



Bimetallic Nickel and Cobalt nanoparticles supported on TiO₂ as catalyst for the synthesis of 2-substituted benzimidazole by reductive amination-cyclization of 2-nitroaniline and aldehydes

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ARTICLE INFO

Keywords:

Thermal assisted reduction
Bimetallic catalyst
Catalytic tandem reaction
Benzimidazole

ABSTRACT

The benzimidazole nucleus finds respectable space and interest among nitrogen heterocycles, whether for its applications or the number of synthetic methodologies employed in their preparation. Recent trends show that interest in the scientific fraternity is now bending towards exploring the use of bimetallic NiCo-based heterogeneous catalysts for the synthesis of benzimidazoles. This work is aimed at the development of new catalytic systems obtained from the H₂-assisted reduction of Ni_xCo_{1-x}TiO₃ mixed oxides to produce bimetallic Ni_xCo_{1-x}/TiO₂ (x = 0.0, 0.1, 0.3, 0.5, and 1.0) catalysts for the tandem selective production of 2-substituted benzimidazole scaffolds from 2-nitroaniline and aldehydes. The physicochemical characterization displayed the formation of the NiCo alloy supported on TiO₂-rutile and the active phase are almost in the zero-valent state after the reduction treatment. The catalytic activity showed that all the catalysts are active in the tandem synthesis of 2-benzimidazole, and the selectivity to the target product is a function of the Ni content in the catalyst. The most efficient and selective system was Ni_{0.1}Co_{0.9}/TiO₂, which remained active after 10 consecutive cycles. The Ni_{0.1}Co_{0.9} composition in the catalyst formulation affords optimal physicochemical properties for enhanced catalytic performance and enables the recyclability ability to produce the target product. Thus, our results provide a valuable and practical method by which aromatic N-heterocycles of pharmaceutical relevance can be obtained via catalytic tandem reaction using non-noble based catalysts.

1. Introduction

2-Substituted benzimidazoles are important organic molecules that serve as building blocks in the preparation of antiviral, anticancer, antiulcer, antihypertensive, antifungal, and antihistamine drugs [1]. Traditionally, these compounds have been obtained by two main synthetic routes: (1) through the coupling of o-phenylenediamines with carboxylic acids or their derivatives using conditions that require high temperatures and strong acidic conditions [2] (2) one-pot synthesis from 1,2-dinitroarenes and aldehydes using a non-noble metal-based catalyst and hydrogen as a reductant [3–5] and (3) from the transfer reduction/dehydrogenation of 2-nitroaniline (2NA) or o-phenylenediamines

(OPHENs) with alcohols [6]. An alternative route that has been developed is the catalytic synthesis of benzimidazoles from consecutive reduction-cyclization-oxidation reactions using 2NAs and benzaldehyde [6–11]. Chao et al. developed AgPd/WO_{2.72} catalysts that realize the synthesis of benzimidazoles from 2NA and benzimidazole at 80°C using formic acid as a reducing agent [12]. Recently, Lin et al. reported a series of cobalt-based carbon supports as catalysts that enable a wide range of highly atom-efficient production of 2-substituted benzimidazoles using H₂ as a reducing agent [13]. In addition, the mechanism and kinetics were demonstrated through experimental and theoretical investigations, as shown in Scheme 1. 2NA was hydrogenated to OPHEN using a heterogeneous catalyst. Subsequently, open condenses with benzaldehyde

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<https://doi.org/10.1016/j.cattod.2025.115416>

Received 15 January 2025; Received in revised form 12 April 2025; Accepted 2 June 2025

Available online 5 June 2025

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(BZ) to produce a 2-(benzylidene amino)aniline (BZA) product. The next pathway involves intramolecular cyclization of the BZA intermediary and subsequent dehydrogenation to yield 2-phenylbenzimidazole (BZI).

Thus, cyclization and oxidative dehydrogenation of BZA can recover H_2 during tandem reactions. This phenomenon is known as pseudo-hydrogen autotransfer or pseudo-borrowing hydrogen, which can provide the temporary transfer of two hydrogen atoms from the BZA to a metallic site on the surface of the catalyst and return those hydrogen atoms to reduce other $-NO_2$ groups to form OPHEN and continue the tandem reaction until the production of the target product. This methodology is a novel and powerful tool for the formation of 2-substituted benzimidazoles.

Remarkably, non-noble-based catalysts have demonstrated excellent results in hydrogenation reactions [14]. Among these, heterogeneous bimetallic nickel-based formulations provide highly efficient and operationally stable catalysts. Lin et al. reported the use of $NiCu/Al_2O_3$ for the N-alkylation of amines with alcohols [15]. Tomer et al. used bimetallic $5Ni-0.5Pd/Al_2O_3$ to afford 90 % conversion and 71 % yield of 1-octylamine (TON = 93) in the amination of 1-octanol with ammonia at $160^\circ C$ for 4 h [16]. However, in the proposed catalytic synthesis of 2-substituted benzimidazoles, H_2 recycled should be used for the reduction of 2NA to avoid the hydrogenation of other molecules, such as BZ ($C=O$ functional group) or BZA ($C=N$ functional group). Liu et al. studied different core@shells based on Ni-Co shells with carbon as a bimetallic catalyst for the hydrogenation of nitroarenes, which produced a highly active and selective system for the hydrogenation of the $-NO_2$ group [17]. In addition, Chen et al. developed a Ni-Co bimetallic formulation that can produce imines or secondary amines by a one-pot hydrogenation-coupling tandem reaction system, controlling the metal composition in the bimetallic formulation [18]. The authors reported that at low Ni content in the bimetallic formulation provides a chemoselective production of imines. This result inspired us to explore this kind of heterogeneous catalyst to produce 2-substituted benzimidazoles because the active phase could promote the formation of the imine encouraging the intramolecular cyclization/dehydrogenation pathway, which enhances the selectivity to the target product (see Scheme 1).

The preparation of bimetallic Ni-Co catalysts require controlled preparation methods to obtain the desired metal composition [19–23]. Among them, the use of precursors such as the ilmenite-like oxide $ATiO_3$, in which the A-site cation is Co or Ni, for the preparation of bimetallic catalysts [24–26]. One interesting feature of these mixed oxides is that their chemical structures can be tuned by partial substitution at the A-sites, which enables the successful production of bimetallic alloys. Moschogiannaki et al. prepared porous Ni-Co supported on titanium nanorods through a solution-based method using ethylene glycol as a photocatalyst for the degradation of ethylparaben, an endocrine-disrupting compound, under simulated solar or visible light irradiation [27]. This method provides an easy synthesis method to produce bimetallic Ni-Co alloys because the catalyst can be prepared easily by a thermally assisted reduction treatment in a manner similar to that reported previously by our research group [26].

In this work, we report the development of novel bimetallic Ni_xCo_{1-x}/TiO_2 prepared by thermal reduction of their corresponding porous quaternary ilmenite-type $Ni_xCo_{1-x}TiO_3$ nanorods precursors

using a wide range of metal concentrations ($0 \leq x \leq 1$). The catalytic activity of the reduced catalysts was evaluated for the synthesis of BZI as a test reaction, employing optimal conditions to provide pseudo-borrowing hydrogen phenomena and improve H_2 recovery during catalytic performance. Among the catalysts examined, $Ni_{0.1}Co_{0.9}/TiO_2$ was the most efficient and selective and was recycled without a significant loss of activity until the 10-reaction cycle or leaching of the metallic species. A series of other aldehydes was probed to evaluate the scope of the obtained catalyst for the production of 2-substituted benzimidazole scaffolds. To the best of our knowledge, this is the first report on the use of quaternary-titanate-based nanorods as efficient catalyst precursors in the preparation of such molecules.

2. Experimental

2.1. General information

Cobalt(II) acetate tetrahydrate ($Co(CH_3CO_2)_2 \cdot 4H_2O$), nickel(II) acetate ($Ni(CH_3CO_2)_2 \cdot 4H_2O$), titanium butoxide ($Ti(CH_3CH_2CH_2CH_2O)_4$), and 2NA were obtained from Sigma-Aldrich. Ethyl acetate, isopropanol, benzaldehyde, and ethylene glycol were obtained from Merck. All purchased reagents were used without further purification. The gases H_2 (99.99 %), He (99.99 %), synthetic air, and nitrogen were provided by Linde Chile.

