Hydrogen-rich gas generation from alcohols over cobalt-based catalysts for fuel cell feeding

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ABSTRACT

The application of potassium promoted Co-ZnO-Al$_2$O$_3$ catalysts prepared by co-precipitation and citrate methods in the steam reforming of ethanol and methanol has been studied. Experimental results of catalytic activity and selectivity of catalysts are reported. The influence of preparation method, potassium addition (1 and 2 wt%) and the reaction temperature (350–600 °C) are the focus of the experimental studies. Potassium promoted catalysts prepared by the co-precipitation method with smaller cobalt active phase crystallites and with potassium deposited on the catalyst surface, are easier and in a higher extend reducible and are more active and selective in the steam reforming of ethanol and methanol than those with large crystallites prepared by the citrate method into which potassium was introduced with all other components. Also, the suppression of carbonaceous deposit formation was observed while potassium was present on the surface of the catalyst. It is found that steam reforming of both alcohols proceeds under comparable conditions and hydrogen yields are maximized in the temperature range of 420–450 °C. Cobalt-based catalysts can be used in the same processor for hydrogen generation from alternatively methanol or/and ethanol for fuel cell applications.

1. Introduction

Catalysis is a key factor in the conversion of liquid or gaseous fuels into hydrogen. Many studies about hydrogen production for fuel cells deal with the use of two types of organic fuels: (*i*) oxygen-containing compounds, such as methanol or ethanol or (*ii*) hydrocarbons, e.g. natural gas, LPG, and gasoline [1–7]. At time when environmental problems are some of the world's biggest concerns, development of new energy conversion technologies is crucial. Steam reforming, in which an alcohol feed is reacted with steam, can generate a hydrogen-rich reformate stream *on-site*. The advantages of alcohols include facile handling and transport, and ability to be synthesized from a variety of biomass feed-stock. Moreover, both methanol and ethanol can be used in the steam reforming reactions under mild operation conditions for producing hydrogen. The reformate gas contains also carbon monoxide, whose concentration must be lower than the tolerance limit of low temperature polymeric electrolyte membrane (PEM) fuel cells (FCs) (50 ppm) or up to 1 vol.% if a high temperature PEM (HTPEM) fuel cell is applied [8]. PEM fuel cells are expected to find application as combined heat and power generation stationary systems, as a substitute for batteries in portable devices and in transportation [9].

In the case of the steam reforming of methanol (SRM), proposed catalysts can be divided in two main groups: copper-based and group 8–10 metal-based catalysts [10,11]. Other metals, like cobalt, have been barely studied in methanol reforming or decomposition [11–15].

In contrast to the SRM, cobalt is a well-known and promising active phase in the steam reforming of ethanol (SRE). There were made extensive studies on developing a catalyst for the SRE which could operate at relatively low temperature without by-products formation, which is also resistant to carbon deposition [16–28]. Catalyst active phase can be deposited on many support types, which can be divided in a few main groups with: (i) acidic, (ii) basic and (iii) redox properties. One of the most popular supports in catalysis is alumina, nevertheless, it is also known from their acidic properties of its surface which are very undesirable in the SRE process. It leads to dehydration of ethanol to ethylene, which is strong precursor for carbonaceous deposit formation on the catalyst what results in its fast deactivation [16–22,25,28,29–32]. Therefore, numerous efforts have been dedicated to explore another active and stable supports, like La$_2$O$_3$, CeO$_2$, ZrO$_2$, MgO, SiO$_2$, ZnO or hydrotalcite [16–43]. The addition of some of those oxides to Al$_2$O$_3$ affects its final acidity.

