

Article

Enhanced Performance of Bimetallic Co-Pd Catalysts Prepared by Mechanical Alloying

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Abstract: Bimetallic catalysts can provide enhanced performance, and Co-based catalysts in particular have been studied in various respects for their activity in the deposition of carbon nanofibers (CNFs). The majority of studies on CNF catalysis use co-precipitation to create alloys, but recent work has demonstrated the suitability of mechanical alloying (MA) by ball milling to reduce cost and increase catalytic activity. This work establishes the unique ability of MA to control the microstructure to produce bimetallic composites, which retain distinct metallic phases that improve catalytic activity. It is demonstrated that Co-Pd alloys reach a maximum in catalytic activity at an intermediate time of mechanical activation, where 30 min of milling outperformed samples milled for 5, 15, 60, and 240 min at a reaction temperature of 550 °C and a 1:4 C₂H₄:H₂ reactant ratio. This indicates there is benefit to retaining the metals in distinct phases in close proximity. Ball milling provides a relatively simple and scalable method to achieve these unique microstructures, and in the optimal condition tested here, the activity toward carbon deposition is increased fourfold over prior work. Furthermore, the minimum temperature for deposition is also reduced. The characteristics of these materials, the effects of milling and annealing, and the underlying mechanisms of deposition are discussed.

Keywords: mechanical alloying; ball milling; carbon nanofiber; catalysis; bimetallic composite; ethylene

1. Introduction

Bimetallic catalysts are known to have distinct performance advantages at lower cost than pure catalysts [1]. The performance of these alloys has been attributed to the varied elemental distribution at the surface, which is often controlled through composition [2], though temperature is also important [3]. In the field of carbon nanofiber (CNF) catalysis, the use of bimetallic catalysts is well documented, with examples including Ni-Cu [3,4], Fe-Ni [5], Fe-Cu [6,7], and many more. Most pertinent to this work, Co has been alloyed with Ag [8] and Cu [9–11] for CNF deposition, and when alloyed with Ag, as little as 1% dramatically increases the conversion of ethylene to solid carbon (as CNFs), but larger quantities do not increase this benefit [8]. It is suggested that Ag introduces electronic perturbations in the alloy that modify the adsorption of ethylene, but alloying also modifies other factors such as the deactivation conditions (e.g., [10]). The controlled addition of sulfur to Co has also been noted to increase CNF deposition rate by surface modification [12], but again, the addition provides diminishing returns.

In prior work on Co-Pd alloys for CNF deposition [13], small additions of Co to Pd, and vice versa, were found to be significantly more efficient toward CNF deposition than the pure metals, but equal mixtures were most effective. The primary difference from other alloy studies in CNF deposition is that, in this system, the two elements were more effective when they were not fully alloyed. Rather, the activity was maximized by coarsely mixing powders of the two metals and using that mixture

in the reaction without further modification. The enhanced deposition activity was attributed to complementary chemistry between the two elements, most likely a combination of differing radical chemistry and a hydrogen spillover effect from the Pd phase to the Co phase [14]. Additional work on that system was of interest since directly controlling the extent of mixing may provide additional insight into the mechanisms and provide a template for other bimetallic catalysts.

Mechanical alloying (MA) has been applied for decades to produce nanostructured alloys and nonequilibrium mixtures that are impractical or impossible by other means [15]. In many studies using MA, the complete refinement and mixing of the elements is the desired outcome, but there are useful properties from incomplete mixtures, also referred to as bimetallic composites. Although unsupported bimetallic alloys are typically produced by chemical methods, including reduction of metallic salts, precipitation of nitrates, or selective leaching/dealloying of ternary alloys [16], these alloys and heterogeneous mixtures may also be created by preventing or interrupting the alloying process. This work applies nanoscale microstructural tailoring to leverage the known benefits of bimetallic catalysts and to investigate interesting phenomena in heterogeneous mixtures.

