



Role of Iron on the Structure and Stability of Ni_{3.2}Fe/Al₂O₃ during Dynamic CO₂ Methanation for P2X Applications

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An energy scenario, mainly based on renewables, requires efficient and flexible Power-to-X (P2X) storage technologies, including the methanation of CO₂. As active Ni⁰ surface sites of monometallic nickel-based catalysts are prone to surface oxidation under hydrogen-deficient conditions, we investigated iron as “protective” dopant. A combined *operando* X-ray absorption spectroscopy and X-ray diffraction setup with quantitative on-line product analysis was used to unravel the structure of Ni and Fe in an alloyed Ni–Fe/Al₂O₃ catalyst during dynamically driven methanation of CO₂. We observed that Fe protects Ni from oxidation and is itself more dynamic in the oxidation and reduction process. Hence, such “sacrificial” or “protective” dopants added in order to preserve the catalytic activity under dynamic reaction conditions may not only be of high relevance with respect to fine-tuning of catalysts for future industrial P2X applications but certainly also of general interest.

Renewable energy sources, such as wind and solar, provide a sustainable solution to the ever-growing demand for energy.^[1] To ensure an overall grid stability, their (seasonal) fluctuations must be balanced.^[2] P2X storage technologies represent one option to overcome this problem. Energy can be stored e.g. as Fischer-Tropsch products, methanol or synthetic natural gas (SNG).^[3] For SNG, the existing and long-ranging gas grid can be used for low-cost storage and distribution. Within the “power-to-gas” process chain, excess renewable electric power is catalytically converted to methane, a chemical energy carrier (Sabatier reaction, [Equation (1)]).^[4]



Renewable H₂ from electrochemical water splitting,^[5] and CO₂, e.g. from biomass gasification or industrial exhaust gases,^[6] can be used as reactants for this catalytic process. The production of hydrogen via electrolysis in a renewable energy scenario depends directly on weather-related fluctuations, especially when produced in decentralized plants with small H₂-buffer tanks.^[1b,2] As these fluctuations are transferred to the reactor bed and the catalytic system, efficient and stable catalysts that can withstand the highly dynamic and demanding P2X conditions are required. Catalysts based on nickel are commonly used and have been extensively studied under stationary reaction conditions, providing satisfactory catalytic activity at low cost.^[7] Recently, the dynamics of these systems have received growing attention in research.^[8] It was concluded that during short-term H₂-dropouts the preservation of the catalytically active Ni⁰ species and especially the removal of oxygen from the catalytic surface were crucial for maintaining the catalytic activity. One possible approach to protect Ni⁰ from forming surface oxygen species is the addition of a second “sacrificial” or “protective” metal with a higher affinity to oxygen, such as iron. Under stationary reaction conditions, we recently found that by addition of iron the catalyst exhibited improved long-term stability and superior CO₂ conversion compared to a monometallic nickel catalyst.^[9] This additionally motivates to characterize the role of iron in detail in such a bimetallic Ni–Fe catalyst, especially under dynamic reaction conditions, as present in P2X applications. By combining X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) as powerful *operando* tools with quantitative product analysis in a single experiment, we aimed at revealing the role of iron in this system. To our knowledge, the role of a “sacrificial” or “protective” metal in order to preserve the catalytically active species has not yet been investigated with in-depth *operando* studies under dynamic reaction conditions for bimetallic Ni–Fe/Al₂O₃ catalysts in the methanation of CO₂.

Therefore, we prepared two model catalysts, consisting of 17 wt% Ni_{3.2}Fe/Al₂O₃ and 17 wt% Ni/Al₂O₃ by precipitation with urea^[9] with similar particle size for good comparability. In order to obtain information about the structural changes of amorphous as well as crystalline phases, we performed alternately *operando* XAS- and XRD experiments at the beamline BM31 (ESRF) using a micro quartz capillary setup^[10] and a micro-GC for quantitative on-line gas analysis (details in ESI, Figure S1). Prior to the catalytic experiments, the catalysts were activated