Moreover, several research groups investigated ethanol reforming on catalysts containing cobalt supported on ZnO or ZnO-Al$_2$O$_3$ [23–29], and alumina is only a small additive to ZnO support and its role is improvement of thermal stability of zinc oxide together with minimalizing the impact of its strong acidic sites. It has been also reported that addition of basic promoters (Li, Na, K, Mg, La and Ce) is very

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effective in improving the performance of catalysts for the SRE [16–19, 27,29,32,35–43]. The main role of alkali dopants in the SRE process is proposed to promote the removal of carbonaceous deposits or inhibit their formation by favouring water adsorption or neutralizing the support acidic sites responsible for ethylene formation and polymerization [17]. Llorca et al. [27] showed that sodium addition (0–1 wt%) to a 10 wt% Co/ZnO catalyst improved the stability of the catalyst in the SRE. Also, bulk cobalt oxide [31] and cobalt oxide supported on stainless steel wires [32] were investigated in the SRE reaction at moderate temperature. While undoped cobalt oxide underwent massive carbon deposition process, potassium was able to stop the over reduction of cobalt oxide and thereby prevent formation of large amount of carbon [32]. Espinal et al. [40,41] studied potassium-promoted (0–2 wt%) cobalt hydrotalcites which were very stable in long-term experiments due to reduction of the number and strength of acidic sites even under high loads of both ethanol and bioethanol. Catalysts were generating only small amounts of carbon deposition. In the later research of Espinal et al. [41] have showed that potassium-promoted cobalt hydrotalcites supported over cordierite and placed in a catalytic membrane reactor with composite Pd-Ag selective membrane performed with very high efficiency. The pure hydrogen has been obtained in the permeate stream. After 650 h of operation no carbon accumulation has been observed, even with very small excess of water vapour in the reaction mixture. They found that it was possibile due to the presence of CoO only, without metallic palladium in their catalyst. Ogo et al. [42] showed that thanks to 1–2 wt% of potassium loading on Co/Al$_2$O$_3$ catalyst, the catalyst performance was stabilized as well as by-product (CH$_4$ and C$_2$H$_4$) and coke formations were suppressed. Authors concluded that potassium addition has had a very positive effect on catalyst performance. The formation of Co^0—CoO core-shell structure over Co/K/ Al$_2$O$_3$ catalyst was effective for improvement of catalyst activity suggesting that the CoO species are highly active in ethanol steam reforming. What is more, in situ IR measurements revealed that thanks to potassium presence the adsorbed ethanol forms stable acetate species, which improves hydrogen selectivity. Alumina support was also modified with other additives like lanthanum and cerium oxides [30]. Nevertheless, according to Ávila-Neto et al. [30], under SRE without excess of water (EtOH:H$_2$O = 1:3 mol:mol), the nature of the support seems to have no direct effect on carbon formation and catalyst deactivation. The good catalytic performance was also showed by catalysts containing cobalt, zinc oxide and aluminium oxide [23,25,26,29,43]. According to Wang et al. [44] addition of Al$_2$O$_3$ to support have two effects. Firstly, it enhances the interactions between cobalt and a catalyst support and, secondary, alumina increases the surface area and improves cobalt particles dispersion. Cobalt catalysts tested in the SRE have been prepared by various methods. These include urea hydrolysis [26], incipient wetness impregnation [22,24,27,34,35,38,39], co-precipitation [23,29,33,40,41,43] and citrate complexation [20,43]. The most popular method is incipient wetness impregnation. The choice of preparation method or solvent is very important in terms of physicochemical properties presented by catalysts. From the results given by Lucredio et al. [22] it can be inferred that the thermal treatment is the most important step in obtaining good dispersion and small crystallites of active phase. Even occurrence of smaller metal crystallites on γ-Al$_2$O$_3$ than on SiO$_2$ support does not allow achieving of better Co/Al$_2$O$_3$ catalyst performance during the SRE. The acid nature of this support influences the performance of the reaction and the dehydration of ethanol is favoured.