Nanoscale multilayer metallic structures of this type may be precisely created through layered deposition [17,18], but a low-cost, scalable method is preferable for bulk applications. Mechanical alloying by accumulative roll bonding can also achieve a nanoscale lamellar structure [19,20], but in many catalytic applications, the relatively low surface area is a disadvantage. Ball milling is capable of producing fine powder that is more suitable for catalysis, and the process can also be relatively rapid. Therefore, MA by high-energy ball milling was used to create lamellar microstructures within loose powder. The degree of alloying is controlled by the milling duration, such that the lamellae can be variously sized or eliminated. The catalytic activity of these alloys is then assessed by CNF deposition rate. The findings indicate that the structure can be suitably controlled to produce unique catalytic properties and that partial mixing of these elements is more effective than complete alloying. This provides unique implications for other material systems and applications that are only practical using MA.

2. Materials and Methods

2.1. Catalyst Preparation

High-energy cryogenic ball milling was performed using a modified SPEX 8000M mixer/mill (SPEX SamplePrep, Metuchen, NJ, USA). For each run, equiatomic mixtures of Pd and Co were added to a 440C stainless steel milling vial with the addition of 440C stainless steel ball bearings (16 at 6.35 mm and 17 at 7.94 mm). The starting materials were Pd (chips, 99.995%) and Co (powder, <150 μm , 99.9%). Each run consisted of 5 g total sample mass for a 10:1 ball:powder mass ratio. The duration of milling was varied for each sample run such that samples milled for 5, 15, 30, 60, and 240 min were produced. All materials were stored, weighed, and transferred to and from the vial under Ar (<1 ppm oxygen, <1 ppm H_2O). To determine the extent of alloying, annealing at the maximum reaction temperature (550 $^{\circ}\text{C}$) was performed by inserting the milled powder into a preheated, single-zone, 50 mm diameter tube furnace (Across International, Inc., Livingston, NJ, USA), and the sample was held at that temperature for 1 h, as measured by a thermocouple mounted directly above the sample boat. Before, during, and after the annealing process the chamber, including the sample, was purged with 5% H_2 (bal. Ar) at a flow rate of 200 sccm.

2.2. Carbon Nanofiber Deposition

To determine the catalytic activity of the samples, carbon deposition was performed on each at 450, 500, and 550 $^{\circ}\text{C}$. Each of these reactions consisted of 50 mg of sample powder placed in an alumina boat and located at the center of a single-zone tube furnace (Across International, Inc., Livingston, NJ, USA). After sample placement, the furnace was ramped to the reaction temperature in 20 min, held for one hour during the reaction, then allowed to cool under nitrogen (99.9999%). Reaction gases

were ethylene (C_2H_4 , chemically pure) and 5% H_2 (bal. Ar) with flow rates of 17.8 sccm and 88.9 sccm, respectively, to achieve a 1:4 $C_2H_4:H_2$ ratio. Gas flow was controlled using digitally programmed MKS G-series mass flow controllers (MKS Instruments, Inc., Andover, MA, USA). Reaction kinetics were determined by measuring the sample mass before and after the reaction, and deposition rates represent the mass gain per gram of catalyst (i.e., mg carbon/mg catalyst). Deposition rates were determined by the average of at least three reactions at each condition. Error bars on those data points represent one standard deviation (plus and minus) from the mean.

2.3. Characterization

Catalyst microstructures were examined using a Zeiss Auriga 60 CrossBeam SEM/FIB (Carl Zeiss Microscopy GmbH, Jena, Germany). These samples were prepared by mounting them in epoxy and polishing with progressively finer grit abrasives, culminating with 1 μm alumina paste. Energy-dispersive X-ray spectroscopy (EDS) mapping was also performed on powder milled for 5 min and then reacted for only 5 min to determine early-stage deposition characteristics. Catalyst powders were also analyzed using a PANalytical X'Pert Pro MPD X-ray diffractometer (XRD) (Malvern Panalytical B.V., Almelo, The Netherlands) with Cu anode (Cu $K\alpha$ wavelength: 1.54 Å). Samples were placed on a low-background substrate. Diffraction patterns were processed by stripping $K\alpha_2$, smoothing, and background subtraction using Xpert Highscore software (also Malvern Panalytical B.V.). All patterns are presented as relative intensities with arbitrary units (arb. units).

