Packed and Monolithic Reactors for the Dry Reforming of Methane: Ni Supported on γ-Al_2O_3 Promoted by Ru

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The Dry reforming of methane (DRM) is as an efficient way for CH₄ and CO₂ valorisation because the produced syngas has an H₂/CO ratio equal to that suitable for the synthesis of oxygenated hydrocarbons and synthetic fuels. The development of Ni (10 wt%) based structured and unstructured catalysts promoted by a small amount of Ru (0.5 wt%) has been investigated. Unstructured catalysts were prepared by wet impregnation method and a combination of wash coating-wet impregnation methods was used for cordierite monoliths. Ru promoted catalyst (Ni–Ru) was remarkable active showing higher reactant conversions and H₂/CO ratio compared with Ni catalyst. Ni–Ru monolith was initially much more active than monometallic Ni stating the positive effect of Ru on maintaining Ni reduced. Reaching steady state condition, Ni rapidly deactivated due to carbon formation, whereas Ni–Ru monolith remained stable confirming that Ru behaves as an efficient and cheap promoter of Ni for DRM.

Keywords: Ni/Al₂O₃, NiRu/Al₂O₃, Structured Catalyst, Dry Reforming of Methane, Carbon Deposition.

1. INTRODUCTION

The CO₂ reforming of CH₄ (Eq. (1)) or dry reforming (DRM) is as an efficient way of recycling two greenhouse gases to syngas.¹

\[ CH₄ + CO₂ \rightarrow 2H₂ + 2CO \quad \Delta H_{298}^{0} = 247 \text{ kJmol}^{-1} \]  

(1)

To date, the DRM industrial implementation is mainly impeded by catalyst deactivation and/or reactor plugging due to the methane cracking (Eq. (2)).

\[ CH₄ \rightarrow C + 2H₂ \quad \Delta H_{298}^{0} = 75 \text{ kJmol}^{-1} \]  

(2)

Therefore, there is a pressing need to increase the catalysts resistance toward carbon deposition, one main being the use of noble metal, such as Pt, Ru and Rh, supported on various oxides.² Among bimetallic systems, best performances are shown by those containing a small amount (<1 wt%) of precious metals keeping the catalyst cost sufficiently low for industrial implementation. Ruthenium is the cheapest precious metal and for this reason can be the ideal choice as a promoter. Ni–Ru catalysts have been studied for the DRM reaction showing very good catalytic activity and stability due to an increased Ni dispersion. As yet, it has not been completely clarified if the effect of Ru is to promote the formation of Ni–Ru alloys or to favour Ni dispersion. Moreover, being the solubility between Ni and Ru metals quite limited, some authors claim a very low Ni sintering resistance by Ru addition.³ Beside the definition of the catalyst proper characteristics, it is also important to fulfil the demands arising from industrial production and process intensification. For this purpose, the use of micro-structured catalysts can offer several advantages over conventional packed bed reactors: increase of mass and heat transfer, lower pressure drop, larger surface-to-volume ratio and compact reactor design.⁴ In the present work we investigated the effect of a small amount of Ru (0.5 wt%) on the catalytic activity and stability toward carbon deposition and Ni oxidation of Ni/γ-Al₂O₃ catalysts for the DRM reaction. Ni and Ni–Ru based catalysts were studied in both powder and structured forms. Cordierite monolith was selected because of its chemical stability and thermal compatibility with alumina catalyst.

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catalyst showed carbon filaments with the typical bamboo like morphology along the channels (Inset in Fig. 1(c)). Some Ni nanoparticles were detached from the γ-Al₂O₃ support and were clearly visible on the tip of the filaments (tip grow mechanism). On Ni–Ru–M catalyst, the Ni nanoparticles were hardly visible even though well dispersed on the support. The carbon filaments seemed to be formed by a base grown mechanism clearly laying on the catalytic layer. Therefore, FE-SEM analysis clarified that the deactivation of the sample Ni–M after 60 h of time on stream was due to the greater amount of C. Moreover these results may be useful to engineer the monolith by using a zone coating of a specially designed catalyst (i.e., with a higher content of precious metal) where there is a greater tendency to form carbon residues.

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References and Notes

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