

Article

Catalytic Hydrogenation of Nitrocyclohexane with CuCo/SiO₂ Catalysts in Gas and Liquid Flow Reactors

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Abstract: Catalytic hydrogenation of nitrocyclohexane proved to be an attractive alternative source of various chemical compounds: cyclohexanone oxime, cyclohexanone, cyclohexanol, cyclohexylamine and dicyclohexylamine. A growing interest in this reaction has been observed in the last few years. Herein, we present the catalytic performance of Cu/SiO₂, Co/SiO₂ and CuCo/SiO₂ in gas and liquid flow nitrocyclohexane hydrogenation. The analysis of synthesized catalysts morphology (BET, TPR, XRD, TEM) in terms of their catalytic behavior allows us to draw general conclusions and determine the optimal conditions for the production of desired products. Application of the monometallic copper leads to the formation of cyclohexanone as the main product, but with low activity. On the other hand, Co/SiO₂ shows high activity but gives cyclohexylamine. Bimetallic system CuCo(3:1)/SiO₂ allows for the efficient production of 100% cyclohexanone at 5 bar and 75 °C.

Keywords: hydrogenation; nitrocyclohexane; flow reactor; cyclohexanone; cyclohexylamine



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1. Introduction

Catalytic hydrogenation is one of the most widely used reactions in modern production, which found application in the fat industry, petroleum refining processes, production of modern materials, synthesis of pharmaceuticals and many others. Decades of research on hydrogenation catalysts have resulted in the development of many active, selective and stable catalytic systems [1]. A lot of patented solutions are based on noble metals. However, every year, more and more catalysts consisting of non-noble metals have been synthesized, tested and developed [1].

Whereas the hydrogenation of aromatic nitro compounds has been widely studied, the hydrogenation of aliphatic nitro compounds still needs to be investigated more thoroughly [2]. Among them, hydrogenation of nitrocyclohexane (NC) seems to be an attractive alternative source of various chemicals: cyclohexanone oxime (essential in the manufacturing of polyamides), cyclohexanol (feedstock in the polymer industry and plasticizers production), cyclohexylamine (a building block for pharmaceuticals), cyclohexanone (a precursor in the production of nylons and resins) and dicyclohexylamine (which found application in the manufacture of antioxidants in rubber and plastics, agrochemicals and corrosion inhibitors). A thorough analysis of research on the catalytic hydrogenation of nitrocyclohexane shows that this seemingly simple reaction could be very challenging due to the vast number of crucial factors. However, the possibility of obtaining numerous valuable chemicals in one reaction seems to be extremely interesting. Those individuals are produced by multi-step processes at elevated pressure and temperature [3–9]. On the other hand, selective hydrogenation of nitrocyclohexane provides the possibility to obtain each of them in a simple one-step process performed under mild conditions [10]. The development of catalytic flow reactors for scientific purposes even increased the applicability of this solution to the chemical industry.

Most of the research concerning the catalytic hydrogenation of nitrocyclohexane has been focused on noble metal catalysts used in batch conditions [11–16]. However, relatively

recently, the activity, selectivity and stability of non-noble catalysts in this reaction have been proved by different research groups [17–19]. Fangbo et al. [18] demonstrated the activity of Ni-based catalysts in the hydrogenation of nitrocyclohexane. On the other hand, Zhang et al. [17] analyzed the activity catalysts containing 15 wt.% of Ni and Fe during batch mode NC hydrogenation at 100 °C and under 10 bar in ethylenediamine as a solvent. They revealed that, depending on the used transition metal, the catalysts were selective to different reaction products. Application of Fe led to the formation mainly cyclohexanone (75% selectivity), Ni gave cyclohexanone oxime as a major product with 59% selectivity [17].

Until now, not a lot of attention has been paid to the nitrocyclohexane hydrogenation in flow mode [19–21]. Moreover, only one of these articles demonstrated activity of the non-noble metals (CuZnAl hydrotalcite derived materials) in the liquid phase continuous flow hydrogenation of nitrocyclohexane at mild conditions (5 or 10 bar and the temperature range 25–145 °C [19]. Despite the growing interest in this topic observed in the last few years, many essential for this reaction factors still need to be determined.

Therefore, this work is a continuation of our previous research on the use of flow conditions in the hydrogenation of nitrocyclohexane with readily available transition metals.

Copper and cobalt-based catalysts proved to be active and selective in the hydrogenation of nitro compounds. Zhang et al. [17] demonstrated that Cu and Co catalysts could be very selective in nitrocyclohexane hydrogenation at 100 °C and under 10 bar in ethylenediamine as a solvent. They showed that Cu catalysts steer this reaction into the formation of cyclohexanone oxime (92% selectivity) and Co into the formation of cyclohexanone (59% selectivity).

The earlier studies concerning the activity of CuCo bimetallic systems in the hydrogenation of CO₂ [22] and transformation of biomass-derived compounds: γ -butyrolactone into 1,4-butanediol [23], lauric acid into lauric alcohol [24] or 2-hydroxymethylfurfural into 2,5-dimethylfuran [25] clearly show the beneficial role of the close interaction or proximity of Cu⁰ and Co⁰. The coexistence of Cu and Co improved the catalytic performance by increasing the activity with maintaining selectivity toward desired product [26–29]. Hence, we wondered CuCo-based catalysts' performance in NC hydrogenation.

Therefore, the main goal of the research was the modification of the catalytic behavior of Cu catalysts by Co addition to increase its activity with the preservation of the selectivity toward desired product. The monometallic and bimetallic catalysts with different Cu:Co ratio were synthesized, characterized and investigated in NC hydrogenation. The firstly reported catalytic results have shown the beneficial role of CuCo formation on their catalytic performance.

2. Results

2.1. N₂ Physisorption Results

The nitrogen adsorption performed at 77 K for each catalyst showed satisfactory specific surface area ~240 m²/g and well-developed porosity, with the dominance of mesopores (Table 1). Moreover, the test for support material (SiO₂) revealed that the applied synthesis procedure does not significantly affect the surface parameters of SiO₂. The similarities in surface parameters between all catalysts eliminate the additional factor in the analysis of the catalytic behavior of tested materials.

Table 1. Cu/SiO₂, CuCo/SiO₂ and Co/SiO₂ physicochemical parameters.

Parameter\Material	SiO ₂	Cu/SiO ₂	CuCo(3:1)/SiO ₂	CuCo(1:1)/SiO ₂	CuCo(1:3)/SiO ₂	Co/SiO ₂
Surface area [m ² /g]	240 ± 5	230 ± 5	230 ± 5	230 ± 5	230 ± 5	230 ± 5
Pore volume [cm ³ /g]	1.0	1.0	1.0	1.0	1.0	1.0
Average pore diameter [nm]	17	17	17	17	17	17

2.2. Temperature-Programmed Reduction Studies (H_2 -TPR)

TPR profiles of the calcined Cu/SiO₂, Co/SiO₂ and CuCo/SiO₂ catalysts are shown in Figure 1. The obtained results are in agreement with the previous observations of Smith et al. [29] for similar materials.

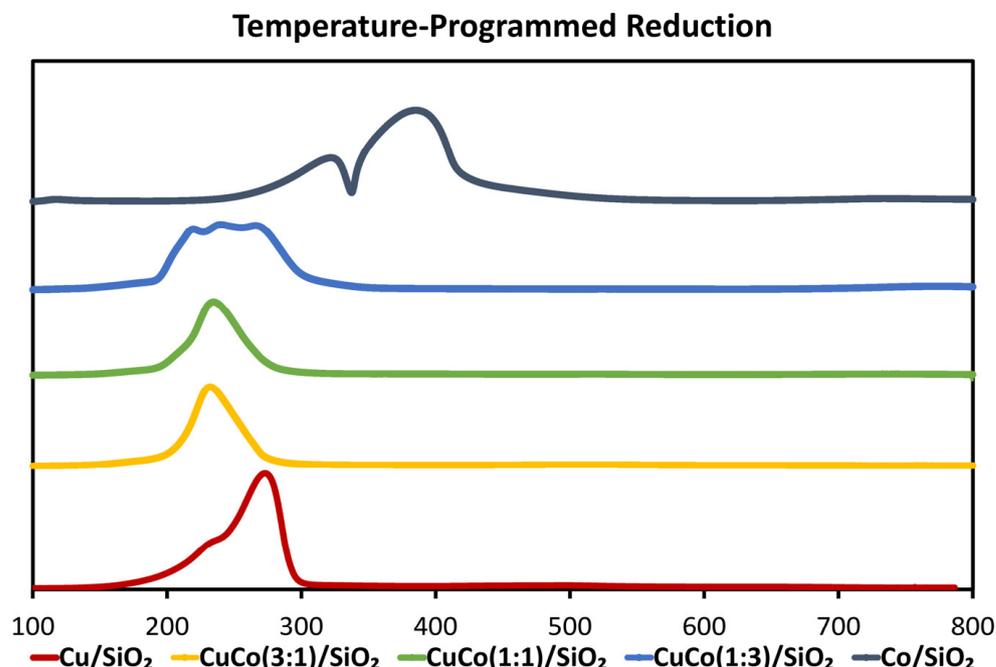


Figure 1. Temperature-programmed reduction of Cu, Co and CuCo catalysts.