2.2. Synthesis of the $Ni_xCo_{1-x}TiO_3$ precursors

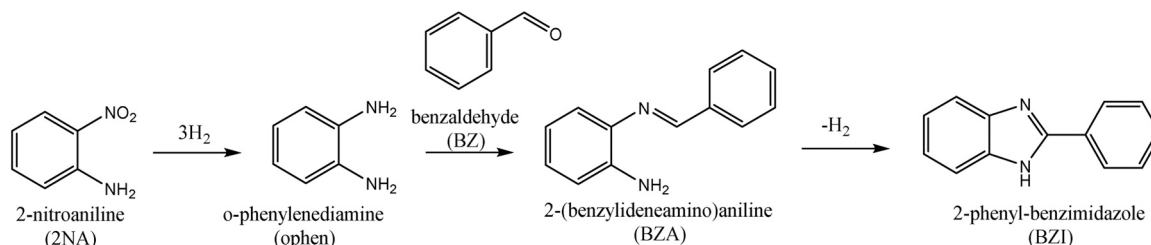
The ilmenite-type precursors with the formula $Ni_xCo_{1-x}TiO_3$ were synthesized using the methodology reported by González-Vera et al. with some modifications [26]. In general, 0.01 mol of $Co(CH_3CO_2)_2 \cdot 4H_2O$, $Ni(CH_3CO_2)_2 \cdot 4H_2O$, and $Ti(CH_3CH_2CH_2CH_2O)_4$ required to achieve a molar ratio of $Co + Ni/Ti = 1$ were dissolved in 60 mL of ethylene glycol/isopropanol (50/50) mixture to form a clear solution of the metal precursors. The nominal molar contents of Ni used corresponded to $x = 0, 0.1, 0.3, 0.5$, and 1. The mixture was stirred for 24 h until a milky dispersion was obtained. Finally, the dispersion was stirred for 10 min and washed with absolute ethanol ($\times 3$) to remove excess ethylene glycol. The recovered solid was dried in an electrical oven at $100^\circ C$ for 12 h and calcined in a static air atmosphere from room temperature to $700^\circ C$ at a heating ramp rate of $5^\circ/min$.

2.3. Synthesis of the Ni_xCo_{1-x}/TiO_2 catalysts

Ni_xCo_{1-x}/TiO_2 catalysts were synthesized using the methodology reported by Bustamante et al. [24]. The calcined material was subjected to an *ex-situ* reduction treatment at $550^\circ C$ using H_2 as the reducing agent for 5 h. Subsequently, the catalyst was transferred to the reactor and quickly immersed in ethyl acetate that had been previously degassed with N_2 to prevent its oxidation. The reduction temperature was selected based on the H_2 -thermal programmed reduction (TPR) results.

2.4. Characterization

Chemical analyses were conducted using inductively coupled plasma



Scheme 1. Proposed reaction pathways for the formation of BZI. Adapted from [10].

(ICP) with an ICP-OES Varian 715-ES instrument. The required amount (0.03–0.05 g) of the samples was previously dissolved in a concentrated $\text{HNO}_3\text{:HCl:HF} = 1\text{:}1\text{:}1$ acid solution and diluted with distilled water until the optimal concentration that aligns with the limit of detection of the equipment.

TPR was performed using a TPR/TPD 2900 Micromeritics system equipped with a thermal conductivity detector (TCD). Two reduction profiles were recorded. In the first (H_2 -TPR1), TPR data was recorded for 0.050 g samples of the calcined $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursors using a 5 % H_2/Ar flow of 40 mL/min and a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 800°C . In the second (H_2 -TPR2), 0.050 g samples of the calcined $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursors were first thermally reduced in the TPR equipment using the same experimental conditions as in the preparation of the $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ materials (pure H_2 flux of 30 mL/min, heating from room temperature to 550°C at $10^\circ\text{C}/\text{min}$ for 5 h). After the reducing treatment, the samples were cleaned at 100°C under an Ar flow for 2 h, and TPR data from a second run using the H_2 -TPR1 conditions was recorded. Thus, the H_2 -TPR1 data represent the complete reduction of Co and/or Ni species in the precursor materials, and the H_2 -TPR2 data represent the Co and Ni reduction in the prepared $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalysts.

The specific areas were calculated using the Brunauer-Emmett-Teller (BET) method from N_2 adsorption-desorption isotherms obtained at -196°C using a Tristar II 3020 surface area and porosity analyzer.

X-ray powder diffraction (XRD) patterns of the $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursors samples were obtained with nickel-filtered $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5418 \text{ \AA}$) using a Rigaku diffractometer and were collected over the 2θ range $20 - 90^\circ$. The reduced $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalyst samples were passivated prior to XRD to avoid continued oxidation during the XRD measurements. Details of the passivation treatment are described in our previous reports [24,26].

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1200 EX II microscope. The precursor and catalyst materials were dispersed on a carbon grid. High-resolution transmission electron microscopy (HR-TEM) images were obtained using a JEOL JEM-300F microscope equipped with scanning transmission electron microscopy (STEM) mode and an energy-dispersive X-ray spectroscopy (EDS) detector.

X-ray photoelectron spectroscopy (XPS) was performed using a SPECS® spectrometer with a PHOIBOS® 150 WAL hemispherical energy analyzer with angular resolution ($< 0.5^\circ$), equipped with an XR 50 X-Ray Al-X-ray and $\mu\text{-FOCUS}$ 500 X-ray monochromator (Al excitation line) sources. The $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursor was reduced *in situ* in the XPS prechamber prior to analysis.

2.5. Catalytic activity

The catalytic activity of the $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ systems in the tandem production of BZI was evaluated using 0.025 g of the catalyst and the necessary amount of substrate to obtain a $\text{mol}_{\text{substrate}}:\text{mol}_{\text{metal(Ni+Co)}}$ ratio of 100, based on the quantities of metals determined from ICP, TPR, and XPS characterization (*vide infra*). All activity measurements were performed in triplicate using a stainless-steel semi-batch reactor Parr® with mechanical stirring using 50 mL of solvent and pressurized at 10 Bar of H_2 pressure and set to the required temperature for 30 min. Then, the reactor was purged and pressurized with Ar at 5 Bar keeping the temperature. To avoid diffusion control and mass transfer, a stirring speed of 800 rpm was used. The reaction products were identified by gas chromatography using a Nexis 2030 instrument equipped with an Rtx-5 Amine capillary column and a flame ionization detector (FID). The conversion was calculated using the calibration curves and the following equation:

$$X_{2\text{NA}}(\%) = \frac{[2\text{NA}]_i - [2\text{NA}]_t}{[2\text{NA}]_i} \bullet 100 \quad (1)$$

where $[2\text{NA}]_i$ corresponds to the initial 2NA concentration and $[2\text{NA}]_t$ is the 2NA concentration at the corresponding time. In addition, the yield of the products was calculated as:

$$Y_{\text{product}}(\%) = \frac{[\text{product}]_{2\text{NA},t}}{\sum [\text{products}]_{2\text{NA},t}} \bullet 100 \quad (2)$$

where $[2\text{NA}]_{2\text{NA},t}$ corresponds to the product from the hydrogenation of 2NA. Other aldehydes were used to synthesize the 2-substituted benzimidazole, and the same operational conditions were used for BZI-based heterocycles production. The products of all reactions were monitored using a Shimadzu single quadrupole GCMS-QP2020 NX gas chromatograph-mass spectrometer (GC-MS) equipped with an Rtx-5 Amine capillary.

Recycling experiments were performed under conditions identical to those mentioned in the kinetic experiments. The catalyst was recovered by centrifugation and was washed with the degassed ethyl acetate (x1) and used in the next cycle up to ten consecutive reaction cycles without regeneration process. Hot filtration tests were performed to evaluate the metal leachate where the reaction was stopped after 30 min of reaction where the liquid medium was extracted from the reactor and centrifuged at 9000 rpm and then the liquid was exposed to the reaction conditions in the absence of the catalyst.

3. Results and discussion

3.1. Precursor and catalyst characterization

ICP-MS analysis was carried out to quantify the total amount of Ni and Co in the catalysts (Table 1). The theoretical and experimental metal contents for Ni and Co were similar, confirming the chemical composition of the proposed materials and the absence of appreciable metal loss during synthesis. The N_2 adsorption-desorption isotherms at -196°C of the ilmenite-type precursor systems show type-III isotherms according to the IUPAC classification [28] (see Fig S1 in Supplementary material). This is a result of high calcination temperatures required in sol-gel synthesis of $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursors which usually gives low surface areas due to formation of larger particles at elevated temperatures. In addition, after the reduction treatment, all the synthesized catalysts displayed specific surface (S_{BET}) values between 5–9 m^2/g which are characteristic of non-porous materials.