3. Results

3.1. Catalyst Preparation

The mixing of Pd and Co was tracked by XRD after each milling time, and the results are shown in Figure 1A. It can be seen that the Pd and Co peaks gradually broaden and lose intensity with increasing milling time, which is consistent with the development of a nanocrystalline microstructure [21] or amorphization (e.g., [22,23]). The peaks for each phase remain distinct until the 240 min milling time where a single, primary peak for single-phase, fcc α Co, Pd [24] appears between the normal positions of Pd and Co. Due to the considerable milling time, the higher-angle peaks are not readily distinguished. It is expected, however, that the alloying process is complete after that duration. This is further supported by SEM results discussed below.

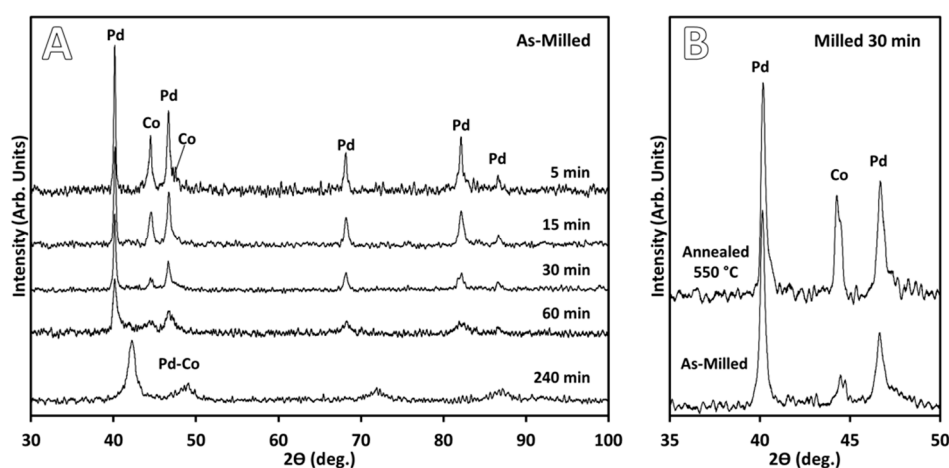


Figure 1. XRD profiles for samples (A) produced using milling times listed, and (B) samples milled for 30 min in the as-milled condition and after annealing at 550 °C for 1 h.

The as-milled microstructure is expected to change at elevated temperature. To determine the extent of change, the sample milled for 30 min was annealed at 550 °C for 1 h. Although catalyst disintegration is expected to occur much faster during carbon deposition, the stability of

the microstructure over the reaction period could still be determined. As shown in Figure 1B, the XRD pattern of the annealed sample is similar to the as-milled condition, which indicates that extensive alloying does not occur. There is a notable increase in the Co intensity relative to the Pd, but both have sharper peaks. The microstructural refinement during milling for such a short duration is expected to affect the two metals differently, especially given their difference in initial form (chips vs powder for Pd and Co, respectively). A slight peak shift is noticeable after annealing, with Pd peaks shifting to higher angles and Co shifting to lower angles. This may be attributable to alloying, as Co has a smaller atomic radius than Pd, but using the Pd (111) peak (at about 40 degrees), the shift is only 0.032° after annealing (from 40.148° to 40.116°). Using Bragg's law, this corresponds to a 0.00017 nm shift in interplanar spacing, which indicates a negligible change in Co concentration in the Pd lattice. This number should not be over-interpreted, as strain relaxation and other factors may also contribute. This general estimation, together with the distinct peak separation in the XRD pattern, supports the conclusion that alloying does not significantly progress during heating to the reaction temperature.

To determine the phase dispersion in the Pd-Co alloys, polished samples were imaged using SEM. As shown in Figure 2, the two metals remain in readily identifiable regions up to 30 min of milling time. After 60 min, the regions are refined to the nanoscale, but there is still a distinction between the phases at higher magnification. After 240 min, no distinguishable phase separation was found at any magnification. Note the scale bar differences between Figure 2A,B and Figure 2C,D,F in order to capture the mixing behavior. Figure 2E is the increased magnification in the inset of Figure 2D. It is evident that the milling process quickly refines the microstructure, but it can be readily controlled.