The maximum Cu/SiO₂ reduction peak is located at 275 °C, with a distinguished sign of another peak at 233 °C. Unsupported CuO usually reduces directly into metallic Cu in a single step, without forming Cu₂O [30,31]. However, multiple peaks during TPR are often observed in the case of supported CuO. Based on the reported data, several possible explanations exist for this phenomenon. Some authors attribute the low-temperature peak to the direct reduction of small particles with low crystallinity into Cu⁰ directly [32,33]. The other explanation involved the presence of CuO species with various hydrogen availability [19]. On the other hand, the subsequent reduction: CuO → Cu₂O → Cu⁰ should also be considered, especially if the ratio between TPR peaks is almost 1:1 [29]. In the case of the presented results (Figure 1), the first one seems to be the most possible.

The TPR profile for the reduction of Co/SiO₂ demonstrates two very-well distinguishable peaks related to sequential reduction: Co₃O₄ → CoO → Co⁰ [34,35]. In the presented results, related peaks are located at 320 °C and 384 °C, respectively. According to the literature data, the second step is strongly affected by the interaction with support material [36]. Powerful interaction of cobalt species with SiO₂ increases the maximum temperature of reduction. The presence of cobalt silicate may increase the TPR maximum up to 900 °C [35]. Based on the obtained results (Figure 1), there is only little support interaction of Co species with SiO₂ in the synthesized Co/SiO₂ catalyst.

Each bimetallic catalyst demonstrated a lower reduction temperature than monometallic Cu/SiO₂ and Co/SiO₂. Only in the case of the catalyst with higher Co concentration (CuCo(1:3)/SiO₂) does the presence of a broad area of hydrogen consumption (190–315 °C) indicate several overlapping reduction processes. The other two bimetallic catalysts showed only one reduction peak with a maximum located at ~235 °C. Such a TPR profile is typical for CuCo/SiO₂ catalysts [37–39]. It could be explained by strong interaction between CuO and Co₃O₄ [37,39,40] or even a formation of Cu_xCo_{3-x}O₄ phase to explain the promoting effect of Cu on Co reduction [38,39]. In general, the addition of Cu into Co/SiO₂ increases the reducibility of cobalt oxides, especially CoO. On the other hand,

adding Co into Cu/SiO₂ decreases the formation of Cu₂O, which is more challenging to reduce [29].

2.3. X-ray Diffraction Results

The XRD patterns obtained for the Cu, Co and CuCo catalysts are shown in Figure 2. Each catalyst demonstrated a diffraction hump between 20 and 25 °C, corresponding to the structure of SiO₂.

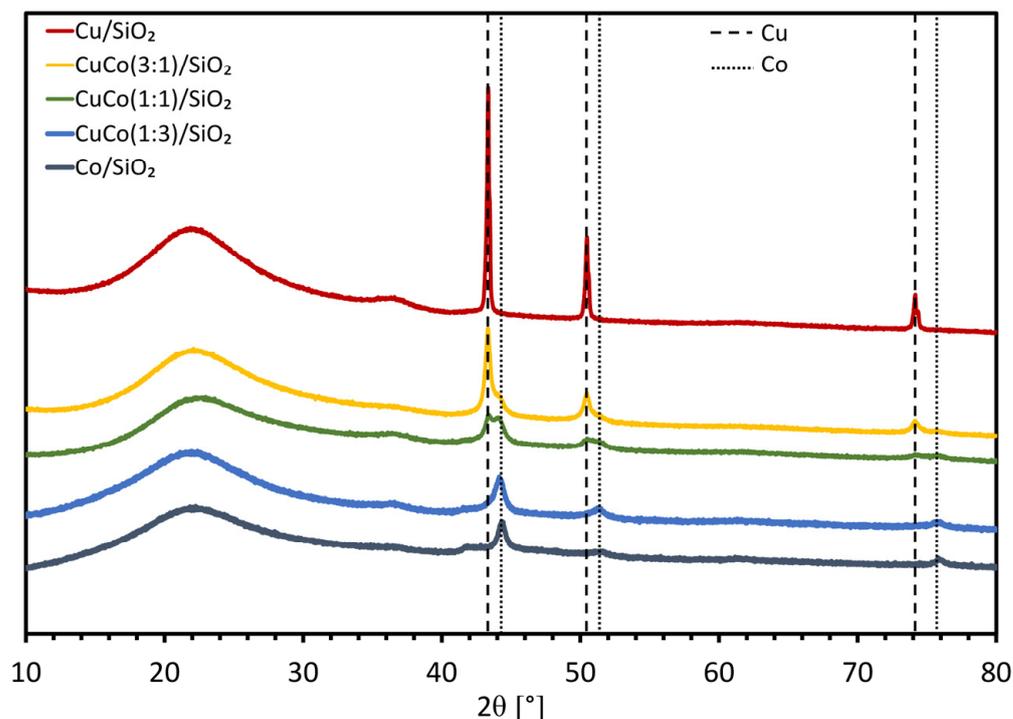


Figure 2. XRD results of CuCo/SiO₂ catalysts.

The activated Cu/SiO₂ catalyst's XRD pattern consisted of three visible diffraction peaks located at 43.3°, 50.5° and 74.3°, associated with Cu(1 1 1), Cu(2 0 0) and Cu(2 0 0). Besides the small signal located at ~36°, there was no evidence of CuO or Cu₂O presence in the sample.

The diffraction pattern obtained for the activated Co/SiO₂ suggests the presence of only the metallic form of Co. Nevertheless, the existence of highly dispersed on the catalysts' surface Co₃O₄ and CoO cannot be excluded. However, thorough studies of the activation process of such catalysts performed by Smith et al. [29] showed similar behavior of the Co/SiO₂ catalysts. CoO starts to convert into cubic Co⁰ phase above 400 °C. The transformation can be completed during a prolonged process at 600 °C [29].

Each bimetallic CuCo/SiO₂ catalyst demonstrated entirely different XRD patterns and hence diverse morphology of their active phases. CuCo(1:3) presented only Co⁰ related diffraction signals. On the other hand, CuCo(3:1) exhibited mainly signals assigned to Cu⁰, with a small sign of Co⁰ in the sample. In both cases, slight shifts of Cu and Co peaks were observed relative to the monometallic catalysts. It could suggest the modification of Cu or Co unit cell by other metal. Because copper and cobalt have limited miscibility, it is highly possible that CuCo alloy is formed in a limited amount, while metal present in excess creates a separate crystalline phase. Different XRD profile was observed for CuCo(1:1)/SiO₂ in which shifted Cu⁰ and Co⁰ signals overlapped. Simultaneously, the intensity of Cu⁰ signal significantly decreased. Such behavior could be associated with the formation of CuCo alloy or high dispersion of Cu nanoparticles on the SiO₂.

2.4. Transmission Electron Microscopy (TEM) Results

TEM images and particle size distribution of monometallic Cu/SiO₂ and Co/SiO₂ are shown in Figure 3. In comparison to the bimetallic catalysts (Figures 4–6), both monometallic systems demonstrated smaller metal nanoparticles.

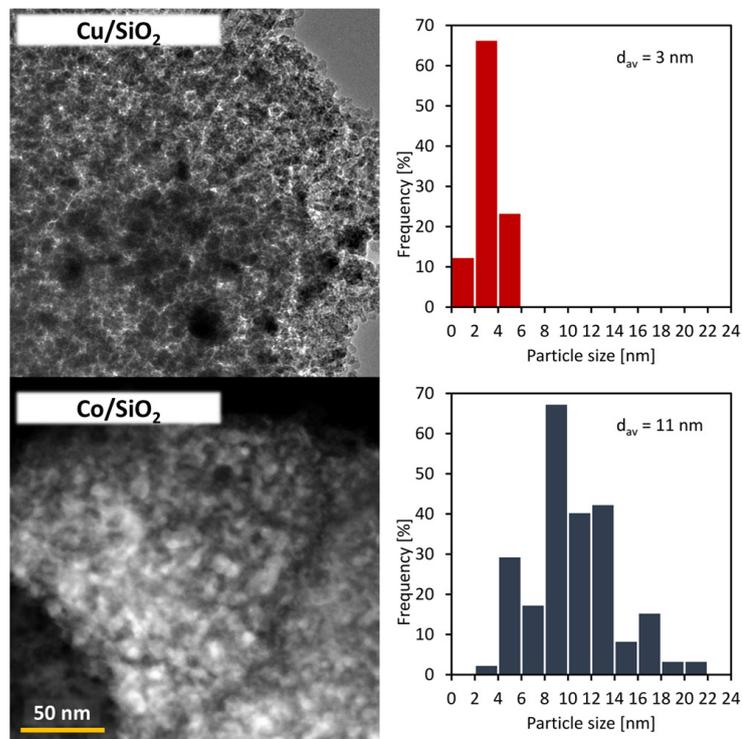


Figure 3. TEM images and particle size distribution of Cu/SiO₂ and Co/SiO₂.