The formation of ilmenite-type structured materials based on $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ was confirmed by XRD (Fig 1a). The diffraction profiles of the NiTiO_3 (ICSD 0–5988) and CoTiO_3 (ICSD 1–6548) ilmenite structures were present in all precursors, showing well-defined and intense peaks. The incorporation of Ni into the bimetallic materials did not result in the appearance of segregated phases of NiO_x , CoO_x , or TiO_x , which could be attributed to the high tolerance to the incorporation of Ni by the CoTiO_3 structure or the segregation of highly dispersed metal oxide phases that were not detected by XRD in the ilmenite structure. Fig 1b shows the XRD patterns of the reduced $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalysts. All systems showed diffraction peaks characteristic of the crystalline phase of rutile- TiO_2 (ICSD 0–9161) attributed to the collapse of the ilmenite structure to produce metallic nanoparticles (NPs) and TiO_2 oxide as a support. No signals corresponding to Ni or Co hydroxides or oxides were observed.

Table 1
Physicochemical characterization of $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$.

Sample	S_{BET} (m^2/g)	ICP ^a	
		% Ni	% Co
Co/TiO ₂	5	-	38.8 (37.8)
Ni _{0.1} Co _{0.9} /TiO ₂	5	4.1 (3.9)	35.9 (34.1)
Ni _{0.3} Co _{0.7} /TiO ₂	6	11.7 (11.3)	28.1 (26.5)
Ni _{0.5} Co _{0.5} /TiO ₂	8	20.0 (18.9)	19.9 (18.9)
Ni/TiO ₂	9	39.0 (37.8)	-

^a Nominal metal contents of Ni and Co are given in parenthesis.

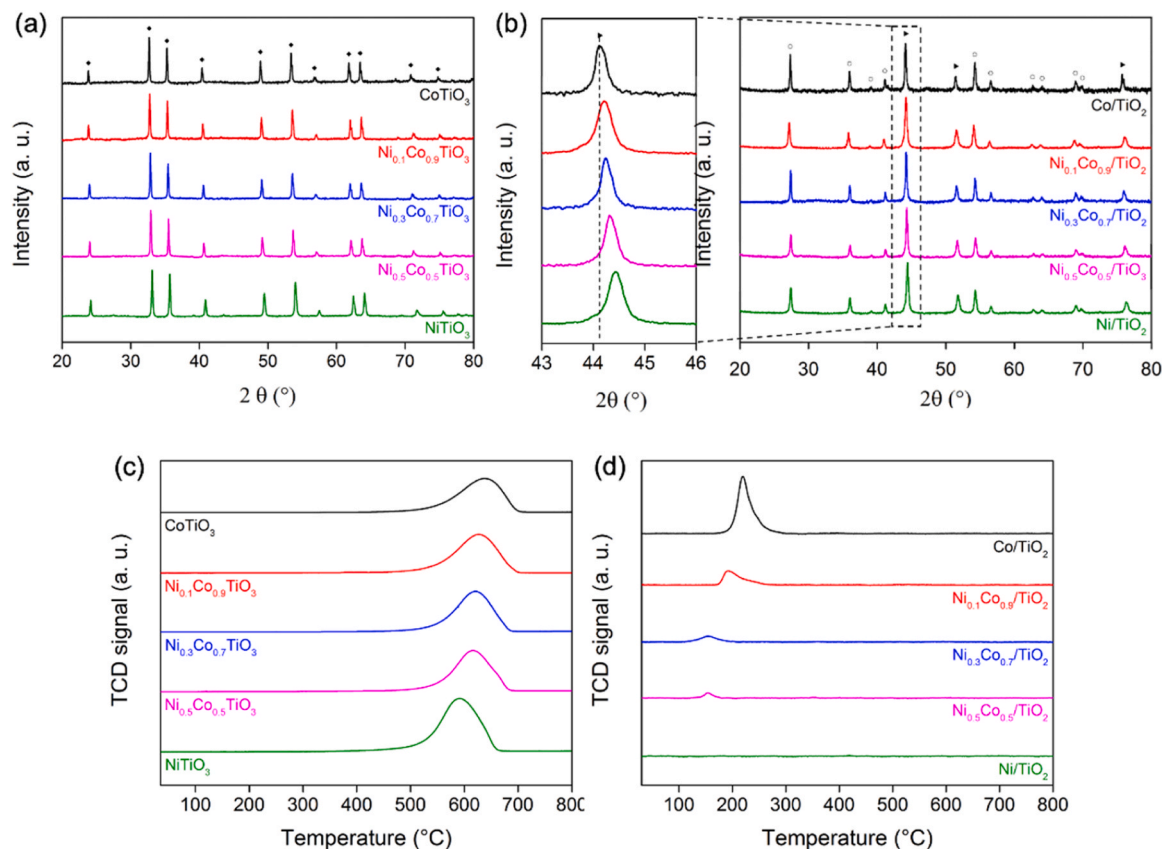


Fig. 1. Characterization of ilmenite $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursor and $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalysts. (a) and (b) XRD $\blacklozenge$ NiTiO_3 (ICSD 1–5988) and CoTiO_3 (ICSD 1–6548), $\blacktriangleright$ Ni^0 (ICSD 5–2231) and Co^0 (ICSD 4–4989) and $\circ$ TiO_2 -rutile (ICSD 0–9161), (c) H_2 -TPR1 and (d) H_2 -TPR2. inset shows an expansion of the $2\theta = 43^\circ - 46^\circ$ range containing the (111) peaks of metallic ni and co.

For the Co/TiO_2 catalyst, three peaks centered at 44.09° , 51.53° , and 75.87° were observed, which were assigned to the (111), (002), and (022) planes of face-centered cubic (fcc) metallic Co, respectively (ICSD 4–4989). The pattern of Ni/TiO_2 had three peaks at 44.47° , 51.84° , and 76.37° , corresponding to the (111), (002), and (022) planes of face-centered cubic metallic nickel, respectively (ICSD 5–2231). In the case of bimetallic $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$, the materials displayed slight variations in the peak position, all of which lie between those of pure fcc Ni and Co, and shifted to higher angles as the Ni content increased (Fig 1b inset), which suggested the formation of a nickel–cobalt alloy [29]. The characteristic peaks of Ni, Co, and Ni–Co for all catalysts were sharp, indicating high crystallinity and large particle sizes.

Fig 1c shows the H_2 -TPR1 profiles of the Ni–Co ilmenite-type materials. The monometallic materials showed a single reduction signal centered between 590 and 640°C for NiTiO_3 and CoTiO_3 , respectively, which are attributed to the reduction of Ni^{2+} or Co^{2+} in the ilmenite crystalline structure [24,26]. In the bimetallic $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursors ($x = 0.1, 0.3$, and 0.5), a similar trend was detected, showing a single reduction peak. However, as the Ni content of the formulation increased, the reduction signals shifted towards the NiTiO_3 reduction temperature (lower temperature). This behavior is attributed to Ni insertion into the mixed oxide structure, which decreases the reduction potential of Co^{2+} in the ilmenite structure [30], where Ni is preferentially reduced on the surface, generating Ni^0 metallic sites that promote the reduction of the second metal by the effect of H_2 spillover, as has been reported by various authors [31,32]. A second thermal treatment was performed to determine the optimal reduction temperature, followed by an *in-situ* reduction treatment to obtain the $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalysts, followed by a second TPR characterization (H_2 -TPR2). Fig 1d shows the reduction profiles, where Co/TiO_2 catalyst displayed one reduction signal at 230

$^\circ\text{C}$ was detected. This reduction signal could be attributed to the reduction of remaining Co cations in intimal contact with the metallic Co metallic assisted by a hydrogen spillover [33]. In the case of Ni/TiO_2 , no-reduction signal was detected, which confirmed the complete reduction of Ni-ilmenite precursor after reduction treatment. The systems with higher nickel contents ($x > 0.3$) have greater reducibility degrees, with minimal reduction signals, which are attributed to the complete reduction of both Co and Ni species, showing a promoting effect on the reducibility of the systems, in line with the XRD results.