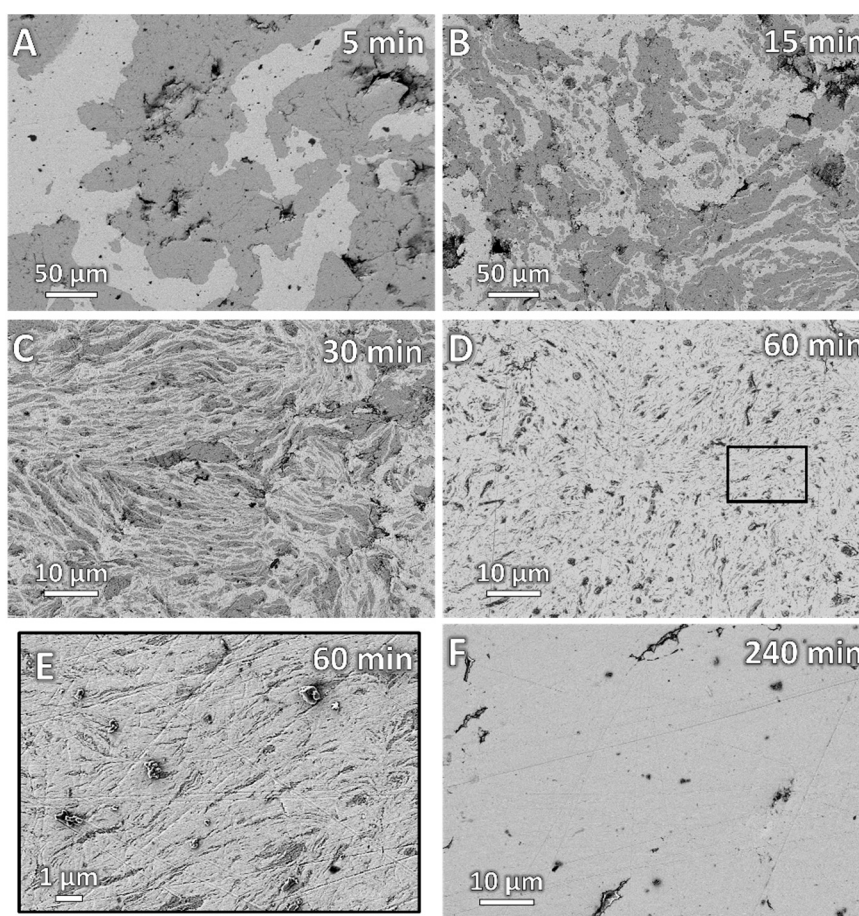


Figure 2. SEM micrographs of polished sections of alloys after milling for (A) 5 min, (B) 15 min, (C) 30 min, (D) 60 min, with (E) high-magnification image of inset, and (F) 240 min. Darker regions of images are Co and lighter regions are Pd. No distinct regions are visible after 240 min.

3.2. Catalytic Performance

Carbon deposition was assessed by the mass gain per unit time during a 1 h reaction. To determine the deposition kinetics, reactions using catalysts of various milling times and various temperature were used, and the results are presented in Figure 3. It can be seen that the milling time has a distinct impact at each of the temperatures tested. Although the deposition rate was the lowest overall at 450 °C, the milling time has the most notable influence. Specifically, only the 15 min and 30 min samples show any notable deposition, and the 30 min milling time is nearly four times higher. The 30 min sample is also the most effective at 500 °C and 550 °C. The 5 min samples are the least effective, with little deposition at any temperature. The activity rapidly rises at 15 min and slowly drops at 60 min and 240 min. These results indicate that the degree of mixing determines the minimum temperature where the catalyst is active and that the overall activity is maximized by partial mixing, such that undermixed or overmixed alloys are less effective. Even at 550 °C, pure Co and pure Pd only resulted in $0.05 (\pm 0.03)$ and $0.79 (\pm 0.08)$ mass gain (mg carbon/mg catalyst), respectively, which is less than the sample milled for 5 min (i.e., 1.38 ± 0.14 mg carbon/mg catalyst).