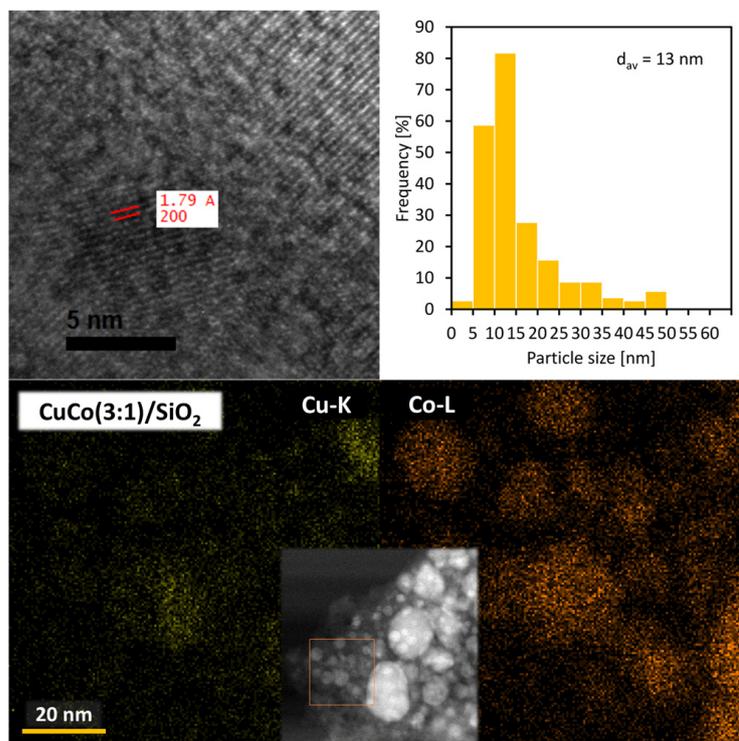


Figure 4. Interplanar distance, TEM mapping and particle size distribution of CuCo(3:1)/SiO₂.

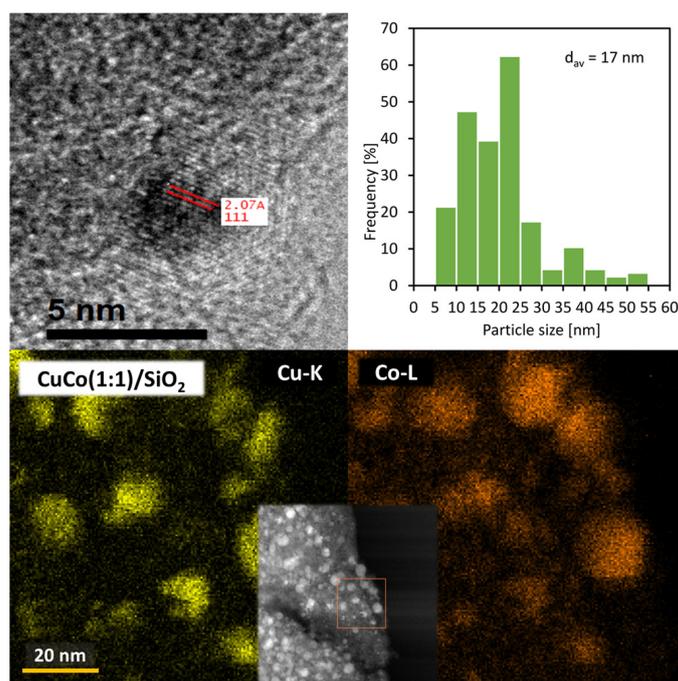


Figure 5. Interplanar distance, TEM mapping and particle size distribution of CuCo(1:1)/SiO₂.

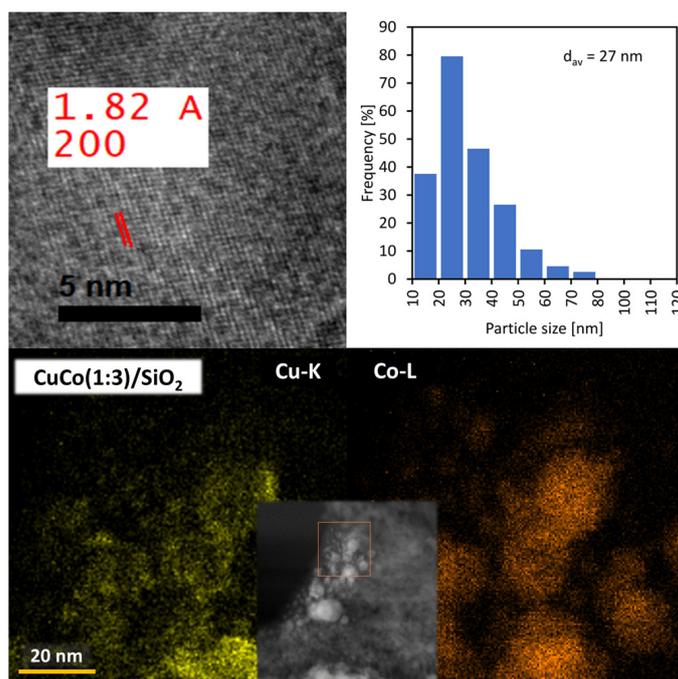


Figure 6. Interplanar distance, TEM mapping and particle size distribution of CuCo(1:3)/SiO₂.

The elemental mapping images, particle size distribution charts and interplanar distances of the bimetallic catalysts are shown in Figures 4–6. Each catalyst presents well-dispersed metal nanoparticles consisting of Cu and Co supported on SiO₂. The dominance of metal with higher concentration in the sample is noticeable. The increasing Co concentration in CuCo/SiO₂ resulted in the growth of formed metal nanoparticles. The average particle size in CuCo(3:1)/SiO₂ was equal to 13 nm, with a relatively narrow distribution. Setting up the Cu:Co ratio to 1:1 did not significantly affect the average particle size but broadened the distribution. Finally, the dominance of cobalt in CuCo/SiO₂ catalysts meaningfully increased the overall particle size. The measured interplanar distances of

nanoparticles in bimetallic systems allowed for determining the presence of CuCo alloy ($\text{Cu}_{0.52}\text{Co}_{0.48}$) in all tested catalysts.

2.5. Catalytic Tests Results

2.5.1. Catalytic Hydrogenation of Nitrocyclohexane in Liquid Flow Conditions

Before catalytic experiments, blank tests with support material in all reaction conditions were performed to eliminate the influence of the reaction conditions on catalytic performance. The obtained results proved negligible activity of SiO_2 in all tested conditions.

The catalytic hydrogenation of nitrocyclohexane in the liquid phase was performed at various reaction parameters (from 1 to 40 bar and from 50 to 125 °C). The selectivity and activity (expressed as C/Co and marked with \diamond) of the tested catalysts are shown in Figures 7–11. Both monometallic and bimetallic catalysts demonstrated satisfactory activity and selectivity to desired products.

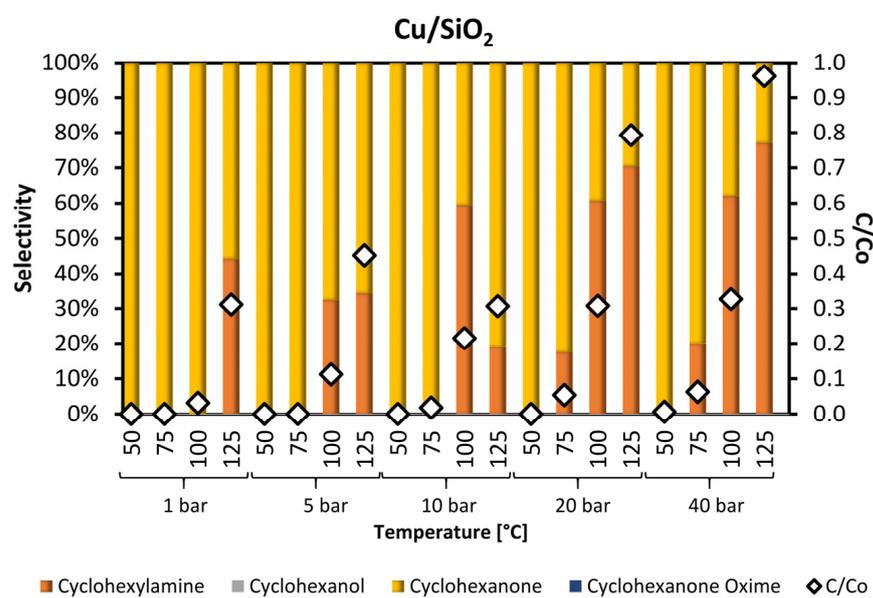


Figure 7. Catalytic hydrogenation of nitrocyclohexane in liquid flow conditions with Cu/SiO₂.

