Catalysis Letters 32 (1995) 387–390

Large enhancement in methane-to-syngas conversion activity of supported Ni catalysts due to precoating of catalyst supports with MgO, CaO or rare-earth oxide

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Received 23 August 1994; accepted 4 January 1995

Supported nickel catalysts prepared using commercial sintered low surface area porous catalyst carriers (containing SiO_2 and/or Al_2O_3) precoated with MgO, CaO or rare-earth oxide show very much higher activity, selectivity and productivity in methane-to-syngas conversion reactions, than the catalysts prepared using catalyst carriers without any precoating. Among the precoating metal oxides, the best performance is observed for MgO.

Keywords: conversion of methane to syngas; supported nickel catalysts; methane oxidation; methane steam reforming; methane CO_2 reforming

1. Introduction

Nickel supported on alumina [1–6] and silica [7] is a commonly used catalyst in the conversion of methane to syngas (i.e. CO and H_2). Highly sintered low surface area (< 1 m^2 g^{-1}) porous catalyst carriers, containing silica and/or alumina, which have high thermal and hydrothermal stability and mechanical strength are most commonly used supports for the hydrocarbon oxidation catalysts and also for the catalysts used in the processes involving drastic reaction conditions (e.g. high temperatures, presence of steam in reaction mixture, sharp temperature changes, etc.). At high temperatures, a solid–solid reaction of Ni or NiO with Al_2O_3 and SiO_2 results in the formation of nickel aluminate (spinel) and nickel silicate phases, respectively, which are catalytically inactive for methane-to-syngas conversion reactions and also difficult to reduce, thus lowering catalytic activity and also causing catalyst deactivation during the high temperature process and/or in the catalyst regeneration cycles. In this communication, we report that the catalytic activity,

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selectivity and productivity of supported nickel catalysts, prepared by depositing NiO on sintered low surface area porous commercial catalyst carriers containing Al_2O_3 and/or SiO_2, in the oxidative conversion of methane to syngas and also in the steam and CO_2 reforming of methane to syngas are drastically increased by precoating the catalyst carriers with MgO, CaO or rare-earth oxides before depositing NiO on them.

2. Experimental

Supported nickel catalysts (tables 1 and 2) were prepared by depositing nickel nitrate on 22–30 mesh size particles of commercial catalyst carriers (sintered low surface area ($\leqslant 0.2\ m^2\ g^{-1}$) porous (porosity: 48 ± 10%) supports, obtained from Norton Co., USA) with or without precoating them by MgO, CaO or rare-earth oxide using incipient wetness impregnation technique, drying and decomposing (or calcining) in air at 900°C for 4 h. The catalyst carriers were precoated with MgO, CaO or rare-earth oxide by impregnating the carriers with corresponding metal nitrate, drying and decomposing as above. (The main components of the supports are as follows: SA 5205, 86.1% Al_2O_3 and 11.8% SiO_2; SA 5218, 86.1% Al_2O_3 and 12.0% SiO_2; SS 5231, 4.1% Al_2O_3 and 95% SiO_2; SC 5531 and SC 5232, 4.7% Al_2O_3, 28.5% SiO_2 and 65.8% SiC.) The methane-to-syngas conversion reactions over the supported nickel catalysts were carried out at atmospheric pressure in a

Table 1
Results on oxidative conversion of methane[a] to CO and H_2 over supported Ni catalysts prepared with or without precoating support by different metal oxides

Catalyst	CH_4 conv. (%)	Selectivity (%)		CO STY ($mol\ g^{-1}\ h^{-1}$)
		CO	H_2	
NiO(12.0 wt%)/SA 5205	3.0	11.1	17.0	0.05
NiO(12.2 wt%)/MgO(5.6 wt%)/SA 5205	94.7	97.5	95.6	13.5
NiO(13.3 wt%)/CaO(9.7 wt%)/SA 5205	82.0	91.9	89.6	11.0
NiO(13.1 wt%)/Yb_2O_3(19.6 wt%)/SA 5205	88.3	95.5	93.2	12.3
NiO(13.4 wt%)/Sm_2O_3(15.3 wt%)/SA 5205	87.2	93.8	91.2	12.0
NiO(14.8 wt%)/SC 5532	<0.1	–	–	–
NiO(12.9 wt%)/MgO(5.2 wt%)/SC 5532	89.0	95.8	97.2	12.5
NiO(18.0 wt%)/SC 5232	3.3	26.4	15.0	0.13
NiO(15.8 wt%)/MgO(7.5 wt%)/SC 5232	91.1	98.9	95.1	13.2
NiO(11.4 wt%)/SS 5231	5.9	39.1	10.0	0.34
NiO(10.3 wt%)/MgO(7.8 wt%)/SS 5231	91.8	95.8	95.1	12.9

[a] Reaction temperature, 800°C, feed, 65 mol% CH_4 and 35 mol% O_2; space velocity, $5.1 \times 10^5\ cm^3$ (at STP) $g^{-1}\ h^{-1}$.