The XPS test was performed to obtain surface electronic states and chemical composition information on the $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ (reduced-passivated) catalysts. The contributions of Ni, Co, Ti, and O were determined from the XPS survey spectrum displayed in the supplementary material (Fig S2). Fig 2 shows the binding energies (B.E.) of the Co $2p_{3/2}$ and Ni $2p_{3/2}$ states for all catalysts. The Co $2p$ spectrum for the Co/TiO_2 system (Fig 2a) is deconvoluted into three components, indicative of two cobalt species on the surface with B.E. of 778.0 eV and 781.0 eV attributed to Co^0 and Co^{2+} , respectively [34] and the characteristic satellite signal for this system type [35]. The B.E. differences allowed the differentiation of the surface contributions of the oxidized (87 %) and reduced (13 %) Co species, as presented in Table 2. As for the monometallic Ni/TiO_2 system (Fig 2b), the Ni $2p_{3/2}$ triplet has a value of 852.6 eV and 855.8 eV which are attributed to the Ni^0 and Ni^{2+} species, respectively [34], and the characteristic satellite signal [35], where the estimated contributions of the Ni^0 and Ni^{2+} species were 29 % and 71 %, respectively. These B.E. are in agreement with those reported in the literature for Co and Ni [36,37] and it is notable that the appearance of Ni^{2+} and Co^{2+} in the XPS spectrum is due to air oxidation of the sub-surface atoms during the analysis [38].

The Co $2p$ spectra of the bimetallic catalysts showed the presence of

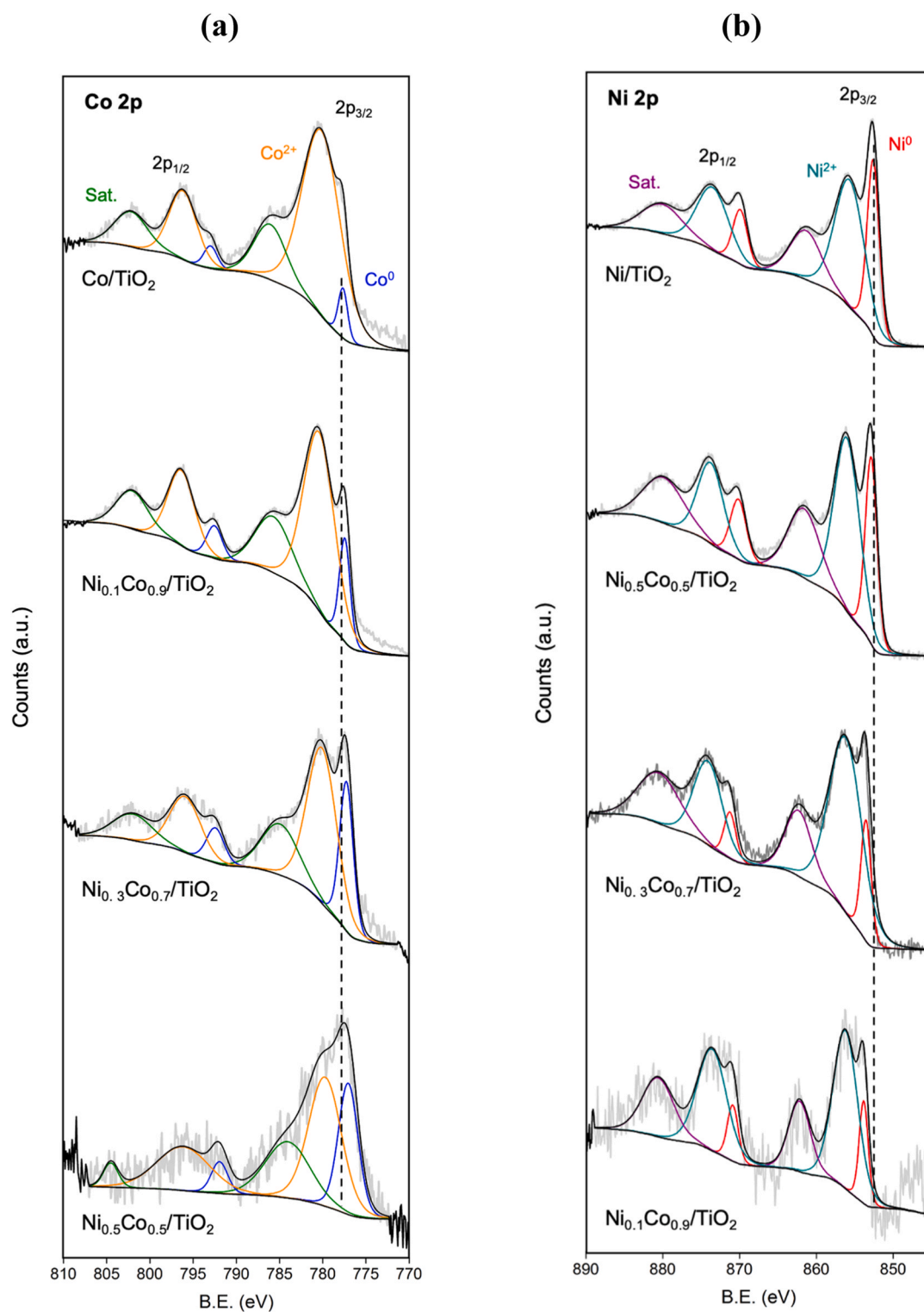


Fig. 2. XPS spectra for the $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalysts of (a) co 2p and (b) ni 2p.

both metallic and oxidized cobalt species and a satellite peak. The B.E. of these Ni–Co catalysts shifted towards lower values as the Ni content increased, and the Co^0 and Co^{2+} species shifted to 777.9 eV and 780.2 eV, respectively, for the higher nickel content catalyst ($\text{Ni}_{0.5}\text{Co}_{0.5}/\text{TiO}_2$). It is notable that the contribution of the Co^0 species had a gradual increase in the presence of Ni, from 13 % to 30 % of reduced cobalt on the surface. These results support the promoting effect of the bimetallic

catalysts on the reducibility compared with that of the Co system, as evidenced by the H_2 -TPR results. This behavior was also observed in the Ni 2p spectrum; the B.E. of Ni/TiO_2 shifted to higher values as the Co content increased. This result further confirmed the presence of the Ni–Co alloy in the bimetallic formulations.

TEM images were recorded to obtain the shape of the nanomaterials and the particle size distribution of the metal NPs in all catalysts is

Table 2XPS characterization of the $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ catalysts.

Catalysts	B.E. (eV)			
	$\text{aNi } 2p_{3/2}$		$\text{aCo } 2p_{3/2}$	
	Ni^0	Ni^{2+}	Co^0	Co^{2+}
Co/TiO_2	-	-	778.0 (13)	781.0 (87)
$\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$	853.8 (16)	856.2 (84)	777.9 (20)	780.3 (80)
$\text{Ni}_{0.3}\text{Co}_{0.7}/\text{TiO}_2$	853.5 (22)	856.2 (78)	777.9 (28)	780.2 (72)
$\text{Ni}_{0.5}\text{Co}_{0.5}/\text{TiO}_2$	853.3 (20)	856.1 (80)	777.7 (30)	780.2 (70)
Ni/TiO_2	852.6 (29)	855.8 (71)	-	-

^a Percentage ratio of $\text{Ni}^0 - \text{Ni}^{2+}$ and $\text{Co}^0 - \text{Co}^{2+}$ in parentheses.

displayed in supplementary material. The $\text{Ni}_x\text{Co}_{1-x}\text{TiO}_3$ precursor systems prepared using the sol-gel methodology show micro-rod morphology characteristics of the methodology used, as displayed in

the supplementary material (Fig S3), and the ilmenite-type morphology. Indeed, the micrographs of $\text{Ni}_x\text{Co}_{1-x}/\text{TiO}_2$ showed that the thermal treatment did not significantly modify the micro-rod-type structure and dimensions of the prepared materials, and the presence of metallic NPs was observed in all systems with an average particle size of 19 nm.

In addition, the monometallic catalysts Ni/TiO_2 and Co/TiO_2 , as well as the bimetallic catalyst $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$, were used to evaluate the surface nature through HR-TEM, as displayed in Fig 3. Co/TiO_2 and Ni/TiO_2 catalysts were chosen as references, and $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$ was characterized because it showed the best catalytic performance in the study reaction (*vide infra*). Analysis of the lattice spacing confirmed the presence of TiO_2 -rutile with an interplanar distance between 0.3213 and 0.3246 nm, characteristic of the (110) planes of the titanium support, in line with the XRD results and ICSD 0-9161 patterns.