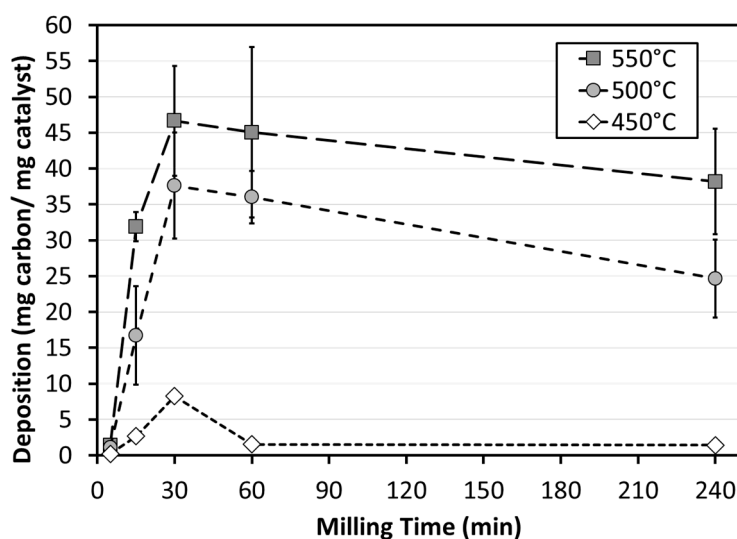


Figure 3. Normalized carbon deposition amounts from Pd-Co catalysts processed using varying milling times and reaction temperatures after a 1 h reaction duration in 1:4 C₂H₄:H₂. All data points have error bars with a magnitude of one standard deviation from the mean.

The nature of the carbon deposition in relation to the metallic phases was of interest, but due to the rapid reaction rates, the particles are quickly consumed. To achieve clear phase separation and deposition characteristics, the powder milled for 5 min was only reacted for 5 min. The results of this deposition are shown below. In Figure 4, EDS is combined with secondary electron (SE) imaging to determine the location of carbon deposition and the underlying composition. It can be seen that the carbon is locally deposited on the particle (Figure 4A) and is in the form of early stage CNF growth (Figure 4B). When the composition of the particle is examined, it is revealed that the carbon is principally located on Co-rich areas (Figure 4C,D). This indicates the Pd is creating favorable conditions for Co-mediated deposition to occur.

