

Recent Advances in Cobalt and Related Catalysts: From Catalyst Preparation to Catalytic Performance

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In our days cobalt, Co, and related catalysts are very attractive because they exhibit a lot of advantages like low cost and high activity in a significant variety of different applications. Cobalt-catalysts are among the most active catalysts for Fischer-Tropsch synthesis and they promote the catalytic activity of the hydrodesulfurization catalysts. Also, they have other significant applications in environmental protection like oxidation of volatile organic compounds, VOC, persulfate activator, ammonia synthesis, electrocatalysis, and many more. Cobalt-catalysts are active, stable, and exhibit significant oxidation-reduction activity, as Co can be found either as Co(II) or Co(III). Also, many molecules can interact with cobalt-supported phase by co-ordination due to partially filled d-orbital. Co-catalysts can be supported in almost all the inorganic supports like alumina, titania, zeolites etc. The cobalt oxide phase can be stabilized onto the surface of the support due to variable interactions between support and cobalt phase. These interactions are crucial for catalytic activity and can be regulated by proper selection of the preparation parameters like the type of support, the Co loading, impregnation method, and thermal conditions.

The energy problem seems to be one of the most serious among the top 10 problems of the humanity. It is more complex since the public discussion about energy is dominated with the climate change. One possible solution is the development of more green approaches for the replacement of fossil fuels. One promising candidate is the development of batteries as clean energy storage and conversion devices. A platinum-based electrocatalyst supported on carbon form is commonly applied in these devices, with the disadvantage of the high cost. It has been reported that the replacement of the expensive Pt with Co and doping of carbon support with N and S heteroatoms can lead to electrocatalysts with excellent performance toward oxygen reduction reaction, oxygen evolution reaction (OER), and hydrogen evolution reaction.

Indeed, the work of Wang et al. [1] clearly showed that a Co, N co-doped carbon material (CoNC) can be competitive of the Pt/C electrocatalyst. The carbon support was prepared from chitin and the Co and N co-doped biocarbon was synthesized by a one-step pyrolysis method, which is a simple and low-cost method. The CoNC exhibits the positive onset potential of 0.86 V vs. RHE and high-limiting current density of 5.94 mA cm⁻². The stability of CoNC is higher in alkaline electrolyte compared to the commercial Pt/C catalyst. The combination of CoNC as cathode with Al-air battery, provides the power density of 32.24 mW cm⁻². These results are promising for the mass production of low-cost ORR catalyst and the utilization of biomass product.

On the other hand the simultaneous presence of cobalt oxides species with Pt metal species can be favorable for the anodic OER reaction. Generally, the OER is characterized by a high onset potential, and it exhibits slow kinetics due to four-electron transfer and oxygen—oxygen bond formation. These factors were the trigger for many researchers to study the substitution of Pt with other oxides. Among them Co₃O₄ is a promising alternative, since it has affordable cost, high abundant in nature, and possess enhanced catalytic performance toward OER in alkaline media.

Indeed, Adesuji et al. [2] have prepared an effective Pt-Co₃O₄ electrocatalyst. Their results showed that the Pt-Co₃O₄-HSs has better performance than Pt-HS. The performance



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of the new electrocatalyst strongly depends on the preparation method. The authors use bicontinuous microemulsions (BCME) for the synthesis of hierarchical superstructures (HSs) of Pt-Co₃O₄ by reduction/precipitation. They use both hydrophilic and lipophilic precursors and prepared PtAq-CoAq, PtAq-CoOi, PtOi-CoAq, and PtOi-CoOi samples (where Aq and Oi stand for the precursor present in aqueous or oily phase, respectively). The lowest onset overpotentials were achieved with PtOi-CoOi (1.46 V vs. RHE). Also, the PtAq-CoAq exhibits the lowest overpotential at a current density of 10 mA cm⁻², equal to 381 mV, significantly lower than the one for Pt-HS (627 mV). The higher Tafel slope was 157 mV dec⁻¹ for PtOi-CoAq. The improvement in OER activity is due to the synergistic effect of electronegative Pt on Co₃O₄, which allows for the formation of Co(IV) intermediate species.

One other interesting application, where the Co has central role, is the Fischer-Tropsch synthesis (FTS). This is a catalytic process where syngas is converted to high-quality fuels. The catalytic elements for this process are Co, Fe, Ni, and Ru. Only Fe and Co are used commercially, since Ru is impractical due to very high cost and low abundance and Ni exhibits higher selectivity for the short-chained hydrocarbons, something that it is not desirable. Cobalt has high activity and selectivity for linear long-chained hydrocarbons, low deactivation rate, and finally, low activity for water-gas shift reaction. The activity of a cobalt catalyst depends on the dispersion and surface availability of Co(0) species, with an optimal particle size of 6–10 nm for Co particles. The partial substitution of Co species with Ni can form alloys with different electronic structure with better performance in the FTS.