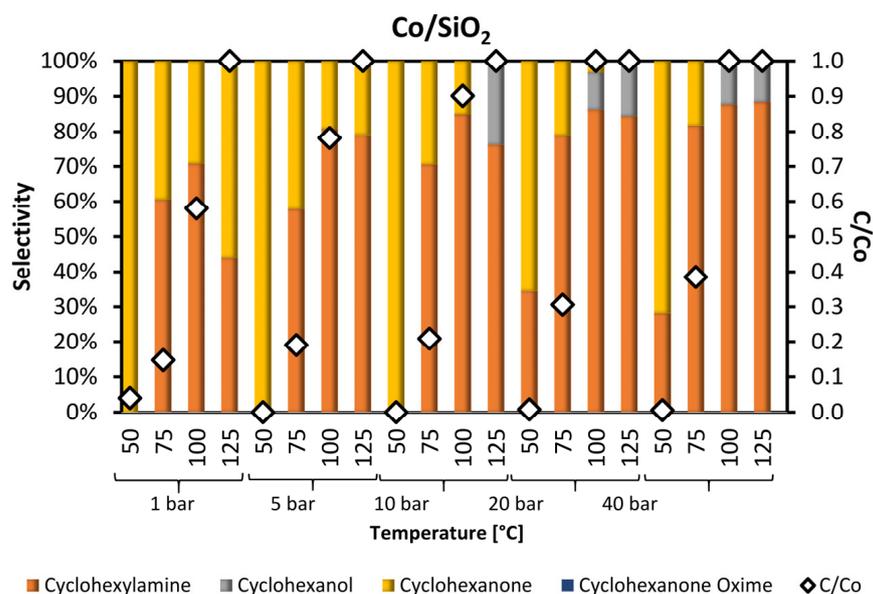


Figure 8. Catalytic hydrogenation of nitrocyclohexane in liquid flow conditions with Co/SiO₂.

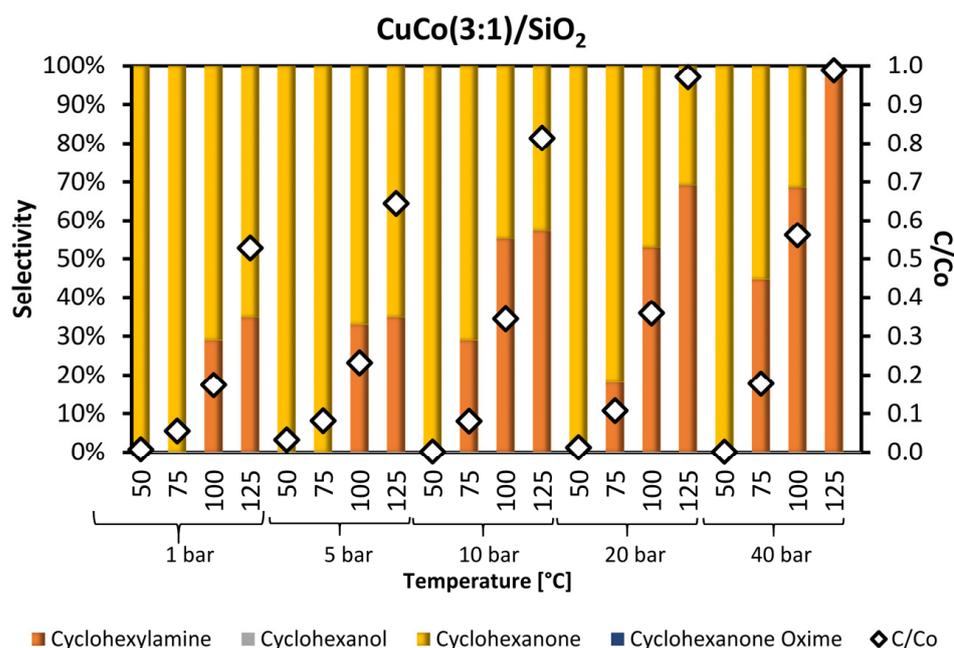


Figure 9. Catalytic hydrogenation of nitrocyclohexane in liquid flow conditions with CuCo(3:1)/SiO₂.

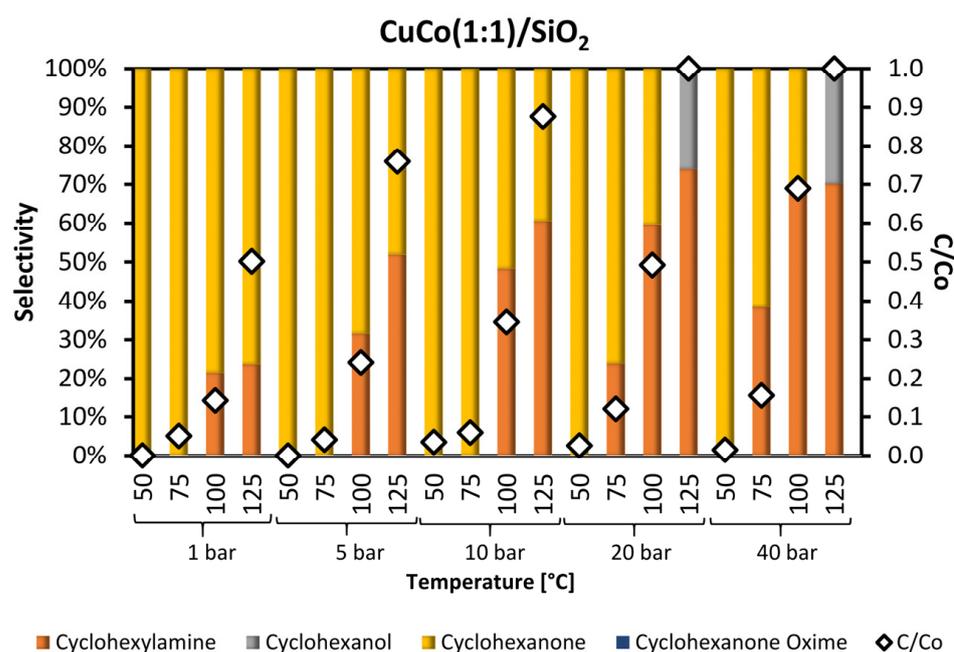


Figure 10. Catalytic hydrogenation of nitrocyclohexane in liquid flow conditions with CuCo(1:1)/SiO₂.

Cu/SiO₂ is generally less active than Co/SiO₂ (Figures 7 and 8). The main product of nitrocyclohexane hydrogenation with Cu/SiO₂ is cyclohexanone (Figure 7). According to the reaction Scheme 1, cyclohexanone formation requires less hydrogen. Hence, the selectivity of this catalyst could be influenced by a reduced amount of dissociated hydrogen on the catalyst surface. However, with simultaneous temperature and pressure increases, the activity of Cu/SiO₂ also increases. On the other hand, its selectivity varies only slightly, and the formation of a higher amount of cyclohexylamine is observable.