Fig. 3a shows a Co/TiO_2 micrograph, where the Co NPs have a spherical shape and displays a visible set of lattice spacings of

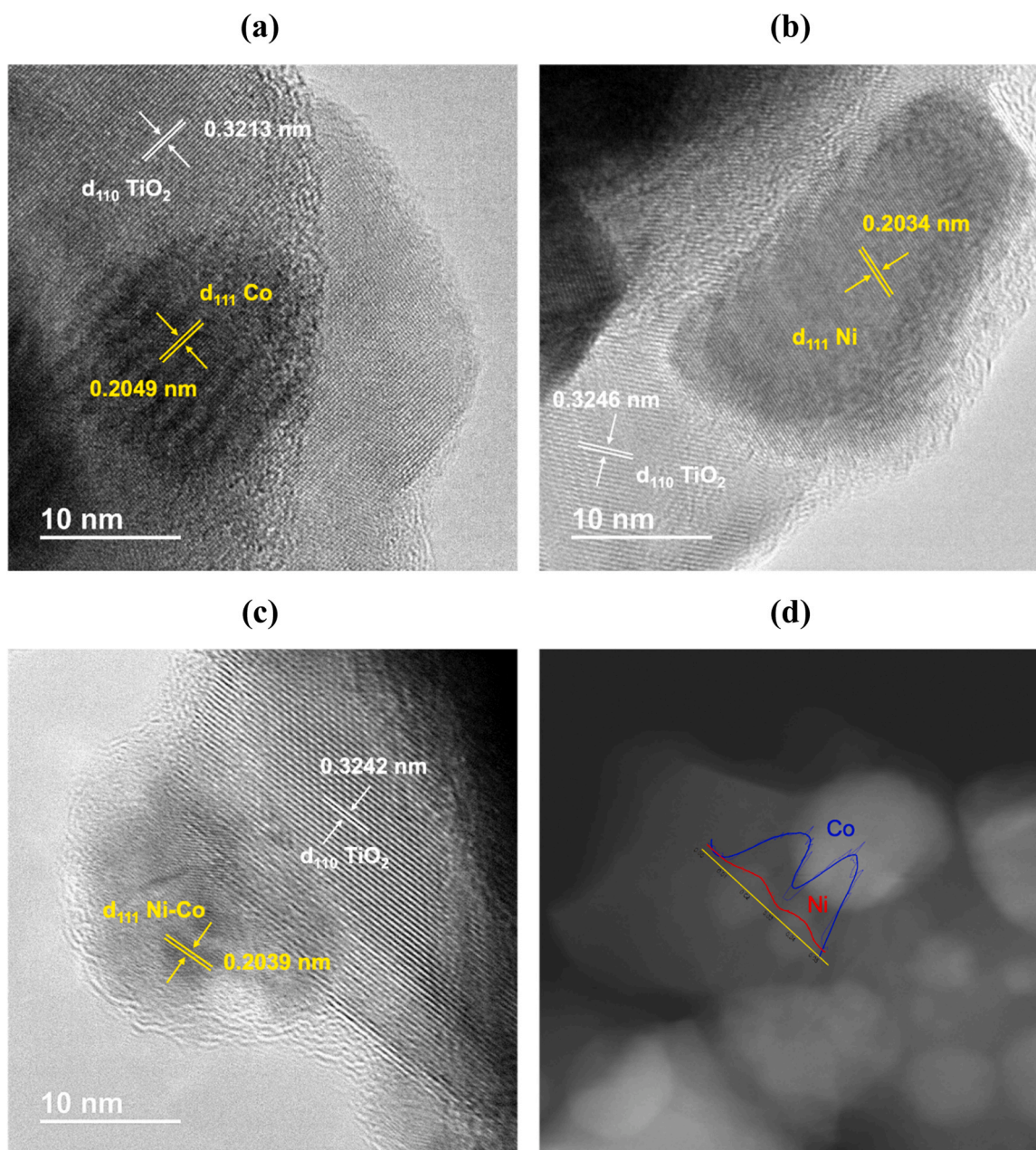


Fig. 3. HR-TEM micrographs of (a) Co/TiO_2 , (b) Ni/TiO_2 , (c) $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$, and (d) compositional line profiles for Ni and Co across the $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$ catalyst along the line marked.

0.2049 nm, which are characteristic of the (111) planes of metallic Co (ICSD 4-4989). Fig. 3b shows that metallic Ni (in the Ni/TiO₂ catalyst) has an interplanar distance of 0.2034 nm, which is characteristic of the (111) plane of metallic Ni (ICSD 5-2231). For the bimetallic Ni_{0.1}Co_{0.9}/TiO₂ (Fig. 3c), an interplanar distance of 0.2039 nm was observed, attributed to the (111) planes of the CoNi alloy reported by several authors [17,29,31] and in line with the patterns in the crystallographic data from ICSD 10-8308. During the synthesis of this bimetallic system, Ni replaces Co atoms in the crystal lattice, causing deformation of the lattice spacing and a decrease in size. This microscopic evidence reveals the lattice configuration of the Ni-Co alloy and confirms the strong interactions between Ni and Co atoms [39]. The compositional line profiles in Fig 3d for Ni and Co across the catalyst show similar intensity profiles for both metals because of the alloy structure. These images are in line with the shifted 2θ values in the XRD characterization and EDS mapping analysis displayed in supplementary material (Fig S4), confirming the contribution of nickel and cobalt in a proportion analogous to the material design.

3.2. Catalytic activity

Catalytic activity studies were performed using a H₂ pressure of 10 bar for 30 min. To start the tandem reaction, 2NA should be hydrogenated to OPHEN and couple with BZ to produce intramolecular cyclization of the BZA intermediary and subsequent dehydrogenation to yield BZI. As control experiments, non-catalyzed, CoTiO₃, NiTiO₃ and TiO₂-rutile commercial and were screened in the BZI (see Fig. S5 in supplementary material). The non-catalyzed reaction displayed a negligible conversion level even at 24 h of reaction (lower than 3.5 %). In addition, CoTiO₃, NiTiO₃ and TiO₂-rutile commercial showed similar results as non-catalyzed reaction. These results demonstrate that the reaction only proceeds in the presence of a metallic site, which is produced after the exsolution of metallic Co and/or Ni from Ni_xCo_{1-x}TiO₃-illmenite-precursor [33]. In the solvents effect in the production of BZI using methanol, ethanol, toluene and ethyl acetate were studied (see Table S1 in supplementary material). The polar protic solvents (ethanol and methanol) displayed reaction products from the solvent oxidation (acetaldehyde and formaldehyde), which produce undesired byproducts. The use of toluene and ethyl acetate provides the target product with a higher selectivity. Hence, we have chosen ethyl acetate to continue the studies due to its environmentally friendly properties. Fig 4 shows the conversion of 2NA (C_{2NA}) and the product selectivity (S_x) for the reductive amination-cyclization of 2NA with BZ using the Ni_xCo_{1-x}/TiO₂ catalysts. During the reaction, 2NA followed pseudo-first-order kinetics (k₀), reaching the maximum conversion after 24 h. The systems were active, with > 90 % conversion for the transformation of 2NA; the higher Ni content catalyst (x > 0.3) showed total conversion for this reaction. However, the selectivity towards the BZI production was < 40 % as a consequence of the accumulation of OPHEN and its condensation to provide the BZA and other intermediates and products. The selectivity showed that only OPHEN was detected as a product of 2NA hydrogenation, which is consumed to lead to BZI formation, which is in agreement with the proposed mechanism for the formation of this N-heterocycle scaffold. On the other hand, the higher Co content catalyst (x < 0.1) achieved more efficiently the product of interest, S_{BZI} > 70 %. In these results, the metallic proportion and alloy formed by the Ni_{0.1}Co_{0.9}/TiO₂ catalyst promoted the catalytic performance. Thus, the presence of metallic Ni in the crystalline structure of the catalysts could influence the electronic and structural properties of the Ni-Co ilmenite-type catalysts, enhancing the active sites and catalytic activity, while metallic Co promotes selectivity, demonstrating a synergy due to the influence of the second metal on the catalyst structure, compared to monometallic systems [40,41]. Helal et al. reported similar results using bimetallic CoNi@C catalysts for the synthesis of various benzimidazoles and found a significant improvement in activity owing to the synergistic effects produced by the presence of both metals

