Ni-Based Catalysts Supported on Mg-Al Mixed Oxides

Ni-based catalysts supported on Mg-Al mixed oxides (Mg(Al)O) have been intensively investigated as catalysts for CH_4 reforming processes (i.e., steam reforming (SMR) and dry reforming (DRM)), which are pivotal actors in the expanding H_2 economy.

1. Introduction

To overcome the identified challenges in catalytic reforming systems, the selection of the catalyst support plays a crucial role during the catalyst development [1][2][3]. In addition to coke limiting ability, reforming catalysts must also meet stringent requirements due to the harsh conditions required of the processes (high temperature, high pressure, and presence of steam) [4][5]. Common oxide supports are Al_2O_3, MgO, and their corresponding mixed oxides [4]. Because of its high surface area, thermal and chemical stability, and strong interaction with Ni, Al_2O_3 is one of the most studied supports [6][7]. Indeed, commercially available catalysts for traditional steam reforming (SMR) are mainly constituted by Ni supported on Al_2O_3 [8]. MgO support is also widely studied, particularly in dry reforming (DRM), because its high basicity is beneficial for adsorbing CO_2, which in turn enhances the reforming activity and the coke removal rate [9][10]. Moreover, the ability of MgO to form a strongly interacting solid solution with NiO improves the catalyst stability and resistance to sintering [11][12].

As for the active metallic constituents, bimetallic systems are attracting considerable research interest thanks to the possible promotional effect of the second (or third) metal on the processes and/or the presence of synergetic effects between the metals [13][14][15]. Particularly for Ni-based catalysts, noble, alkaline, and rare earth metal promoters are the subjects of many studies and demonstrate promising improvements. Among those, the addition of small amounts of noble metals to Ni catalysts is beneficial while remaining cost competitive [16]. The addition of Pt, Ru, and Pd improves reducibility, may provoke an auto-activation of the catalyst, and reduces the coke formation [16]. On the other hand, the addition of Group 11 metals (Au, Ag) reduces the Ni activity but extends the catalyst's lifetime by inhibiting the coke formation [17].

In addition to the selection of the active metal, support, and promoters, the way the catalyst is prepared also plays an important role in determining its morphological and structural features and, as a result, its catalytic performance [17][18][19]. This is particularly true when preparing Mg-Al mixed oxides, which can form several crystal phases and can have different morphological characteristics [20][21]. Hence, a thorough understanding of each parameter in traditional synthesis procedures as well as the exploration of innovative preparation approaches are both highly desirable to improve homo- and bimetallic Ni catalysts supported on Mg(Al)O for SMR and DRM.

Metal–support interaction is arguably one of the most critical aspects impacting both the activity and the stability of heterogeneous catalysts, especially when used in high-temperature processes. The interaction of Ni with the support is a somewhat textbook example of the tradeoffs to be considered when preparing a heterogeneous catalyst. If, on the one hand, a weak interaction is good for the catalytic activity because it does not impair the Ni reducibility, it may be insufficient to stabilize the nanoparticles against sintering [22][23]. It is also true, however, that it is hard to obtain small Ni nanoparticles, and thus a high number of catalytically active sites with Ni interacting too weakly with the support can be found. In other words, a strong interaction with the support helps suppress the overgrowth of the particles, thereby enhancing their stability at high reaction temperatures, but could also lead to Ni nanoparticles that are hard to reduce, which may limit the availability of metallic Ni [19][24].

2. Ni-Support Interaction in Ni(M)/Mg(Al)O Catalysts

Ni-based catalysts are generally prepared as NiO followed by reduction, but the final form of the catalyst is heavily influenced by the composition of the Mg(Al)O support because Ni interacts very differently with Al and Mg oxides.

NiO is known to form a stable spinel nickel aluminate with Al_2O_3 after heat treatment, denoted as $NiAl_2O_4$ [25]. In Ni-Al-O systems, three phases of Ni-Al_2O_3 can be observed: "free" NiO particles, NiO weakly interacting with Al_2O_3, and $NiAl_2O_4$ spinel. The order is based on the strength of interaction between Ni and Al. Temperature-programmed reduction (TPR) can be used to identify the phases of Ni in Al_2O_3. Due to the difference in bond strength, each phase displays reduction features in a specific temperature range. Reduction peaks occurring between 300 and 350 °C are originated by the reduction of "free" NiO to metallic Ni, whilst weakly interacting NiO-Al_2O_3 is reduced around 500–600 °C. The reduction of Ni^{2+} present in the spinel phase ($NiAl_2O_4$) can only be observed at temperatures higher than 800 °C. The formation of such three phases depends largely on calcination temperature, Ni loading, and the preparation method. Generally, high calcination temperatures favor the formation of spinel phases with stronger interaction between Ni and Al_2O_3 [26][27].