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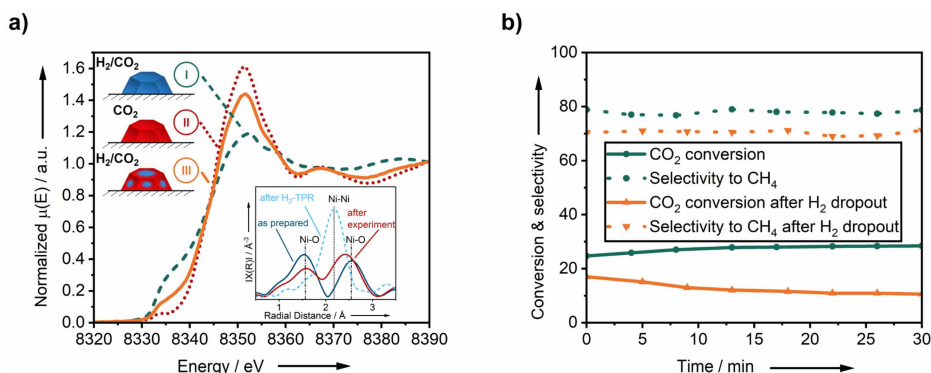


Figure 1. Operando Ni–K edge XANES spectra and k^2 -weighted FT-EXAFS spectra after activation and after the experiment (a), simultaneously measured catalytic performance (b) of Ni/Al₂O₃ during methanation of CO₂ before (I), during (II) and after (III) a simulated H₂-dropout. Reaction conditions: T = 350 °C, p = 1 bar, 30 mL min⁻¹ total flow; Methanation: H₂/CO₂/N₂ = 4/1/5, H₂-dropout: CO₂/N₂ = 1/9.

by temperature-programmed reduction (TPR) with H₂. The experiments were performed at 350 °C and atmospheric pressure. Experimental details including further time-resolved data are given in the ESI.

As an extreme case for dynamic reaction conditions during P2X applications, we simulated H₂ dropouts for 70 minutes in the reactant feed gas mixture during the methanation of CO₂. When we performed the experiment with the monometallic Ni/Al₂O₃ catalyst, we achieved a CO₂ conversion of 28% (79% selectivity to CH₄, see Figure 1b) under stationary reaction conditions (350 °C, 1 bar). The only detected by-product was CO. Since no differences between the Ni–K XANES spectra (Figure 1a, for time-resolved see Figure S2 in the ESI) recorded after TPR (–) and during methanation (– –) were observed, the catalyst remained stable during CO₂ methanation. When we simulated hydrogen-lean conditions resulting from a H₂-dropout (•••), the shift of the pre-edge feature (Ni⁰ at 8333 eV) and the increasing whiteline at 8350 eV in the Ni–K XANES spectra in Figure 1a indicate that nickel is in the oxidation state 2+. According to linear combination analysis (LCA), ~96% of the Ni⁰ species were oxidized to Ni²⁺. As it is difficult to distinguish between oxygen and carbon species by EXAFS, we simultaneously followed the formation of NiO or NiCO₃ species by XRD. NiO (2 Θ = 11.7° and 19.5°, cf. Figure S2d) was the only detectable oxidized nickel phase, thus, a significant formation of carbonates during the H₂ dropout using technical grade CO₂/N₂ could be excluded. During the subsequent methanation step, ~35% of Ni⁰ were recovered (~76% Ni⁰ before H₂ dropout) resulting in a CO₂ conversion of 11% (~28% before H₂ dropout). Since only minor sintering occurred (crystallite size estimated by Scherrer equation: 3.4 nm to 3.9 nm) and the decrease in Ni⁰ species directly correlates to the loss in activity, we can conclude that the active species for the conventional Ni-based catalyst is the reduced Ni⁰. The oxygen species either originating from CO₂ dissociation,^[8c,11] or from oxygen impurities in the technical grade gas feed might be responsible for the formation of the NiO species and are therefore critical for monometallic nickel catalysts.