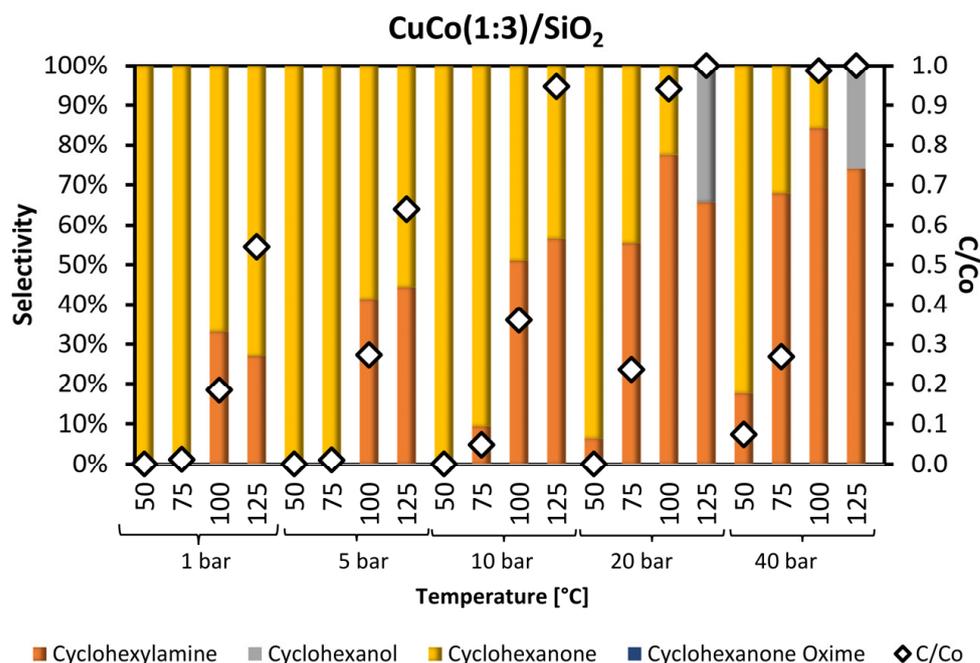


Figure 11. Catalytic hydrogenation of nitrocyclohexane in liquid flow conditions with CuCo(1:3)/SiO₂.

Monometallic Co/SiO₂ showed significantly higher activity in nitrocyclohexane hydrogenation (Figure 8) than its copper counterpart. Independently from the applied conditions, this catalyst steers the reaction into the formation of cyclohexylamine. At the temperature and pressure above 10 bar and 100 °C, cyclohexanol was detected as an additional product. No other products of nitrocyclohexane hydrogenation (cyclohexyl-cyclohexylidene amine, dicyclohexylamine) were observed.

Each bimetallic catalyst showed a different catalytic performance from the monometallic ones (Figures 9–11). However, the influence of each metal seems to be apparent. Regarding the overall catalytic activity, bimetallic systems are much like the more active Co/SiO₂. Nevertheless, the selectivity of CuCo/SiO₂ catalysts seems to be determined by the copper presence. Cyclohexanone is a dominant product of nitrocyclohexane hydrogenation at lower temperatures and pressures. An increase of the reaction conditions also switches selectivity into the formation of cyclohexylamine, which is especially visible for the samples with higher Co content (CuCo(1:3)/SiO₂). However, the formation of other nitrocyclohexane products (cyclohexyl-cyclohexylidene amine, dicyclohexylamine) was not observed.

Detailed analysis of the results obtained at various temperatures and pressures allowed us to determine the best conditions for the production of cyclohexylamine and cyclohexanone. Stability tests with selected catalysts were performed at determined parameters (Figures 12 and 13). The samples were collected at regular intervals. Co/SiO₂ allowed cyclohexylamine production at 10 bar and 125 °C, with over 90% selectivity for 5 h without any signs of deactivation. CuCo (3:1)/SiO₂ demonstrated similar stability at 5 bar and 75 °C during the formation 100% of cyclohexanone.

2.5.2. Catalytic Hydrogenation of Nitrocyclohexane in Gas Flow Conditions under Atmospheric Pressure

Each catalyst tested in the liquid continuous-flow reactor was also tested in gas flow conditions (Figures 14–18). Despite the differences between these two catalytic reactors and different reaction conditions, all the catalysts maintained similar selectivity to specific products.

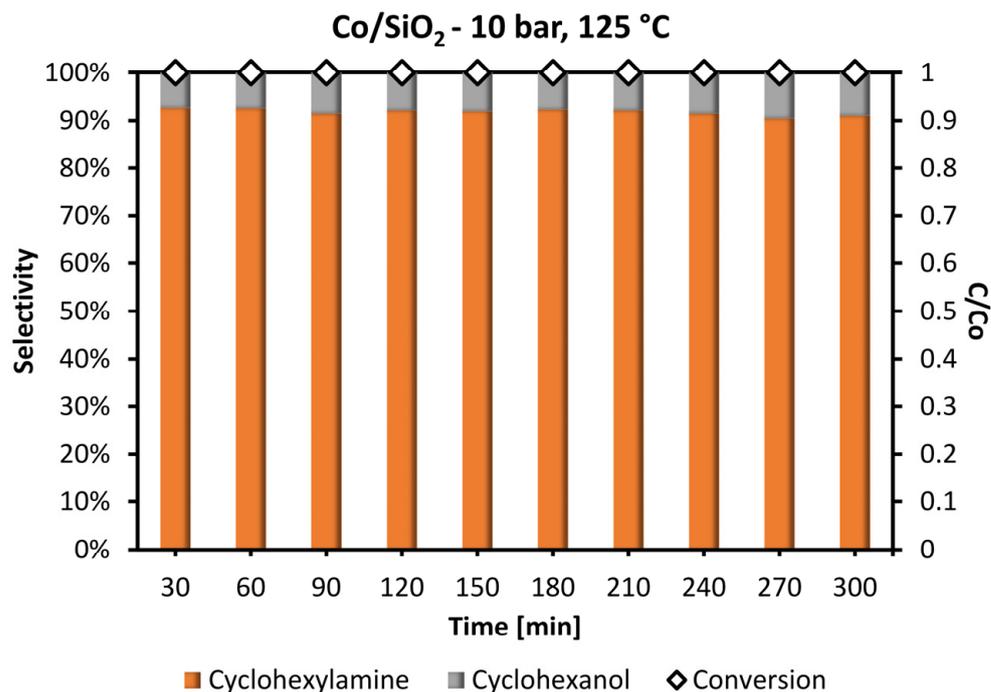


Figure 12. Stability test of Co/SiO₂ in catalytic hydrogenation of nitrocyclohexane in liquid flow conditions (10 bar, 125 °C).

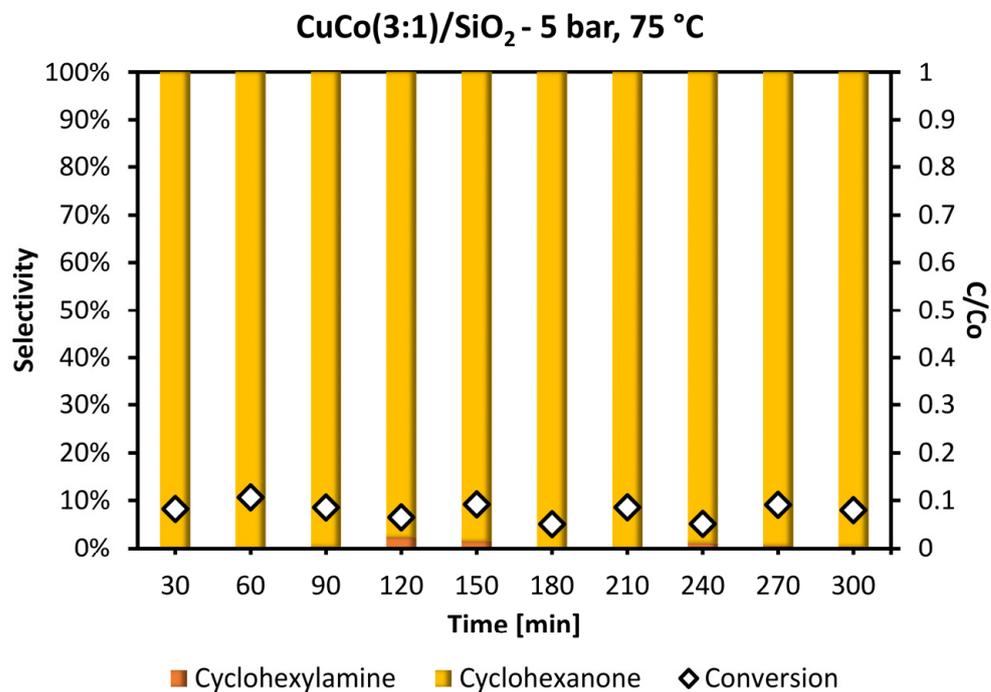


Figure 13. Stability test of CuCo(3:1)/SiO₂ in catalytic hydrogenation of nitrocyclohexane in liquid flow conditions (5 bar, 75 °C).

Monometallic Cu/SiO₂ demonstrated negligible activity in the hydrogenation of nitrocyclohexane with approximately 60% selectivity to cyclohexanone (Figure 14). On the other hand, Co/SiO₂ showed significantly higher conversion (~80%) and steered this reaction into the formation of cyclohexylamine (Figure 15).