According to another statement proposed by Lucredio et al. [22] Co$_3$O$_4$ on Al$_2$O$_3$ is found to be interacting with the Al$_2$O$_3$, which impedes aggregation of Co species during the reduction process and thus decrease the metal particle size. It is a known fact that active metal particle size plays a key role in determining catalyst stability during the SRE. The preparation route should lead to the formation of small and stable metal particles. This can be achieved by methods that promote the interaction between the metal particles and the support. However, depending on

the characteristics of the support, the reduction of metal oxides (e.g., especially Ni and Co oxides) can be hindered due to strong interactions with the support. In addition, the formation of non-reducible mixed oxides such as cobalt aluminate during the calcination or activation steps can also hinder reduction [17,18]. According to results reported by Barroso et al. [25] the main phases showed on XRD patterns of CoZnAl catalysts after calcination at high temperature (700 °C) are ZnAl$_2$O$_4$ and CoAl$_2$O$_4$. These phases are also visible on the TPR profiles where reduction occurs in high temperature regions. According to authors the improved behaviour of cobalt-rich catalysts was related to the presence of Co$_3$O$_4$. To achieve the effect of cobalt oxide phase supported on the ZnO-Al$_2$O$_3$ phase lower calcination temperature seemed to be reasonable.

The goal for this work is a catalyst for *on-site* production of hydrogen-rich gas from alcohols, ethanol or/and methanol, by their steam reforming proceeded in the same processor, at the same (or very similar) process conditions, at as low as possible process temperature. Both alcohols could be alternatively used as a feed in hydrogen small generators for fuel cell applications. In the case of the SRE, bioethanol fermentation broth was used. It is obvious that transporting a feedstock rich in water over long distances, to large installations producing hydrogen from ethanol at industrial scale, could not be recommended from economical point of view. However, our proposition is concerned with *on-site* production of hydrogen-rich gas in small generators for scattered fuel cell applications. Bio-ethanol almost everybody can make by himself and after filtration only it can be ready for use as a feed for the generator. The opinion is also expressed [45] that by circumventing the distillation step, the process of reforming crude ethanol (i.e. fermentation broth) provides us with the ability to produce H$_2$ from crude ethanol solution in a cost effective manner.

Aiming to obtain catalysts with favourable properties for the SRE and the SRM, the effects of potassium promotion and preparation method of cobalt/zinc oxide materials were studied. A small amount of alumina was used to stabilize catalyst performance. Two series of catalysts were prepared, the first one by using the co-precipitation method and the second – by using the citrate method. Potassium was incorporated into catalysts in one step along with cobalt, zinc and alumina in the case of the citrate method. For catalysts prepared by the co-precipitation method, potassium was added by incipient wetness impregnation. Our earlier studies of Co-ZnO-Al$_2$O$_3$ catalysts have shown that the optimum amount of cobalt active phase for the SRE is approximately 24 wt.% [23].

2. Materials and methods

2.1. Catalyst preparation

The first series of cobalt catalysts was prepared by co-precipitation from Zn(CH$_3$COO)$_2$, Al(NO$_3$)$_3$ and Co(CH$_3$COO)$_2$ aqueous solutions. The precipitation was accomplished at 40 °C by addition of (NH$_4$)$_2$CO$_3$ solution, drop by drop, under continuous stirring of the suspension. After ageing of the precipitate at 55 °C for 3 h, the suspensions were filtered. The filtrates were washed with absolute ethanol, in order to remove water. The obtained solids were dried overnight at 110 °C and then calcined at 400 °C for 6 h. Potassium (1 or 2 wt%) was added by incipient wetness impregnation using an aqueous solution of KNO$_3$. After impregnation, potassium-doped catalysts were dried over night at 110 °C and then calcined at 400 °C. The catalysts: unpromoted, promoted with 1 wt% and 2 wt% of potassium were labelled as 0 K-P, 1 K-P, and 2 K-P.

Concerning the catalysts prepared with the citrate method, citric acid was added to an aqueous solution that contained all the required salts, Zn(CH$_3$COO)$_2$, Al(NO$_3$)$_3$, Co(CH$_3$COO)$_2$ and KNO$_3$. The molar ratio of metal ions (Zn^{2+} + Al^{3+} + Co^{2+} + K$^+$)/citric acid was 1/1. The resultant solutions were evaporated on a water bath. The obtained solids were dried at 110 °C and then calcined at 400 °C for 6 h. The