To protect the active Ni⁰ species from oxidation by surface oxygen species, we modified the catalyst by adding a second metal which, compared to Ni, thermodynamically favors the formation of an oxide species. In this case iron was used, as bimetallic Ni–Fe/Al₂O₃ catalysts recently showed promising activity and long-term stability in the stationary methanation of CO₂.^[9,12] In this study, the prepared 17 wt% Ni_{3.2}Fe/Al₂O₃ catalyst reached 56% CO₂ conversion (97% selectivity to CH₄, see Figure 2d) during methanation of CO₂ at 350 °C at 1 bar, which was significantly higher compared to the monometallic nickel catalyst (28%, see Figure 1b). After 60 minutes of CO₂ methanation (full data set, cf. ESI in Figure S3), a H₂-dropout was applied for 70 minutes using the same gases, setup and reaction conditions as for the monometallic Ni catalyst. During the H₂ dropout, the increasing whiteline intensities in the Ni–K and Fe–K XANES spectra (Fe–K measured in fluorescence mode) in Figure 2 and Figure S4 demonstrated a slight oxidation of Ni⁰ to Ni²⁺ (~7% to 11%) and of Fe⁰ to Fe²⁺ (~33% to 47%). This moderate oxidation is also visible in the operando XRD pattern (Figure 2c), where the intensity of the Ni (200) reflection at 2 Θ = 15.95° slightly decreased during the H₂ dropout. A slight shift of the Ni(200) reflection was observed, which might represent the formation of a Ni-rich alloy, as some Fe migrated to the surface under formation of Fe²⁺.^[13] We can assume that mainly FeO was formed, similar to the oxidation of the monometallic nickel catalyst due to oxygen species present during the H₂ dropout. The preferential oxidation of iron suggests that the less-noble metal acts as a “protective” element in relation to nickel. In addition, according to DFT calculations,^[14] iron can migrate out of a Ni–Fe alloy to the surface to form FeO, if a monolayer of oxygen is present. This explains the hint for dealloying we observed during hydrogen-lean conditions resulting in a larger amount of surface oxygen species in the catalyst bed. Hence, we observe that iron protected the reduced Ni⁰ species from major oxidation by FeO formation, as illustrated in Figure 3 and assumed in the concept of the “protective” less-noble metal dopant. After 70 minutes of H₂ dropout conditions, the catalyst was re-exposed to methanation conditions. Surprisingly, in the

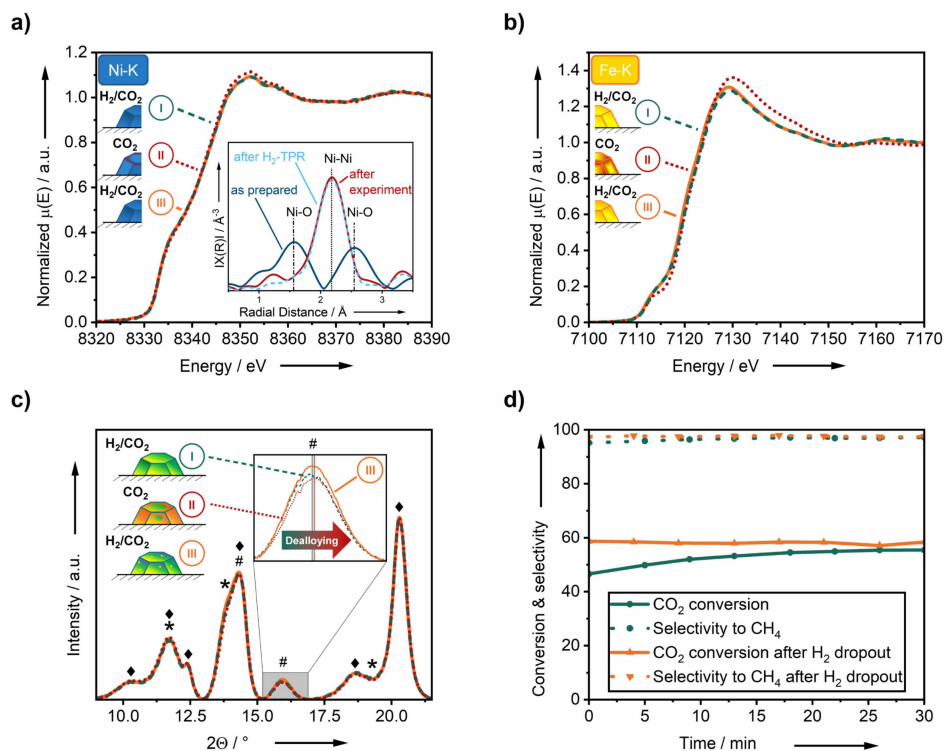


Figure 2. Simultaneously recorded *operando* Ni–K edge XANES spectra, as well as k^2 -weighted FT-EXAFS spectra after activation and after the experiment (a), Fe–K fluorescence spectra (b), XRD with $\lambda = 0.4943 \text{ \AA}$ (c) and catalytic performance (d) of Ni–Fe/ Al_2O_3 before (I), during (II) and after (III) a simulated H_2 -dropout; Ni (#), NiO (*), γ - Al_2O_3 (♦). Reaction conditions: $T = 350^\circ C$, $p = 1 \text{ bar}$, 30 mL min^{-1} total flow; Methanation: $H_2/CO_2/N_2 = 4/1/5$, H_2 -dropout: $CO_2/N_2 = 1/9$.