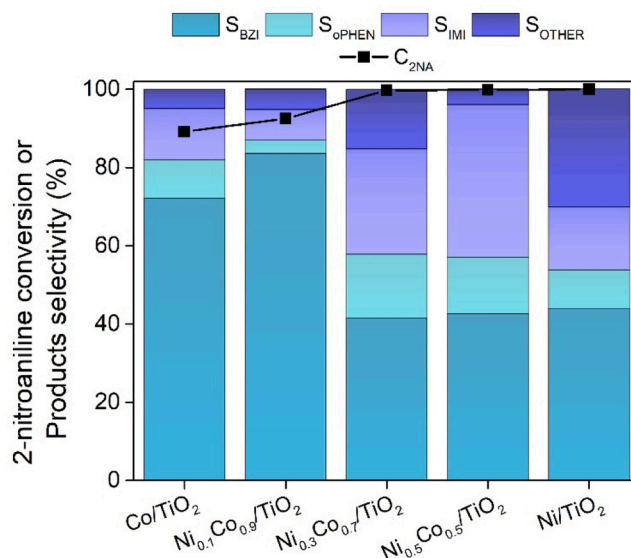


Fig. 4. Conversion and product distribution of Ni_xCo_{1-x}/TiO₂ systems in the reductive amination-cyclization of 2NA with BZ. Reaction conditions: catalyst (0.025 g), 2NA (2 mmol), BZ (2 mmol), ethyl acetate (50 mL), for 30 min after change to Ar (5 bar), 150°C until 24 h. the data was obtained based on 2NA consumption.

[42].

Ni_{0.1}Co_{0.9}/TiO₂ was selected for more specific kinetic studies because of its catalytic performance. To ensure the analysis, the reaction monitoring over time (Fig S6) displayed that, as the conversion of 2NA increases, OPHEN is formed as a primary product. After reaching a maximum, the concentration of OPHEN dropped in line with the formation of BZA as well as the formation of BZI with no detection of other reaction intermediates. This result is in line with previous work reported by Rodenes et al. on the hydrogenation of 1,2-dinitroarene in the presence of a MoS₂-based catalyst [3]. The main step in obtaining the benzimidazole scaffold was 2NA hydrogenation, and hydrogenation kinetic studies were carried out for the 2NA hydrogenation with and without BZ. In both cases, the reactions were performed at 10 bar H₂ pressure, samples were collected during the first 30 min, and a pseudo-first-order reaction was assumed to fit the kinetic data of the hydrogenation of nitroarenes [43–45]. Fig 5a shows the kinetic profiles used to calculate the pseudo-first-order apparent rate constant (k_a) of both experiments. The 2NA and 2NA+BZ hydrogenation constants are 0.0032 min⁻¹ and 0.0093 min⁻¹ respectively. This suggests that 2NA hydrogenation in the presence of BZ undergoes a synergistic effect that allows preferential hydrogenation of the –NO₂ group over the C=O group during the catalytic reaction. Some studies have shown that this behavior is related to the competitive adsorption of nitroarenes with aldehydes at the active sites of the catalyst, allowing selective reaction products to be obtained via nitroarene hydrogenation [46,47].

Furthermore, temperature effect studies were performed to determine the apparent activation energy (E_{aa}) of the reductive amination-cyclization of 2NA and BZ using the Arrhenius equation [48]. For this purpose, four temperatures between 100°C and 160°C were used. Fig 5b shows a direct temperature dependence where k'_{160°C} > k'_{140°C} > k'_{120°C} > k'_{100°C}. Based on the calculated rate constants, E_{aa} was determined to be 47.17 kJ/mol. This calculated energy was significantly lower than that of the Co/CNT catalysts reported by Lin et al., who obtained an E_{aa} of 65 kJ/mol for BZI synthesis from the reductive amination-cyclization of 2NA with BZ [13]. This result supports the increase in catalytic performance when using a bimetallic system with low Ni content.

The versatility of the Ni_{0.1}Co_{0.9}/TiO₂ catalytic system was tested in the production of 2-substituted benzimidazole derivatives. The reductive amination-cyclization reaction was carried out using 2NA as the

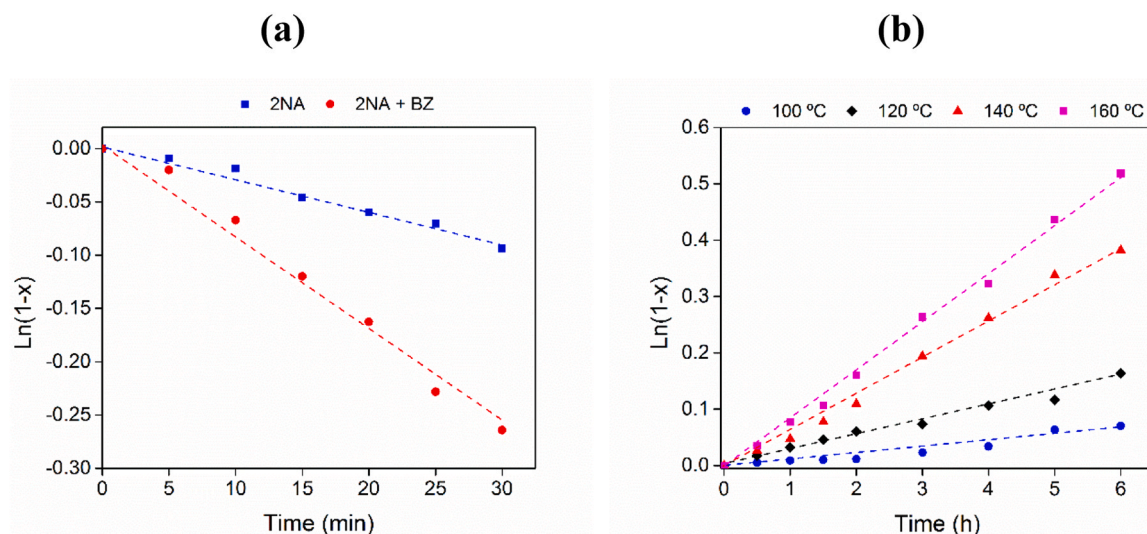


Fig. 5. Kinetic studies on the $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$ catalyst. (a) Kinetic profiles in the 2NA and 2NA+BZ hydrogenation and (b) effect of reaction temperature on the reductive amination-cyclization of 2NA and BZ by the $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$ catalyst. Reaction conditions: catalyst (0.025 g), 2NA (2 mmol), BZ (2 mmol), ethyl acetate (50 mL), H_2 (10 bar) for 30 min after change to Ar (5 bar), 150 °C until 6 h.

