low selectivity. In recent years, noble/non-noble bimetallic systems have attracted interest, achieving high catalytic activity and enhanced selectivity.³ Furthermore, although no clear mechanistic explanation is present in the actual literature, the presence of NaOH in the reaction mixture is known to increase the activity and enhance the H₂ production.⁴

Herein, an iridium–cobalt–cerium (IrCoCeO_x) composite was synthesized and compared to CoCeO_x, CeO₂, and IrCeO₂ to probe the performance of the metal-oxide interfaces in batch N₂H₄·H₂O decomposition. The combination of kinetic batch results, comprehensive characterization by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and HR-TEM and density functional theory (DFT) help us elucidate the role of Ir/CoO interfaces in boosting N₂H₄·H₂O decomposition and promoting H2 production. Moreover, operando attenuated total reflectance infrared (ATR-IR) analysis was employed to investigate the nature of adsorbates at the solid–liquid interfaces of IrCoCeO_x. The formation of Co-hydroxyl and -imido species was directly correlated to the enhanced H₂ productivity through preferential breakage of the N–H bond of N₂H₄·H₂O due to NaOH.

Results and Discussion

From the kinetic experiments, see Figure 1a, we observed that the catalyst is active only when Co is present. Moreover, the presence of Ir clearly boosted the performances, resulting in a 5-fold increasing of catalytic activity. The effect of NaOH was also demonstrated for IrCoCeOx comparing the reaction performed in aqueous NaOH and pure H₂O, see Figure 1b. Here, the effect of the base is clear in enhancing the activity and H₂ selectivity. The combination of different characterization techniques (i.e. XPS, CO-DRIFT and XANES) and especially the tandem analyses of the FT-EXAFS (Figure 1c) signal



revealed a Co-Ir charge transfer. Considering the complete inactivity of the Ir/CeO_2 , we attributed the performances enhancement to such interaction. This was also confirmed by density functional theory calculation, using NH₃ as a probe molecule to investigate the active sites. Mechanistic insights on the role of NaOH at the Ir/CoO interface were obtained through operando ATR-IR. NaOH operates on the catalyst surface, enhancing the cooperation between vicinal Brønsted basic (Co–O–Co) and Lewis acidic (O–Co–O) sites of the Ir/CoO interface, inducing a preferential breakage of the N–H bond, i.e., higher H₂ productivity, through Co hydroxyls and imido groups, see Figure 1d.



Figure 1. Kinetic profiles for the batch N_2H_4 · H_2O decomposition reaction: **(a)** Comparison between catalysts (NaOH 0.5 M) and **(b)** Effect of NaOH on IrCoCeOx. **(c)** k2-weighted Ir–L3 and Co–K edge phase shift corrected FT-EXAFS of IrCoCeOx and **(d)** Phase resolved ATR-IR spectra from modulation experiments of N_2H_4 · H_2O decomposition on IrCoCeOx in water (blue) and 5:1 mol/mol of NaOH (red).

In conclusion, two different take home messages emerge from this study: (1) CoOx is the active phase of the catalyst, and Ir induces an enormous increase in the activity and H_2 selectivity, (2) the presence of NaOH can greatly enhance the catalytic properties of the material. In our case this effect is due to concerted role of vicinal Brønsted basic and Lewis acidic sites, which induces a higher H_2 selectivity due to the preferential breakage of the N-H bond of hydrazine.

References

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