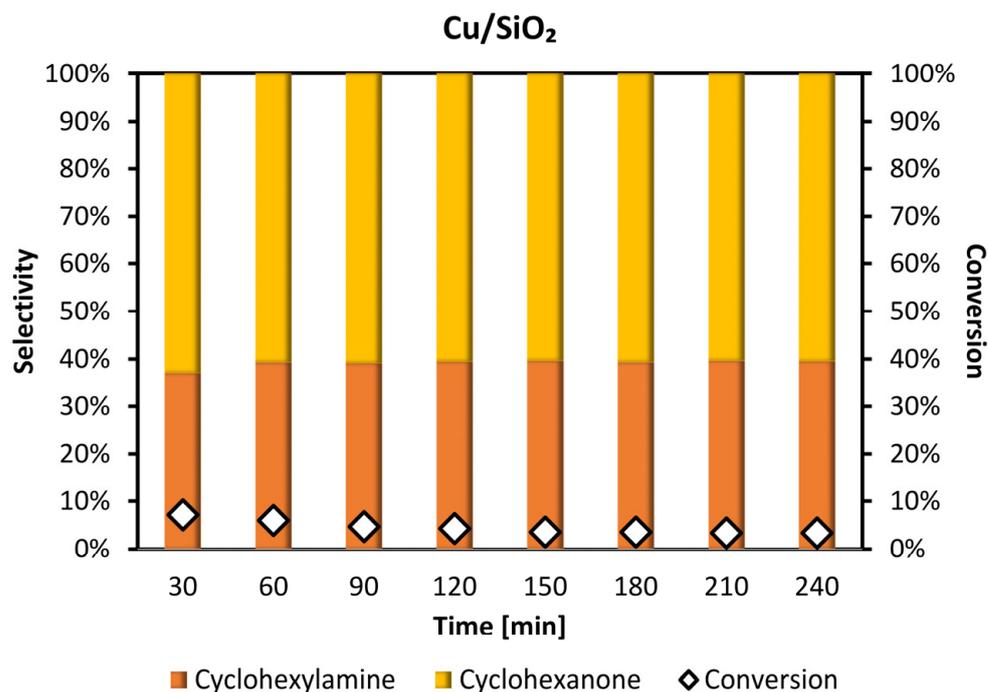


Figure 14. Catalytic hydrogenation of nitrocyclohexane in gas flow conditions with Cu/SiO₂.

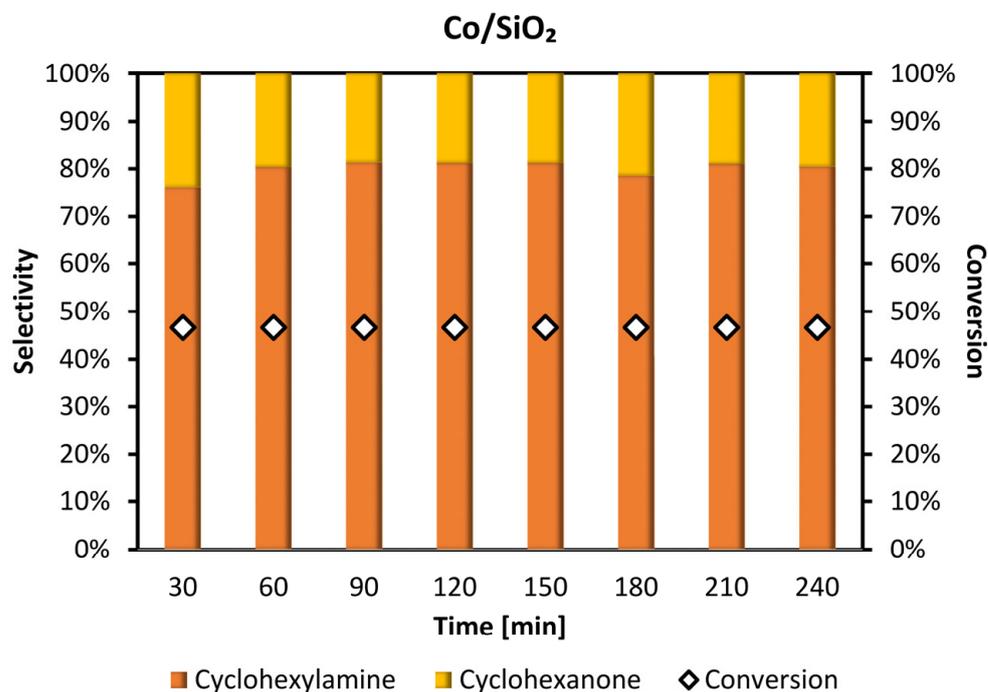


Figure 15. Catalytic hydrogenation of nitrocyclohexane in gas flow conditions with Co/SiO₂.

The results obtained for bimetallic catalysts are different from monometallic ones. However, the comparative analysis of catalytic performance allowed us to observe some correlation between their activity and the activity of the former ones. As in the case of experiments performed in liquid flow conditions, the lowest conversion among the bimetallic catalysts was demonstrated by CuCo(3:1)/SiO₂ (Figure 16). Determination of Cu:Co ratio for 1:1 in CuCo/SiO₂ catalysts gave ~50% selectivity to cyclohexylamine and cyclohexanone with 35% conversion (Figure 17). On the other hand, the most active was the CuCo(1:3)/SiO₂ with the highest concentration of Co.

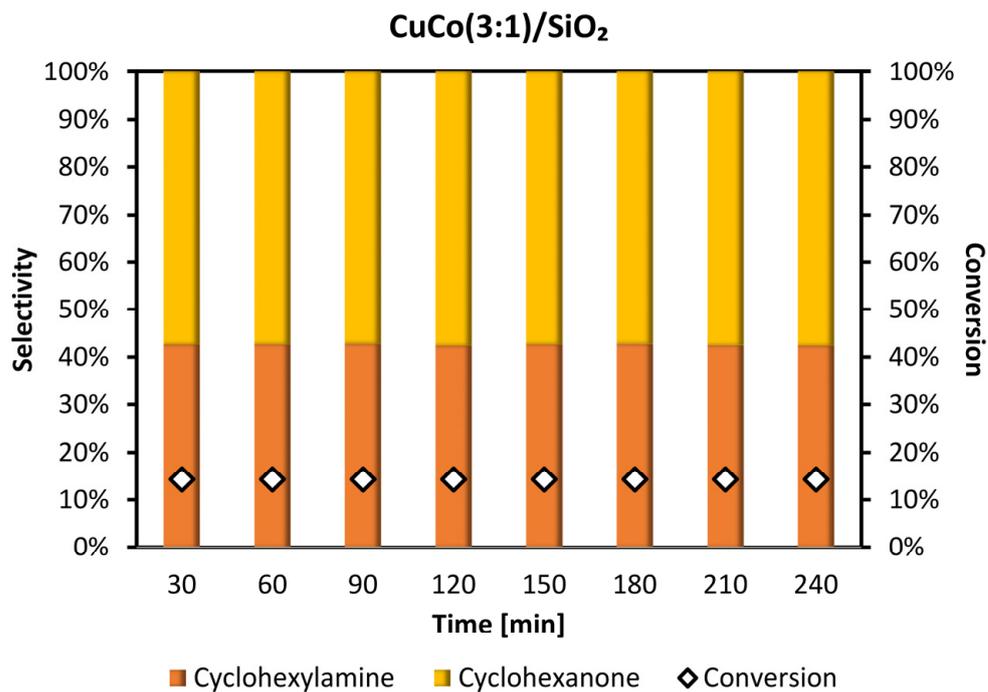


Figure 16. Catalytic hydrogenation of nitrocyclohexane in gas flow conditions with CuCo(3:1)/SiO₂.