With MgO, NiO can form an ideal NiO-MgO solid solution in the whole range of concentrations due to the similar ionic radii of Ni^{2+} (69 pm) and Mg^{2+} (72 pm) [28]. In the solid solution, the interaction of Ni with MgO is particularly strong, resulting in a Ni phase much harder to be reduced. Conventionally, the reduction of NiO-MgO occurs above 800 °C with long reduction times.

In addition to the interactions between Ni and each oxide component, the mixed oxide itself can also form the $MgAl_2O_4$ spinel phase during the catalyst synthesis [29][30], which provides high surface area, good thermal stability, and strong interaction with Ni [19].

Another important aspect of Mg(Al)O systems is the ability to form hydrotalcite. Hydrotalcite is a double-layered lamellar hydroxide (LDH) of Mg and Al with the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ [31]. It is demonstrated that materials derived from hydrotalcites are promising for various catalytic processes including CH_4 reforming [32][33].

3. Monometallic Ni/Mg(Al)O Catalysts for SMR and DRM

3.1. Synthesis of Ni/Mg(Al)O Catalysts by Conventional Approaches

3.1.1. Effect of Ni Loading and Composition Ratio

Ni loading and composition ratio play an important role in the characteristics of the catalysts: High Ni loadings may imply higher activity, but they may result in larger particles, which promote coke formation [34][35][36][37][38].

The study by Guo et al. showed that a catalyst with a low Ni content is not stable in DRM, while the conversion is positively correlated with Ni content only up to 15 wt.% [39]. As expected, above that loading, the coke formation becomes severe. A similar trend of coke deposition was found by Alipour et al. while studying impregnated Ni/Mg(Al)O catalysts obtained by wet impregnation [40]. They showed that after calcination, NiO segregated when above the 15 wt.% of Ni loading. The amount of carbon deposited scaled with the Ni content, but the reforming activity did not. Catalysts prepared via co-precipitation showed a similar behavior [41].

Qi et al. used Ni/Mg(Al)O prepared by the co-precipitation technique and tested them in SMR in comparison with wet impregnated catalysts with varied divalent/trivalent cation molar ratios (Ni+Mg)/Al in the precursors [42]. They reported that the optimal (Ni+Mg)/Al molar ratio in the LDH precursor for SMR is three. The resulting catalyst exhibited the best activity because of its high surface area and high Ni dispersion upon reduction.

3.1.2. Effect of Heat Treatment

Both calcination and reduction conditions have a major impact on the physicochemical properties of the resulting catalyst. As stated earlier, higher calcination temperatures favor the formation of stable phases, such as spinel $NiAl_2O_4$ or NiO-MgO solid solution. A high calcination temperature can enhance the stability and interaction between components but can also decrease the surface area, thus causing a collapse of the pores, and particle sintering [43][44][45][46]. On the contrary, low reduction temperatures may not guarantee the generation of sufficient active species. Hence, various studies have been devoted to the influence of thermal pretreatments on the final structure of the catalysts.

The calcination temperature was studied on NiO-MgO systems for DRM [47][48]. At low calcination temperatures, the material contained weakly interacting NiO species, while at 800 °C NiO bonds strongly with MgO in the form of a solid solution. The strong interaction increases the strength of CO_2 absorption at low reaction temperatures, thus enhancing the activity and stability of the catalyst. The effect of Mg precursors and heat treatment was also studied by Ruckenstein and Hu [49].

3.2. Synthesis of Ni/Mg(Al)O Catalysts by Advanced Methods

Besides the more common methods mentioned above, other approaches aimed at obtaining strictly controlled morphological, structural, and textural properties of both the metal active phase.

Among them, the sol-gel method has been extensively investigated [50][51][52][53]. The catalysts obtained via this approach are typically characterized by high surface area, narrow size distribution, high thermal resistance, and homogeneous composition of the mixed oxides when compared to conventional synthesis methods [54][55]. González et al. utilized LDHs prepared in this way as precursors for DRM [56]. Upon mild thermal treatment, the hydrotalcite collapsed and formed nanosphere structures of mixed NiO and Mg(Ni)AlO periclase without the formation of $NiAl_2O_4$. The catalyst with 15 wt.% Ni and calcined at 650 °C showed the best activity and low carbon formation in DRM.