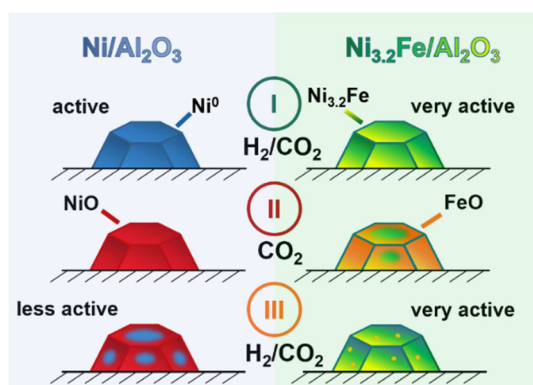


Figure 3. Comparison of the structural changes in a monometallic Ni/ Al_2O_3 and a bimetallic $Ni_{3.2}Fe/Al_2O_3$ catalyst before, during and after a simulated H_2 -dropout during methanation of CO_2 .

bimetallic Ni_xFe_y/Al_2O_3 catalyst both nickel and iron regained the initial oxidation states, as depicted by the XAS data shown in Figure 2a and Figure 2b. However, the dealloying observed during the H_2 dropout might not be entirely reversible, as the Ni(200) reflection in Figure 2c seemed not to fully return to its initial position. Nevertheless, and in contrast to the monometallic Ni catalyst (Figure 1b), the activity of the bimetallic Ni–Fe catalyst was immediately regained after switching to methanation conditions, reaching 58% CO_2 conversion (98% selectivity to CH_4), as demonstrated in Figure 2d. The slightly higher

activity might be related to the increased amount of iron sites at the surface of the catalyst after the H_2 dropout which might change the mechanism of CO_2 activation and its reaction intermediates, as observed during DRIFTS studies on Ni–Fe catalysts.^[15]

In conclusion, the comparison of a monometallic Ni/ Al_2O_3 and a bimetallic $Ni_{3.2}Fe/Al_2O_3$ model catalyst under dynamic reaction conditions by using an advanced combination of *operando* XAS and XRD with quantitative on-line product analysis elucidated the important role of iron. During the simulated H_2 -dropout the monometallic nickel catalyst was prone to form surface oxygen species resulting in an irreversible formation of NiO leading to catalyst deactivation during the subsequent methanation step. This provides evidence that Ni^0 sites e.g. at edges/corners of the particles, that are prone to oxidation, are protected or assisted in the re-reduction. By introducing the concept of adding a less-noble “sacrificial” or “protective” metal, such as iron, we were able to preserve the catalytically active species and revealed in detail the role of iron by using advanced X-ray based techniques: The active Ni^0 species was protected from oxidation during the simulated H_2 dropout by preferential formation of FeO (Figure 3). Surprisingly, both metals were completely reduced again in the subsequent methanation step. This resulted in a fully recovered catalytic activity. The use and the understanding of the role of less-noble metals as dopants in order to preserve the active catalytic species from deactivation due to oxidation under transient reaction conditions represents a major step forward in

the design of future P2X catalysts and may be used as a concept in other applications as well. Our results furthermore show that it is very important to establish such structure-activity relationships by a) using complementary synchrotron-based *operando* techniques such as XAS and XRD to characterize both amorphous and crystalline phases and b) combining them in one experiment with quantitative product analysis, since the structure depends on the reaction conditions.

Further in-depth *operando* spectroscopic studies would be helpful to deepen the investigation both with respect to the role of iron in the CO₂ activation mechanism and of less noble promoters as sacrificial metal dopants to generalize the concept.

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Conflict of Interest

The authors declare no conflict of interest.

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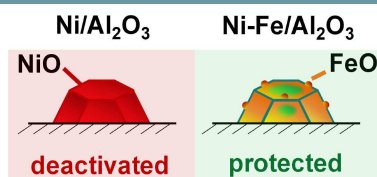
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COMMUNICATIONS

Iron as protective hero: In an energy scenario based on renewables, new and efficient storage technologies, such as Power-to-Gas (PtG) are needed. However, monometallic Ni catalysts are highly sensitive to dynamic reaction conditions, as present in Power-to-X applications. In this *operando* study we investigated the deactivation of a Ni-based catalyst and unraveled the protective role of “sacrificial” iron in a Ni_{3,2}Fe catalyst during dynamic methanation of CO₂.



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