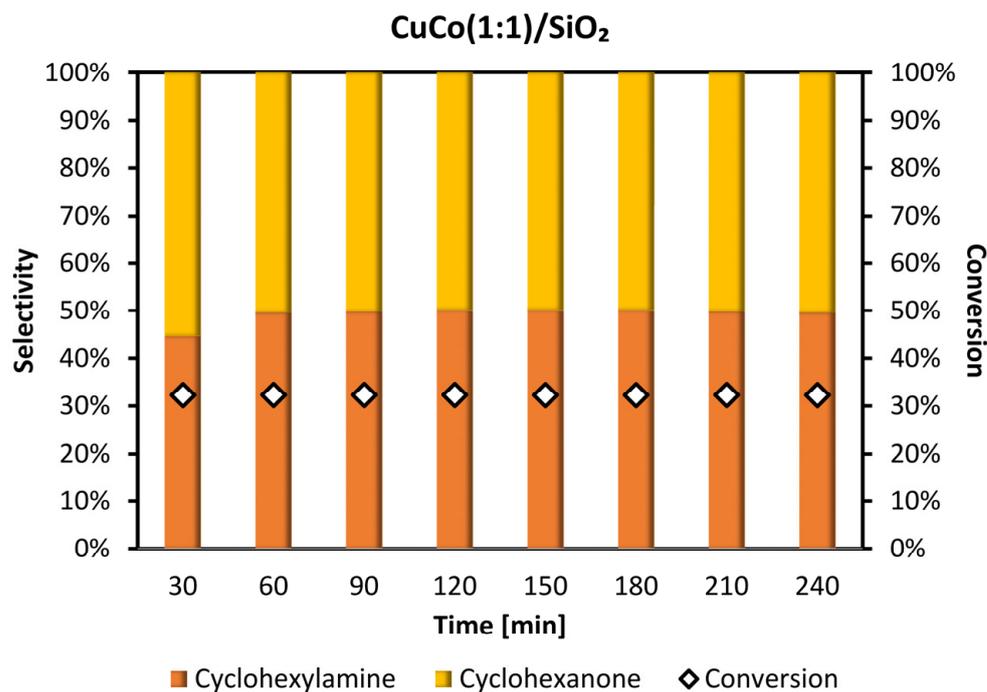


Figure 17. Catalytic hydrogenation of nitrocyclohexane in gas flow conditions with CuCo(1:1)/SiO₂.

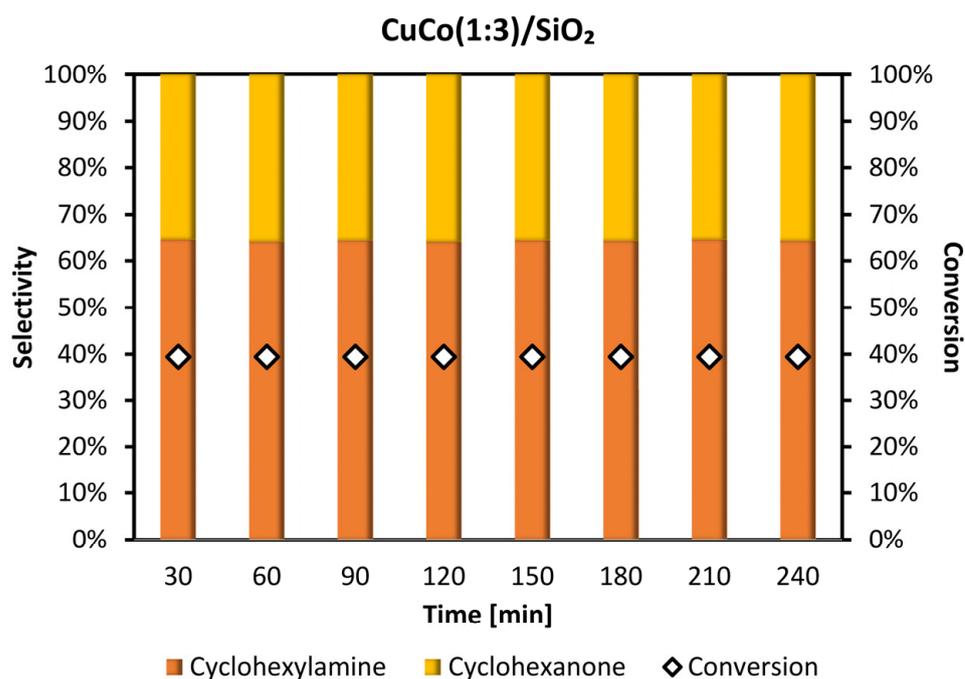


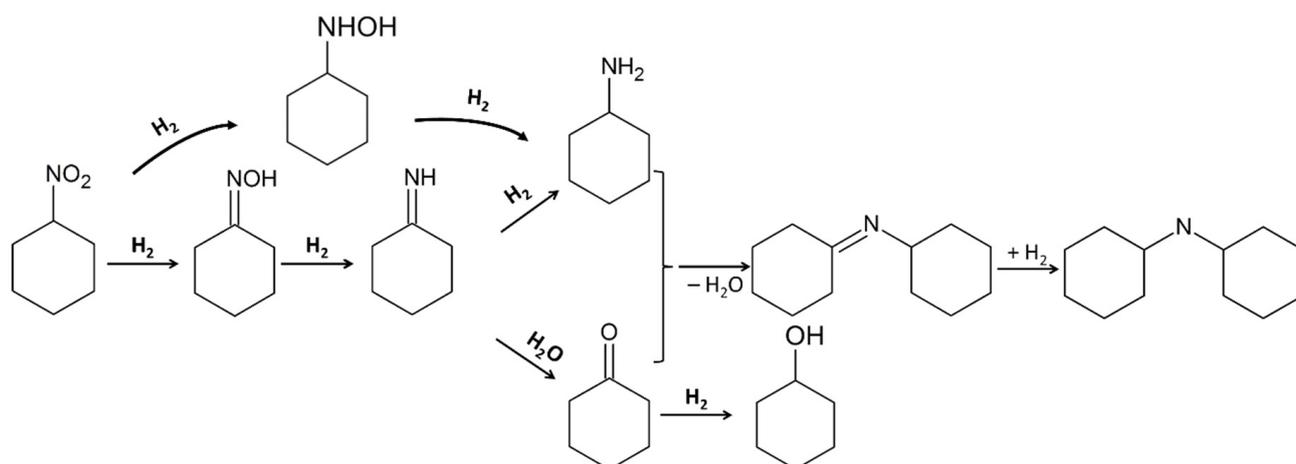
Figure 18. Catalytic hydrogenation of nitrocyclohexane in gas flow conditions with CuCo(1:3)/SiO₂.

2.6. Catalytic Hydrogenation of Nitrocyclohexane—Mechanism

Catalytic hydrogenation of nitrocyclohexane is still an under-researched area. Most of the research groups concerning this process proposed their own mechanisms. All of them were summarized by Kowalewski et al. [10]. In general, the nitrocyclohexane hydrogenation process could be presented as in Scheme 1. However, based on the mechanistic studies of Yao et al. [18], verifying the course of nitrocyclohexane hydrogenation is essential. Hence, the catalytic performance of the selected catalysts was examined at specific reaction conditions (40 bar, 100 °C). The results summarized in Table 2 confirmed that nitrocyclohexane hydrogenation on CuCo catalysts occurs by the pathway presented in Scheme 1.

Table 2. Cu/SiO₂, CuCo/SiO₂, and Co/SiO₂ physicochemical parameters.

Reactant	Nitrocyclohexane	Cyclohexanone Oxime	Nitrocyclohexane + Cyclohexanone Oxime
Catalyst		Products	
Cu/SiO ₂	Cyclohexylamine Cyclohexanone	Cyclohexanone	Cyclohexylamine Cyclohexanone Dicyclohexylamine
Co/SiO ₂	Cyclohexylamine Cyclohexanol	Cyclohexylamine Cyclohexanone Dicyclohexylamine	Cyclohexylamine Cyclohexanone Dicyclohexylamine
CuCo(1:1)/SiO ₂	Cyclohexylamine Cyclohexanol	Cyclohexylamine Cyclohexanone Cyclohexanol Dicyclohexylamine	Cyclohexylamine Cyclohexanone Dicyclohexylamine



Scheme 1. Catalytic hydrogenation of nitrocyclohexane [17,20].

3. Discussion

Despite the high applicability of nitrocyclohexane hydrogenation, the number of available studies is still limited. Nevertheless, a growing interest in this topic has been observed in the last few years [17–19]. However, to the best of our knowledge, there is no study concerning the comparison of the catalytic performance of any catalyst in gas-flow and liquid-flow conditions. Hence, the presented research seems to be unique in this field and may be an inspiration for further investigation.

Most of the research on the catalytic hydrogenation of nitrocyclohexane is focused on reactions performed in batch reactors [11–18]. Moreover, the reaction conditions applied by various research groups are not consistent with each other. Hence, even a comparison of results obtained in the same reactor type could be challenging. Nevertheless, taking into account the concentration of used reactants, the mass of the used catalyst, and the time needed to achieve a similar conversion, a general comparison of catalysts' performance can be made.

The analysis of the catalytic performance of Cu/SiO₂, Co/SiO₂ and CuCo/SiO₂ catalysts allowed for drawing some conclusions.

The chosen catalyst synthesis method (incipient-wetness impregnation) did not change the support material properties. Hence, the influence of the specific surface area and porosity was not considered in the comparison of catalytic performance of Cu, Co and CuCo in the nitrocyclohexane hydrogenation (Table 1).