Table 2
Results on steam and CO_2 reforming of methane to CO and H_2 over supported Ni catalyst prepared with or without precoating support by MgO

Catalyst	Steam reforming[a]			CO_2 reforming[b]		
	CH_4 conv. (%)	CO select. (%)	H_2/CO ratio	CH_4 conv. (%)	H_2 select. (%)	H_2/CO ratio
NiO(12.0 wt%)/SA 5205	<0.1	–	–	46.2	95.1	0.9
NiO(12.2 wt%)/MgO(5.6 wt%)/SA 5205	97.8	91.7	3.59	95.5	~100	1.0

[a] Reaction temperature, 800°C; feed, 39 mol% CH_4 and 61 mol% H_2O; space velocity, 22590 cm^3 (at STP) g^{-1} h^{-1}.

[b] Reaction temperature, 800°C; feed, 50 mol% CH_4 and 50 mol% CO_2; space velocity, 8600 cm^3 (at STP) g^{-1} h^{-1}.

conventional continuous flow quartz microreactor (with i.d. of 4 mm and 9 mm for the oxidative methane conversion and steam/CO_2 reforming of methane, respectively), kept in a tubular furnace (i.d. 25 mm). The reaction temperature was measured by a chromel–alumel thermocouple located in the catalyst bed. Before the reaction, the catalyst was pretreated in situ at 900°C in a flow of pure N_2 (50 cm^3 min^{-1}) for 1 h. The water from the product stream was condensed at 0°C. The feed and the product gases were analyzed by an on-line gas chromatograph, using a spherocarb column.

3. Results and discussion

A comparison of the results (tables 1 and 2) reveals that, in all the three methane-to-syngas conversion reactions, the catalytic activity (i.e. methane conversion), selectivity and space time yield (STY) or productivity of the supported nickel catalysts are drastically increased due to the precoating of the catalyst carrier with MgO, CaO or rare-earth oxide, before supporting (or depositing) NiO on them. The observed drastic improvement in the catalyst performance due to the precoating is attributed to the formation of a protective layer of the precoated metal oxide between the reactive component (e.g. Al_2O_3, SiO_2, etc.) of the support and the deposited NiO, thus eliminating or drastically reducing the chemical interactions between them and consequently the formation of catalytically inactive binary metal oxide phases (e.g. $NiAl_2O_4$, Ni_2SiO_4, etc.) by solid–solid reactions between NiO and Al_2O_3 or SiO_2 from support. When NiO is directly deposited on the supports (without precoating), an extensive formation of these binary metal oxide phases has been observed. Also, even though these directly supported nickel catalysts were reduced before reaction by hydrogen at 500°C for 1 h, no improvement in the catalyst activity and selectivity was observed. Apart from providing a protective layer, the precoating of support (which results in an increase in the surface area) is also expected to result in an increase in the dispersion of nickel oxide in the supported catalyst. It may also be noted that the unsupported NiO–MgO (Ni/Mg = 3.0), NiO–CaO (Ni/Ca = 3.0) and NiO–Yb_2O_3 (Ni/Yb = 1.0) mixed metal oxide catalysts showed excellent performance in the oxidative conversion of methane to syngas [8–10]. However, when these catalysts are directly supported on SA 5205, their catalytic activity is found to be greatly reduced. This clearly shows the importance of forming a protective layer (by the precoating of support) between support and NiO in the supported Ni catalysts in order to avoid chemical interactions between the support components and NiO.

The results (table 1) show that the best catalyst performance in the oxidative methane-to-syngas conversion is observed when the catalyst carrier is precoated with MgO. This is mostly due to the formation of a protective layer of stable $MgAl_2O_4$ (spinel) and/or $MgSiO_3$ phases between the support surface and the active catalyst.

4. Summary

We report here our preliminary studies disclosing the beneficial effect of precoating of catalyst support (containing Al_2O_3 and SiO_2) with MgO, CaO or rare-earth oxide before depositing nickel oxide on the support, in the preparation of supported nickel catalyst. Because of the precoating there is a very large increase in the methane-to-syngas conversion activity/selectivity of the supported nickel catalysts due to the elimination or drastic reduction in the formation of catalytically inactive $NiAl_2O_4$ (spinel) and/or Ni_2SiO_4 phases resulting from the chemical interactions between NiO and Al_2O_3 and/or SiO_2 from support at high temperatures. Among the alkaline and rare-earth metal oxides used for the support precoating, the best performance is shown by MgO, due to formation of stable protective layer of $MgAl_2O_4$ (spinel) and/or $MgSiO_3$ between the support surface and the active nickel catalyst.

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