In the study of Martinelli et al. [3] the effect of cobalt substitution with nickel was systematically investigated for the FTS. Catalysts with different Ni/Co ratios were prepared, characterized with various physicochemical techniques, and tested in a continuously stirred tank reactor for more than 200 h. The authors have found that substitution of Co with Ni did not significantly modify the morphological properties of the mixed catalyst. There is intimate contact between nickel and cobalt, strongly suggesting the formation of a Co-Ni solid oxide solution in each case. Moreover, TPR-XANES indicated that nickel addition improves the cobalt reducibility by systematically shifting the reduction profiles to lower temperatures. The FTS tests revealed that the bimetallic system has a lower initial activity. However, carbon monoxide conversion continuously increased with time on-stream until a steady-state value (34–37% depending on Ni/Co ratio). This value is very close to the undoped Co/Al₂O₃ catalyst. Due to the Ni hydrogenation activity the bimetallic catalysts exhibited slightly higher initial selectivity for light hydrocarbons. Taking in mind the difference in price between cobalt and nickel, the substitution of Co with Ni in a ratio Ni/Co equal to 25/75 can lead to a better performance catalyst compared to the activity/price value.

Different bimetallic catalysts with Co can also be applied in several applications. In the work of Karakhanov et al., [4] a bimetallic MnCo catalyst, supported on the mesoporous hierarchical MCM-41/halloysite nanotube composite, was synthesized and tested for the selective oxidation of *p*-xylene to terephthalic acid (TPA). The MnCo catalyst was prepared by wetness impregnation method using the acetic salts of Mn(II) and Co(II) ions with a nominal molar ratio of Mn/Co equal to 1/10 and real value 1/8.6. Both metals were present as oxides and they interact with the support surface groups. The catalyst was tested in the liquid-phase oxidation of *p*-xylene, a multi stage radical oxidation process. Its kinetics is strongly affected by the reaction conditions. As a rule, *p*-xylene conversion to *p*-toluic acid proceeds fast, whereas oxidation to TPA is a slow highly activated process. The tests were performed under the best condition of AMOCO process. Both homogeneous and heterogeneous catalysts give a quantitative conversion and similar product distribution with TPA yield of about 95% within 3 h but with lower Mn and Co content for the solid catalyst. Comparing the TOF number heterogeneous catalyst has 3.8 times higher TOF value proving the high efficacy and superiority of the heterogeneous catalyst. The reaction pathway is passed through the intermediate alcohol formation. The intermediated radicals are not deactivated with Co(II) species due to their high interactions with the support

surface groups, while the intermediate products can be further oxidized by O_2 or Br radicals catalyzed by the Co(II) species.

The interactions of Co(II) species with the support surface groups are very important for the physicochemical characteristics and the activity of the supported Co catalysts. For example the interactions of the Co(II) ions with the surface $-OH$ groups of the Al_2O_3 can change the local structure of the deposited Co species. This is also valid for the case of TiO_2 . Indeed the interfacial deposition of Co(II) species on the titania surface has been investigated and it was found that the mode of Co(II) ions deposition depends on the surface coverage. In the case of titania the main deposition mechanism is the formation of mononuclear/oligonuclear inner sphere complexes. No interfacial precipitation occurs in contrast with the Co(II)- Al_2O_3 system. This mode of deposition leads to low content of Co catalysts. In a recent published paper [5] it was shown that the proper regulation of the impregnation conditions can increase the Co content. Specifically, the application of high initial basicity in the impregnation solution and high equilibration time can increase the Co content. The physicochemical characteristics of the prepared catalyst were superior of the corresponding catalyst prepared with conventional impregnation method. The Co oxide phase is more reducible, exhibit higher degree of interaction with the surface $-OH$ groups, different ratio of Co(III)/Co(II) species and higher surface coverage. The above characteristics result in a more active catalysts for the degradation of sulfamethaxazole using sodium persulfate as oxidant.

The importance of the different local structure of the Co species on the surface of different supports was pointed out in the study of Bellmann et al. [6]. In this study, different supports were used for the preparation of Co-supported catalysts. Specifically, ZSM-5, Na-ZSM-5, Al-SBA-15, and $Al_2O_3-SiO_2$ were used. UV-Vis spectroscopy and FTIR spectroscopy of pyridine and CO adsorption were applied to determine the nature of Co species in the above materials. It was found that the all Co-zeolite samples contain two types of Co(II) species located at exchange positions as well as in oxide-like clusters independent of the Co content, while in Co/Al-SBA-15 and Co/ $Al_2O_3-SiO_2$ only Co(II) species in oxide-like clusters occur. Finally, the UV-Vis spectra exhibit that not exclusively isolated Co(II) species were present and the characteristic triplet band is not only related to γ -, β -, and α -type Co(II) sites in the zeolite but also to those dispersed on the surface of different oxide supports. These observations clearly denote that for proper characterization of the formed Co species, the use of complementary methods is required.

It is clear that the cobalt catalysts can be used in broad applications. Among their advantages is the low-moderate price and the high abundance of Co. The deposition of Co(II) species in different supports leads to the preparation of highly active and dispersed catalysts. The local environment of the deposited Co species can be regulated through the preparation conditions and stabilized by the interactions with the support surface sites. The applications of cobalt catalysts is not limited to those presented in this book but it is a very active field of research, with promising results. On the other hand, further research is highly needed, especially to obtain better insight into the different processes, in order to develop more active catalysts tailored to the reaction conditions.

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