In general, despite the well-known activity of copper catalysts in hydrogenation reactions [30] (superior to cobalt catalysts [41]), Cu/SiO₂ turned out to be significantly less active in the catalytic hydrogenation of nitrocyclohexane, both in gas and liquid flow reactors. However, Cu/SiO₂ demonstrated unique selectivity to cyclohexanone (Figures 7 and 14), while Zhang et al. [17] showed that Cu/SiO₂ in batch reactor steers nitrocyclohexane hydrogenation into the formation of cyclohexanone oxime (92 % selectivity with 74 % conversion). On the other hand, in our previous studies with CuZnAl hydrotalcite-derived materials [19], it was demonstrated that Cu nanoparticles steer this reaction into the formation of cyclohexylamine. However, CuZn nanoparticles could direct nitrocyclohexane hydrogenation into the production of cyclohexanone with a high yield [19]. Hence, the results obtained for Cu/SiO₂ (Figures 7 and 14) suggest that, in the case of cyclohexanone as a desirable product, modification of copper nanoparticles should be considered. The experiments with products of nitrocyclohexane hydrogenation on Cu/SiO₂ (Table 2) indicated that the high yield to cyclohexanone strongly depends on the dominant presence of cyclohexanone oxime. The simultaneous presence of cyclohexanone oxime and nitrocyclohexane on the catalyst surface allows for the formation of cyclohexylamine and dicyclohexylamine. Therefore, efficient production of cyclohexanone

requires a rapid transformation of nitrocyclohexane into cyclohexanone oxime, which limits their coexistence on the catalyst's surface.

Co/SiO₂ catalyst was previously tested in nitrocyclohexane hydrogenation in a batch reactor by Zhang et al. [17], and it turned out to be almost inactive and selective to cyclohexanone. However, Co/SiO₂ used in gas and liquid flow reactors steered the nitrocyclohexane hydrogenation into the formation of cyclohexylamine (Figures 8 and 15). The other hydrogenation product—cyclohexanol was also detected at higher pressures and temperatures (Figure 8). Considering the proposed reaction pathway (Scheme 1) and the results obtained at lower temperatures and pressures (Figure 8), the presence of cyclohexanol results from the further hydrogenation of cyclohexanone. Such catalytic behavior confirms the great activity of Co/SiO₂. Moreover, the extended experiment showed the high stability of this catalyst in the production of cyclohexylamine (Figure 12).

All bimetallic catalysts are more active than Cu/SiO₂ and less active than Co/SiO₂ in gas and liquid flow catalytic reactors. Nevertheless, despite the increased activity through the presence of cobalt, their selectivity is determined by copper. The obtained EDS images (Figures 4–6) show the coexistence of copper and cobalt species, which indicates the synergistic effect in CuCo/SiO₂ catalysts previously observed for CuCo catalysts by Marcos et al. [22] and Gou et al. [24]. Thorough literature analysis suggests limited mutual miscibility of Cu and Co. However, XRD measurements suggest the formation of CuCo alloy to some extent, while the metal present in excess creates a separate crystalline phase. Moreover, the measurement of interplanar distance confirmed the existence of CuCo nanoparticles on the SiO₂ surface (Figures 4–6). Such bimetallic nanoparticles demonstrated higher activity than Cu, keeping selectivity toward cyclohexanone characteristic for monometallic copper. For example, CuCo(3:1)/SiO₂ allows for a very efficient formation of cyclohexanone (100% of the selectivity, 9% conversion) at 75 °C under 5 bar for several hours, without signs of deactivation (Figure 13), while Cu/SiO₂ shows 100% selectivity but only 0.2% conversion (Figure 7).

4. Materials and Methods

4.1. Catalysts Synthesis

Commercially available SiO₂ (Davison 62) was used as a support material in the synthesis of Cu, Co and CuCo catalysts. In the first step, it was washed with deionized water and dried for 24 h at 110 K. In the next step, SiO₂ was pre-calcined in air at 723 K for 4 h.

All catalysts were prepared by incipient wetness impregnation using Cu(NO₃)₂ • 6H₂O (Chempur, Piekary Śląskie, Poland) and/or Co(NO₃)₂ • 6H₂O (Chempur, Piekary Śląskie, Poland) as metal precursors. The precursors were impregnated into support material using a rotary beaker with simultaneous heating provided by an infrared lamp for 24 h, until complete evaporation of the solvent.

Afterwards, the catalysts were calcined at 500 °C for 3 h (ramp 3 °C/min). Prior to the catalytic reactions, catalysts were activated in 10 % H₂/Ar at conditions determined by TPR measurements.

4.2. Surface Analysis—BET

The porosity and surface area of the catalysts were determined by Micromeritics ASAP 2020, employing the BET (Brunauer-Emmett-Teller) and BJH (Barret-Joyner-Halenda) methods and nitrogen as adsorbate. Measurements were performed at 77 K, and they were preceded by evacuation step—3 h at 573 K.

4.3. Temperature-Programmed Reduction

Temperature programmed reductions of catalytic systems were performed in a glass gas flow system equipped with a thermal conductivity detector (TCD). A sample of the material (0.1 g) was placed on the quartz frit in the quartz reactor, which was heated to 1100 K (ramp 10 K/min) in the stream of 10% H₂/Ar.

4.4. X-ray Diffraction (XRD)

X-ray powder diffraction patterns (PXRD) were collected using a PANalytical Empyrean Series 2 diffractometer equipped with a spinner and a silicon zero background holder. Cu-K α radiation was used with an X-ray tube operating at 40 kV and 40 mA.

4.5. Transmission Electron Microscopy (TEM)

TEM experiments were performed on the electron microscope Titan G2 60–300 kV (FEI, Tokio, Japan) equipped with EDAX EDS (energy-dispersive X-ray spectroscopy) detector. Microscopic studies of the catalysts were performed at an accelerating voltage of the electron beam equal to 300 kV. The sample was prepared by dispersion in pure alcohol using an ultrasonic cleaner; a drop of this suspension was placed on carbon films on copper grids.

4.6. Catalytic Activity Tests

The liquid-phase catalytic hydrogenation was performed using ThalesNano H-Cube Pro continuous-flow micro-reactor with an HPLC pump. Nitrocyclohexane (>95%, TCI) solution in ethanol (99.8% pure from Avantor Performance Materials, Gliwice, Poland) was flown through CatCart[®]70 cartridge with 0.1 g of a catalyst. The hydrogen was generated in situ via water electrolysis. Catalytic hydrogenation of nitrocyclohexane was conducted with each catalyst over a wide range of temperatures (50–125 °C), in the pressure range from 1 to 40 bar and flow rate of 0.5 mL/min and H₂ flow rate 60 mL/min. All of the reaction samples were taken at steady state conditions at regular intervals. Substrate conversion and product formation were analyzed by gas chromatography (GC) Bruker 456 GC equipped with FID detector and BP 1 60 \times 0.25 \times 0.25 column.

The gas-phase catalytic hydrogenation of nitrocyclohexane under atmospheric pressure was performed in a specially-designed glass gas-flow system equipped with independent H₂ and Ar lines. The catalyst (0.1 g) was placed on a quartz frit in a glass reactor. All catalytic experiments were performed at 100 °C in the 10% H₂/Ar mixture. Nitrocyclohexane (200 μ L/h) was introduced into the reaction mixture via a syringe pump (New Era NE-300). The analysis of the reaction progress was performed by gas chromatograph (HP-5890II, Santa Clara, CA, USA) with switching valve, FID detector and BP1 30 \times 0.25 \times 0.25 column.

5. Conclusions

The demonstrated results are further evidence of the high potential applicability of the gas and liquid flow nitrocyclohexane hydrogenation for industrial applications. Monometallic and bimetallic catalysts consisting of Cu and Co active phases proved to be active, stable and selective in nitrocyclohexane hydrogenation, both in a gas and liquid continuous-flow reactor. Cu nanoparticles steer nitrocyclohexane hydrogenation into the formation of cyclohexanone, but with low activity in gas and liquid phase. On the other hand, the application of Co nanoparticles leads to the production of cyclohexylamine as the main product. The catalytic performance of bimetallic systems strongly depends on the ratio between Cu and Co. The addition of a small amount of Co into Cu significantly increases catalyst's activity in comparison to Cu/SiO₂ (from 0.2% to 9% conversion at 5 bar and 75 °C). While Co increases the activity of CuCo(3:1)/SiO₂ catalyst, Cu has a much more significant effect on its selectivity. Finally, the optimal composition of the metallic phase Cu:Co = 3:1 gave 100% of cyclohexanone at 75 °C under 5 bar, showing very high and stable conversion for several hours. Further addition of Co leads to higher overall activity but affects the selectivity toward the desired product of CuCo(1:1)/SiO₂ and CuCo(1:3)/SiO₂. For these catalysts, the products of complete hydrogenation were obtained.

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