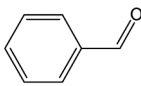
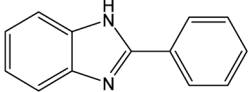
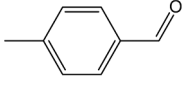
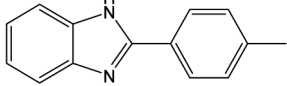
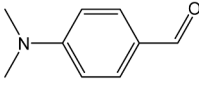
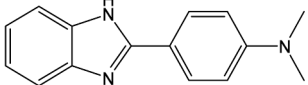
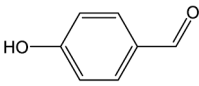
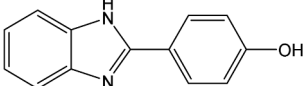
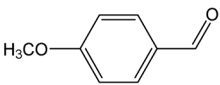
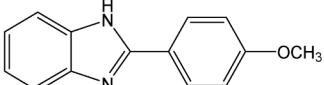
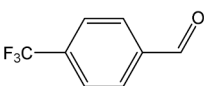
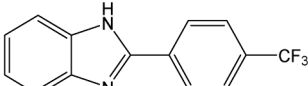
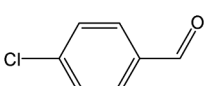
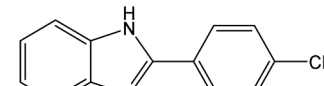
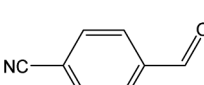
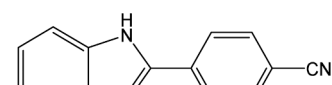
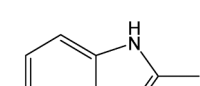
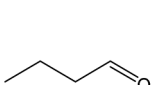
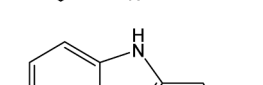
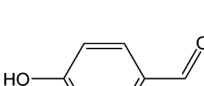
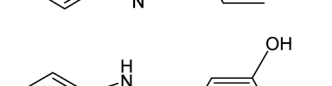
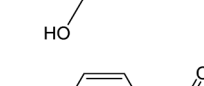
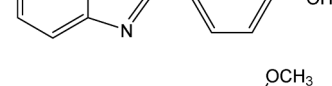
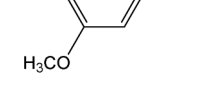
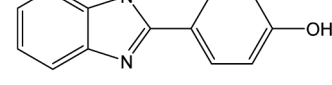
reagent with different aldehydes under the previous reaction conditions using a stoichiometric ratio of both reagents. The conversion and selectivity values for the substituted benzimidazoles are listed in Table 3. First, the reductive amination-cyclization of o-dinitrobenzene with BZ was tested to evaluate the hydrogenation capacity of the $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$ catalysts. The results displayed a lower conversion level in comparison with 2NA (entry 1) while similar selectivity to the target product was detected. We suggest that H_2 pseudo-borrowing step, from the cyclization and oxidative dehydrogenation, is not enough to provide a complete reduction of the o-dinitrobenzene at the evaluated conditions. In basis of this result and aiming to develop a synthetic route that leverage the H_2 pseudo-borrowing in the production of 2-substituted benzimidazoles, we decided employ use of 2NA instead of o-dinitrobenzene, as starting reagent. The introduction of a substituent (independent of its electronic nature) allowed us to obtain derivatives of the 2-substituted benzimidazole. Substituted benzaldehydes with electron density donor groups ($-\text{CH}_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{OH}$, and $-\text{OCH}_3$) showed a significant decrease in the transformation of the nitro compound to obtain the compound of interest (Entries 2–5), with $C_{2\text{NA}} < 75\%$ and $S_{\text{p-BZI}} < 84\%$, presenting mainly accumulation of the intermediate OPHEN and BZA during the process. When using OH-BZ curiously, selectivity towards the higher substituted product was obtained ($S_{\text{OH-BZI}}$ of 82 %), the BZA-intermediate allowed the intramolecular hydrogen bond formation that stabilized the structure and promoted the nucleophilic attack of the second N atom for the formation of the substituted benzimidazole. The introduction of electron density withdrawing groups ($-\text{CF}_3$, $-\text{Cl}$, and $-\text{CN}$) into the aromatic aldehyde allowed to obtain $C_{2\text{NA}} > 90\%$. However, the selectivity towards the production of 2-substituted BZI was 72 %, 64 %, and 53 % (Entries 6–8), this change in selectivity was produced by the accumulation of OPHEN and delaying the formation of BZA as a consequence of the increase in the aldehydes electrophilic character of the $\text{C}=\text{O}$ group [49]. This electronic effect increased the formation of undesirable N-alkylated 2-substituted benzimidazole as by-product. From a mechanistic point of view, once OPHEN is formed, in addition to a condensation step with aldehydes, the synthesis of N-alkylated 2-substituted benzimidazole should involve either the coupling of two aldehydes with OPHEN to produce N,N' -(1,2-phenylene)dialkylimine, followed by cyclization, and oxidative dehydrogenation (Scheme S1). Aliphatic aldehydes (entries 9 and 10) were explored in the synthesis of benzimidazoles. In both cases, almost a complete conversion of the initial 2NA was achieved, and similar selectivity towards the target product were observed. It is important to

note that 1-alkyl-2-phenyl-1H-benzo[d]imidazole were detected in traces ($< 3\%$). Bio-based alkoxy aldehydes (entries 11 and 12) were also evaluated, rendering a conversion level of 68 % in both examples and high selectivity to the target product ($> 78\%$). It was evidenced that the catalyst is compatible with the presence alkoxy aldehydes avoiding the formation of N,N' -(1,2-phenylene)dialkylimine derivatives. Furthermore, the chemoselectivity of other potential reducible groups has been studied using cinnamaldehyde (entry 13) as bio-based α , β -unsaturated aldehyde reaching good selectivity to the target product and detecting as by-product the hydrogenation of $\text{C}=\text{C}$ moiety reaching a selectivity to the 10.4 % to 2-hydrocinnamyl-benzimidazole. For this last substituent, we carried the reaction using the hydrocinnamaldehyde (entry 14) to understand the selectivity observed in entry 13. It is important to note that the reaction increased the selectivity to the target product and OPHEN or BZA were detected. These results are auspicious since this product is marketed as Diabazole, which is a spasmolytic, vasodilator, and hypotensive drug with cardiovascular applications [3]. Furthermore, furfural is an important bio-based aldehyde obtained from the valorization of lignocellulosic biomass [50]. Fortunately, this aromatic aldehyde is used as a building block for the preparation of the fungicide Fuberidazole [1]. Hence, the reductive amination-cyclization of furfural with 2NA (entry 15) reached 94 % of conversion level and 87 % of selectivity to Fuberidazole product.

3.3. Catalytic stability

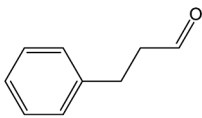
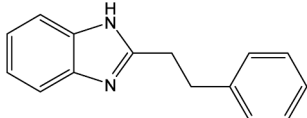
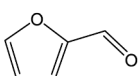
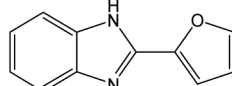
The catalytic stability and recyclability of the $\text{Ni}_{0.1}\text{Co}_{0.9}/\text{TiO}_2$ catalyst were investigated in the 2NA reductive amination-cyclization with BZ. The procedure consisted of carrying out ten consecutive cycles under the same reaction conditions; the catalysts were recovered by filtration after each batch reaction, and the catalytic performance, chemical composition, and physicochemical properties were evaluated. The 2NA conversion and BZI selectivity as functions of the number of experimental runs are shown in Fig 6a. The catalyst showed great stability and remained unchanged up to the tenth cycle when the catalytic activity was $> 90\%$ and $> 80\%$ 2NA conversion and BZI selectivity, respectively. The conversion level and selectivity to produce BZI displayed similar values even at 6 h of reaction demonstrating that the catalysts preserve its efficiency even at low conversion levels. In addition, X-ray diffraction (XRD), transmission electron microscopy (TEM), and inductively coupled plasma (ICP) were performed on the recovered catalyst to determine its physicochemical nature after recycling. Fig 6b shows the

Table 3Conversion and product distribution of Ni_{0.1}Co_{0.9}/TiO₂ catalyst in the reductive amination-cyclization of 2NA with aldehyde for the production of BZI derivatives.

Entry	Aldehyde	BZI derivative	Nitroarene Conversion (%)	S _{ophem} (%)	S _{IMI} (%)	S _{BZI} (%)	S _{others} (%)
1			92.5 68.4 ^a	10.4 10.5 ^a	6.0 4.4 ^a	83.6 85.1 ^a	– –
2			75.4	23.5	10.4	66.1	–
3			72.6	30.1	6.4	63.5	–
4			71.2	15.6	17.3	67.1	–
5			74.0	5.1	21.2	73.7	–
6			91.4	–	11.3	53.5	35.2
7			98.6	–	18.7	64.3	17.0
8			95.9	–	14.5	72.2	13.3
9			99.4	–	–	98.1	1.9
10			98.4	–	–	99.1	0.9
11			77.2	18.6	2.5	78.9	–
12			70.2	7.3	8.6	84.1	–
13			98.1	5.6	10.4	73.6	10.4

(continued on next page)

Table 3 (continued)

Entry	Aldehyde	BZI derivative	Nitroarene Conversion (%)	S _{ophem} (%)	S _{IMI} (%)	S _{BZI} (%)	S _{others} (%)
14			99.3	4.5	9.4	83.6	2.5
15			93.7	6.0	3.8	87.0	3.2

Reaction conditions: catalyst (25 mg), 2NA (2 mmol), aldehyde (2 mmol), ethyl acetate (50 mL), H₂ (10 bar) for 30 min and Ar (5 bar), 150°C, 24 h.

^a 1,2-dinitrobenzene was used as starting material.