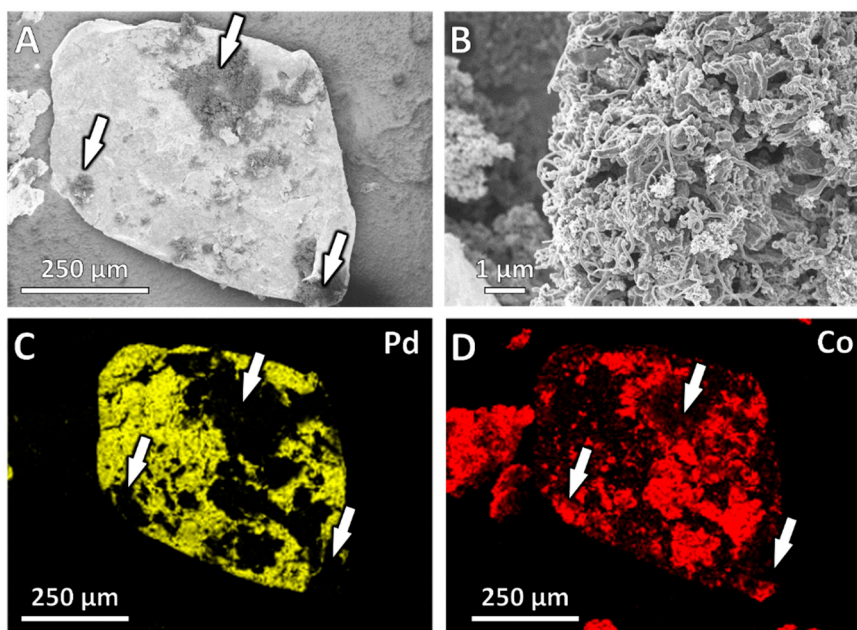


Figure 4. Pd-Co sample milled for 5 min and reacted at 550 °C for 5 min in 4:1 C₂H₄:H₂. Secondary electron images of (A) the catalyst particle and (B) magnified image of the carbon deposited. EDS maps of (C) Pd and (D) Co corresponding to particle image in (A). White arrows indicate carbon deposits.

4. Discussion

4.1. Catalyst Preparation

Ball milling is a versatile technique that can be used to generate nanostructured and nonequilibrium alloys. This can be a valuable tool in catalyst development, as immiscible elements and composite phases can be mixed and refined to create combinations not possible by other means. The characteristics of the materials being mixed and the milling conditions are both critical to the outcome of the process. The alloying/mixing process varies depending on whether the ingredients constitute a ductile-ductile, ductile-brittle, or brittle-brittle combination [25]. For instance, highly ductile metals being milled at room temperature will rapidly mix, but they tend to cold weld to the milling media and container.

Surfactants can be used to prevent this, but contamination from the surfactant [26] may be detrimental to the catalytic properties. Traditional co-precipitation methods are also susceptible to contamination from the starting materials, such as chloride or nitrate precursors [9]. Where beneficial, ball milling may actually be used to intentionally incorporate trace impurities. As done here, cryogenic milling can be used to reduce cold welding with less contamination, though any ball milling process is subject to some contamination from the attrition of the milling vial and media [27]. Any source of contamination can result in a change of activity and selectivity in catalysis, so it should be carefully monitored in these processes, especially at longer milling times and higher temperatures. Although cryogenic milling provides an increase in the rate of microstructural refinement and greater solid solubility extension [25], it does add complexity. Even with extensive cryogenic milling, highly immiscible combinations, such as Cu-W [28] or Cu-Ta [29,30], may not be achievable, though solid solubility can be extended significantly [31,32]. The fine-scale dispersion of insoluble phases was among the first applications for ball milling [33], and it may continue to be valuable in functional applications. Industrial applications often employ low-energy ball milling in large, horizontal, “tumbler” mills, and any deviation from the process parameters used here will have to be studied on a case-by-case basis to determine the optimum conditions for creating bimetallic composites.

4.2. Catalytic Performance

In the Co-Pd system, the ability to create lamellar composites provides a useful increase in catalytic activity. Although Co and Pd are fully soluble [24], the alloying process can be interrupted by short-term cryogenic processing, such that thermal energy for diffusion is minimized. This may be particularly important in highly soluble systems since localized impact temperature during milling can be hundreds of degrees Centigrade [25]. Heat during processing is not the only complicating factor. In the preparation Ni-Cu catalysts by ball milling [34], it was noted that even when distinct phases remain after milling, they are fully alloyed at modest temperature (i.e., 200 °C), which is well below the reaction temperature of 550 °C. Therefore, the long-term stability of the catalyst may be compromised. Complete alloying does not occur in the Co-Pd mixtures after annealing at 550 °C for 1 h, and this is attributable to slower interdiffusion in the Co-Pd system [35]. The catalyst in CNF deposition is rapidly consumed, so long-term microstructural stability is less of a factor.

The separation of the Co and Pd phases dictates the catalytic performance, and there are indications the Pd enhances the reactivity of Co. There are two primary mechanisms that are suggested: (1) Pd promotes the reduction Co oxides by the activation and migration of hydrogen, or (2) Pd produces radical gaseous species more favorable to react with Co. In regard to the reduction of Co oxides by Pd, this process has been studied in various aspects by Noronha et al. [14,36]. Specifically, during the reduction of mixtures of PdO and Co₃O₄, the presence of metallic Pd promotes the reduction of Co₃O₄. It was also noted that gasification of the graphite support contributed to the direct reduction of the oxides [14]. Additionally, the behavior of Pd as a carbon “sponge” during dehydrogenation of ethylene has been noted [37], thereby providing additional hydrogen for reduction.