Another attractive synthesis approach is the aerogel method. This approach enables the synthesis of exceptionally high surface area and thermally stable materials [57]. Suh et al. used aerogel Al_2O_3 as supports for DRM [58]. The high surface area Al_2O_3 was prepared by supercritical CO_2 drying of alcogels. The aerogel-based Ni/Al_2O_3 catalysts showed high activity and enhanced stability against coking compared to the impregnated ones. The scholars assigned such improvements to the high surface area and uniform distribution of the active sites. The follow-up paper investigated the metal loading on this aerogel catalyst, again highlighting that too a high metal content resulted in large particle sizes, which in turn promote coke formation [37].

4. Bimetallic Ni-M/Mg(Al)O Catalysts for Reforming Reactions

4.1. Bimetallic Ni-M/Mg(Al)O Catalysts for SMR

Bimetallic catalysts are a promising area of research because they have improved properties compared to their parent metals, resulting in some cases in catalysts with higher selectivity, activity, and stability. Precious metals with high reforming activity and low coking tendency have been studied as promoters for Ni-based catalysts [59][60][61][62][63][64]. Among different synthesis methods reported for CH_4 reforming catalysts (i.e., self-combustion, ion exchange, sol-gel, microemulsion, precipitation, wet impregnation, and colloidal), precipitation and impregnation methods are the most common ones [65][66][67][68][69].

The role of Pt as a promoter in Ni/Mg(Al)O catalysts has been investigated in different synthetic ways both for metal deposition and support preparation. Foletto et al. reported a catalyst synthesized by the sequential impregnation method while using the sol-gel method via alkoxide hydrolysis to synthesize the Mg(Al)O support [70]. XRD analyses revealed that as the calcination temperature of the support increased, the size of the crystallites rose exponentially, and the formation of the spinel phase occurred at temperatures higher than 600 °C. The formation of the pure spinel phase and a higher resistance to sintering were observed for calcination temperatures exceeding 700 °C. The catalytic activity of the catalyst as a function of different Pt content showed that 0.1 wt.% Pt is optimal compared to catalysts at higher Pt loadings. According to TPR results, Ni reduction peaks shifted to lower temperatures for small amounts of Pt (0.05–0.1 wt.%), while no significant changes were observed when increasing the Pt content.

4.2. Bimetallic Ni-M/Mg(Al)O Catalysts for DRM

The presence of a metallic phase is necessary for the dissociative adsorption of CH_4 and for the generation of H_2 as well as chemisorbed carbon species during DRM. Some bimetallic systems are also capable of lowering the activation energy of the rate-limiting step [71][72]. A kinetic study by Niu et al. revealed that the addition of Pt to Ni reduces the activation energy for CH_4 dissociation and lowers moderately the CO_2 dissociation barrier energy, resulting in higher catalytic activity [73]. Re and Ru have been also described as active sites for CO_2 activation, which, due to their electron-rich properties, can donate electrons to the CO_2 antibonding orbitals and facilitate the reaction by weakening the C-O bond [74].

In another impregnation synthesis process, Pt was loaded on a Ni/Mg(Al)O catalyst using glow discharge plasma pretreatment after impregnation and before calcination [75]. Such treatment was useful to improve the Ni dispersion but inhibited its reduction. The addition of Pt helped in this sense and in fact the bimetallic, plasma-treated Pt-Ni/Mg(Al)O catalyst demonstrated a higher conversion of both the reactant and a higher H_2 yield. An improved resistance toward coke formation was also reported by the scholars. The presence of Pt resulted in smaller Ni NPs in the fresh materials, while the plasma treatment was critical to prevent sintering. It is worth noting the filamentous carbon formations on the spent Ni/Mg(Al)O catalyst, which on the contrary cannot be seen on the spent P-Ni-Pt/Mg(Al)O catalyst. The scholars suggest that this was due to the presence of Pt more than the plasma treatment, and specifically to an altered dissociative adsorption capacity of CH_4 [76][77].

In general, many alloying effects of Ni-based catalysts with base metals and Ni-based catalysts with noble metals have been reported in DRM and SMR to improve the dispersion and reducibility of the supported metal, modify the catalytic performance such as activity and selectivity, and improve the resistance to carbon deposition, sulfur poisoning, sintering, and so on.

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