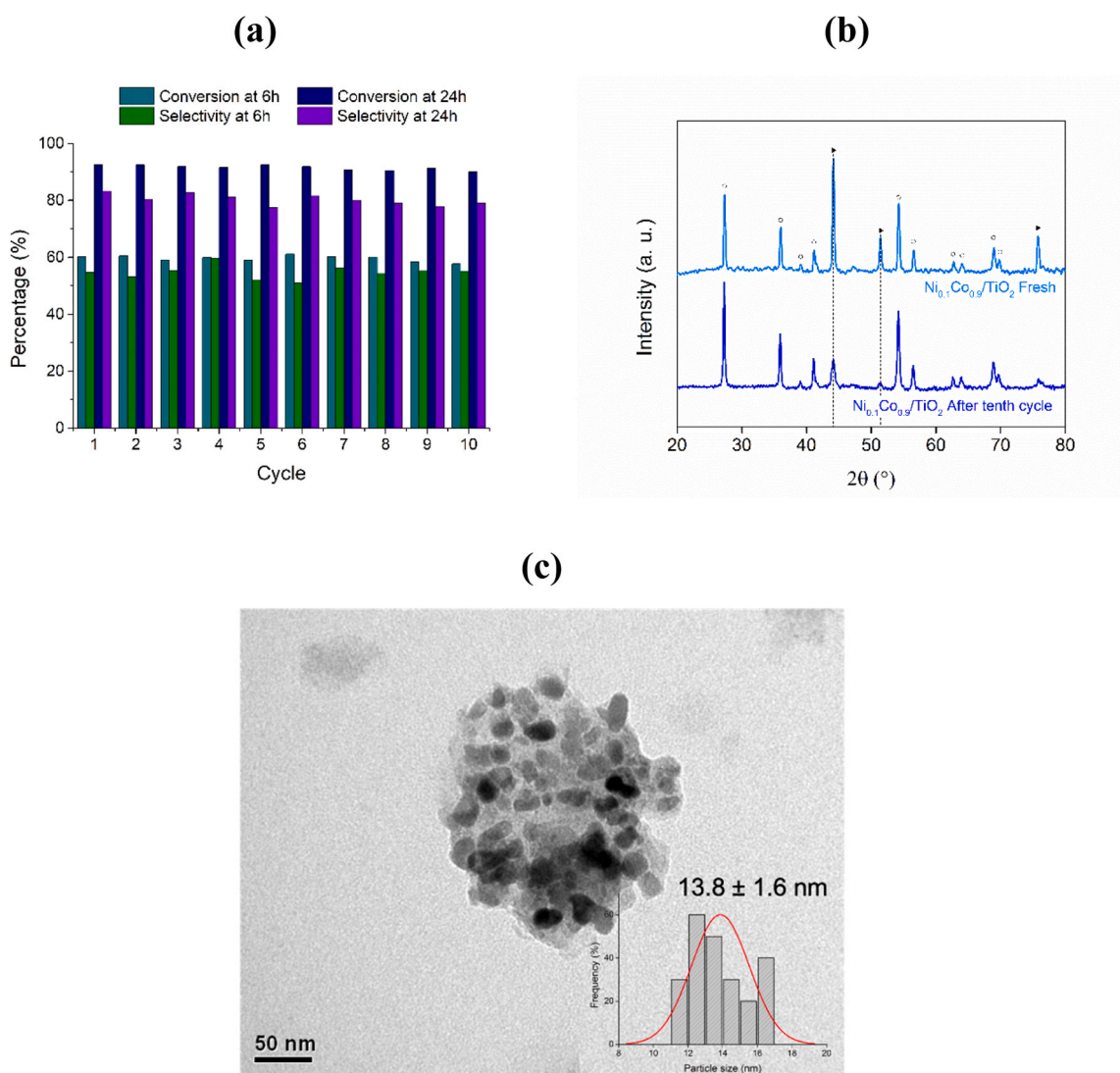


Fig. 6. Recycling of catalyst of Ni_{0.1}Co_{0.9}/TiO₂ catalyst on the reductive amination-cyclization 2NA with BZ. (a) Catalytic stability for the 2NA conversion and BZI selectivity at 6 and 24 h, (b) XRD characterization for the fresh and used catalyst, and (c) TEM micrograph of the catalyst after the tenth catalytic cycle.

XRD patterns of the fresh and used catalysts. A decrease in the signal intensity at 2θ angles of 44.36°, 51.69°, and 76.12° attributed to the Ni–Co alloy (ICSD 10–8308) is observed, whereas the diffraction peaks consistent with TiO₂-rutile remain unchanged. Non-catalytic activity in the conversion of 2NA was confirmed by a hot-filtration test after the third cycle (supplementary material, Fig S7); the catalyst retains its

conversion level after separation from the liquid phase. An ICP-MS analysis was performed on the catalyst recovered in the last cycle to determine the post-reaction metal content. Surprisingly, the metal content decreased from 4.1 % to 2.7 % and from 35.9 % to 25.4 % for Ni and Co, respectively, indicating the leaching of the metal into the liquid phase in higher cycles.

The TEM image of the spent catalyst shows an evident collapse of the microrod structure and particle sizes of < 14 nm after the tenth cycle (Fig 6c). Both Ni–Co alloy oxidation and solid-structure breakdown produced disaggregated catalyst particles because of the hydrothermal reaction. Although the reaction was performed using ethyl acetate as a solvent, the *in situ* formation of H_2O on the catalyst surface as a result of $-NO_2$ group hydrogenation could be responsible for active phase oxidation/hydration upon cycling, analogous to the results reported in previous works [26].

These results suggest that during consecutive reaction cycles, the active phase is lost by the disaggregation of the catalysts producing micro- and/or nano-particles, which could be lost in every wash. According with the proposed deactivation mechanism, we suggest that the activity and selectivity after ten catalytic cycles, displayed by $Ni_{0.1}Co_{0.9}/TiO_2$ system, are due to the strong metal–support interaction effects between the residual NiCo bimetallic nanoparticles in contact with the TiO_2 support [24,26,33].

4. Conclusions

The bimetallic NiCo catalysts supported on TiO_2 -rutile derived from the reduction of the ilmenite-type precursor $Ni_xCo_{1-x}TiO_3$ proved to be highly efficient for the reductive amination-cyclization of 2NA with benzaldehyde, yielding the corresponding BZIs under moderate operating conditions, employing ethyl acetate as the solvent. The bimetallic $Ni_{0.1}Co_{0.9}/TiO_2$ catalyst promoted selective catalytic tandem reaction to produce the desired benzimidazole compared to the Ni and Co monometallic systems, proving that the enhanced catalytic performance of this catalyst was due to the Ni–Co alloy, evidenced by XRD, XPS, HR-TEM, and catalytic activity. This catalyst demonstrates high activity and selectivity in the reductive amination-cyclization of a series of para-substituted aromatic aldehydes. Finally, operational stability tests showed that the optimal catalyst was stable during continuous operation cycles and remained unchanged until the tenth cycle at 24 h of reaction. The results provide evidence that $Ni_{0.1}Co_{0.9}/TiO_2$ have practical potential as highly recyclable catalysts to produce of 2-substituted benzimidazole scaffolds of pharmaceutical relevance via catalytic tandem reaction using non-noble based catalysts.

CRedit authorship contribution statement

Tatiana M Bustamante: Writing – original draft, Validation, Supervision, Formal analysis. **J N Díaz de León:** Validation, Supervision, Formal analysis, Data curation. **Lucía Camarena:** Methodology, Formal analysis, Data curation. **Marcelo E Domine:** Writing – review & editing, Validation, Supervision, Investigation. **Cecilia C Torres:** Writing – original draft, Resources, Project administration, Formal analysis, Conceptualization. **Cristian H Campos:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis. **Daniela González-Vera:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Edgardo Leal-Villarreal:** Visualization, Investigation, Data curation.

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.

Acknowledgments

The authors would like to thank the ANID projects FONDECYT 1231352 and FONDECYT 1231395. D. González-Vera is grateful for her doctoral scholarship ANID 21200167 and ITQ (UPV-CSIC) for support during her research stay, and E Leal thanks Grant ANID 21220327. L. Camarena and M.E. Domine thanks Spanish government

(PID2021–125897OB-I00) for financial support. The authors would like to thank to David Domínguez by his expert technical assistance in the XPS analysis and the Institute of Applied Economic Geology of the University of Concepción for providing the facility to perform mineralogical analyses in the X-ray Laboratory.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2025.115416

Data Availability

Data will be made available on request.

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