Although the enhanced reduction of Co may contribute, it is not expected to be the primary factor. Dehydrogenation of hydrocarbons can result in catalyst deactivation by numerous mechanisms [38]. The choice of the hydrocarbon and the introduction of hydrogen to the gas feed has been studied for varying carbon feedstocks, such as in work by Kim et al. [39], where ethylene, methane, and acetylene were studied under varying deposition conditions. There, it is suggested that the manner of interaction of the hydrocarbon and the catalyst and the promotional effect of hydrogen are both important. Hydrogen is repeatedly noted in CNF literature to inhibit poisoning/fouling of the catalyst and to change the structure of the resulting CNFs (e.g., [7,40,41]) by modifying the wetting behavior of the catalyst. It is plausible that the use of an alternative carbon feedstock, such as ethane (C₂H₆), may pre-empt the hydrogenation of ethylene and provide suitable activity, but the varying role of hydrogen in deposition kinetics, including in reactions involving methane and other alkanes, indicates it is important as a separate reactant.

As an alternative to the simple reduction of Co, the so-called complementary chemistry mechanism suggests that the two metals, operating independently, provide a synergistic improvement in deposition rate. As described in the introduction, the benefits of true alloys are well-documented. Indeed, even here, the production of a fully alloyed catalyst after 240 min of milling provided significant improvement over the alloy milled for only 5 min. In the original work on this system [13], the pure metals were effectively inert (Pd was also studied separately [42] under these conditions), and as the mixture approached a 50-50 ratio, the rate peaked at about 150 mg/hr. Given the standard 12 mg catalyst load in that work, this represents an 11.5 deposition ratio (mg carbon/mg catalyst) over 1 h, which is a noteworthy improvement. The deposition ratio in this work peaked above 45, which is about 4 times higher. Evidently, the phase separation distance is critical. It is also controllable by ball milling, and therefore tunable catalysts can be created from bimetallic composites.

It was observed in the catalyst milled for 5 min and reacted for 5 min (Figure 4) that growth occurs on Co first. The disproportionate benefit of Pd to Co was observed in the prior work [13] by applying powder of one metal to foil of the other. When that was done, the deposition on Co foil in the presence of Pd powder was significantly improved, while deposition on Pd foil with Co powder was limited. While the details of that will not be repeated here, the importance is emphasized by these findings. Together with prior work on Pd where an initiation period was observed before fiber

growth, it is expected that Pd provides a catalytic effect to convert ethylene and hydrogen to a more favorable chemistry for Co to catalyze deposition, and as the reaction continues, Pd also becomes active in that deposition. Although there is undoubtedly some level of alloying, the principal benefit comes from maintaining distinct phases. While the primary focus of this study is the capability of mechanical alloying to produce enhanced bimetallic catalysts, it is expected that further investigation of the catalytic processes can be used to enhance the kinetics even more, possibly while using less Pd. Most importantly, this work establishes the unique opportunities in catalyst design made possible by mechanical alloying through ball milling.

5. Conclusions

The use of alloys to improve catalytic performance is well documented, but the creation of bimetallic composites provides unique challenges and opportunities. The challenge is to create microscale or nanoscale lamellar structures using a simple, scalable method. The opportunities include unique, nonequilibrium alloys, nanoscale composites, and other microstructural tailoring to optimize selectivity, reduce process temperature, or otherwise improve catalytic efficiency. By examining varying milling times, the level of mixing can be controlled to achieve a faster CNF deposition rate. Specifically, after 30 min of milling, the deposition rate was higher than either shorter or longer milling times. Characterization by XRD and SEM reveals that the phases are distinct after milling and annealing to the highest deposition temperature of 550 °C. The benefit of these bimetallic composites is thought to be primarily driven by a promotional effect of Pd on Co. This work uniquely demonstrates the utility of mechanical alloying by ball milling to produce functional bimetallic composites.

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