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NOTE

Beneficial Effects of Noble Metal Addition to Ni/Al_2O_3 Catalyst for Oxidative Methane-to-Syngas Conversion

Ni/Al_2O_3 in its reduced (i.e., Ni^0) form is an active catalyst commonly used in the steam reforming and oxidative conversion of methane to syngas (i.e., CO and H_2) (1–5), which is a process of great practical importance. The as-prepared/calcined form of the catalyst contains a catalytically inactive $NiAl_2O_4$ phase, which is difficult to reduce. Hence, the oxidative methane-to-syngas conversion reaction on the calcined catalyst occurs or starts only at high temperature (about 750°C) (3). However, the reaction on calcined Ni/MgO (6), Ni/CaO (7), and Ni/rare earth oxide (8) catalysts is found to start at much lower temperatures because of their ease of reduction during the initial reaction period. From a practical point of view, the reaction on the calcined Ni/Al_2O_3 should start at lower temperatures. Supported noble metal catalysts (9–13) have also been used extensively for the oxidative conversion of methane to syngas. In this communication, we report our preliminary results which reveal that the oxidative methane-to-syngas conversion reaction on calcined (i.e., unreduced) Ni/Al_2O_3 can be made to start at temperatures much lower than 750°C and the catalyst performance can also be improved to some extent by adding noble metal (e.g., Pt, Pd, or Ru) to the catalyst.

The preparation of Ni (18.7 wt%)/Al_2O_3 catalyst in unreduced form has been described previously (5). The noble-metal-containing catalysts (Table 1) were prepared by impregnating Ni/Al_2O_3 or Al_2O_3 (HARSHAW-AL-U104) with noble metal chloride, drying, and calcining at 930°C in air for 4 h. The oxidative methane-to-syngas conversion over the unreduced catalyst (20 mg) was carried out in a continuous microreactor (i.d. 4 mm) made up of quartz at 1 atm, using a feed consisting of pure methane and oxygen with a CH_4/O_2 molar ratio of 2.0 and a total space velocity (measured at STP) of 5.6 ($\pm$0.2) $\times 10^5$ $cm^3 \cdot g^{-1} \cdot h^{-1}$. The reaction temperature was measured with a Chromel–Alumel thermocouple in the catalyst bed. The water from the reaction products was separated by condensing at 0°C. The feed and product were analyzed by an on-line GC with a Spherocarb column. The reaction start temperature, T_S, for each catalyst was determined by noting the temperature at which the reaction was initiated, indicated by a sudden increase in the catalyst temperature of a few degrees and also an increase in the reactor outlet gas flow rate, forming reaction products (confirmed by analysis) when the catalyst temperature was increased slowly (5°C min^{-1}). After measuring the reaction start temperature, the catalyst reaction was carried out under steady state by increasing the reaction temperature to 800°C and then also by decreasing the temperature. A 50% reduction in the particle size of the Ni/Al_2O_3 and $Pt–Ni/Al_2O_3$ catalysts has produced no significant change in the observed T_S or methane conversion, indicating no influence of either inter- or intraparticle mass transfer on the reaction.

The results in Fig. 1 and Table 1 reveal the following. The addition of noble metal to the Ni/Al_2O_3 catalyst causes:

—a drastic decrease in T_S, depending upon the noble metal and its concentration (T_S decreases with increasing noble metal concentration); and

—an increase in both catalytic activity and CO selectivity (without significantly affecting the H_2 selectivity) for the case of Pt or Ru addition but a substantial decrease in the activity, selectivity for CO and H_2, and CO productivity (or space-time yield) with increasing concentration of Pd in the catalyst.

It may be noted that, when the heating cycle is repeated after the experimental runs (Fig. 1), the dotted curves in the figure are retraced. Although T_S is lowest for $Pd–Ni/Al_2O_3$, the performance of this catalyst in the reaction is inferior. The performance of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts as compared to the other Ni-containing catalysts is also very poor. The activity of Ru/Al_2O_3 is also lower than that of $Ru–Ni/Al_2O_3$.

Data on the hydrogen chemisorption uptakes [obtained by a pulse chemisorption technique using pure H_2 pulses for the Pt- and Ru-containing catalysts and using diluted H_2 (6% H_2 in Ar) pulses for the Pd-containing catalysts, after reducing the catalyst *in situ* with hydrogen at 350°C for 1 h] on the noble-metal-containing catalysts are presented in Table 2. A comparison of the H_2 chemisorption data for pure or Ni-containing catalysts indicates that the H_2 chemisorption uptakes and consequently the dispersion

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TABLE 1

Effect of Noble Metal and its Concentration in Ni/Al_2O_3 (Unreduced) Catalyst on its Reaction Start Temperature T_s and Activity/Selectivity (at 800°C) in the Oxidative Conversion of Methane to Syngas

Catalyst (in calcined form)	Concentration of noble metal (Wt%)	T_s(°C)	CH_4 conversion (%)	Selectivity (%)		CO STY ($mol \cdot g^{-1} \cdot h^{-1}$)
				CO	H_2	
Ni/Al_2O_3	0.0	790	84.0	95.7	96.6	13.00
$Pt-Ni/Al_2O_3$	0.1	605	84.8	96.9	94.8	13.40
	0.5	530	87.3	97.2	95.6	13.71
	2.5	420	88.1	96.5	97.5	14.10
$Pd-Ni/Al_2O_3$	0.1	520	79.0	97.1	93.0	12.39
	0.5	460	76.5	95.5	90.2	11.80
	2.5	400	70.3	93.4	86.6	10.61
$Ru-Ni/Al_2O_3$	2.5	530	90.8	98.8	97.7	14.49
Pt/Al_2O_3	2.5	425	54.7	93.9	70.2	8.30
Pd/Al_2O_3	2.5	405	46.5	92.0	60.2	6.91
Ru/Al_2O_3	2.5	530	74.0	95.1	95.1	11.40

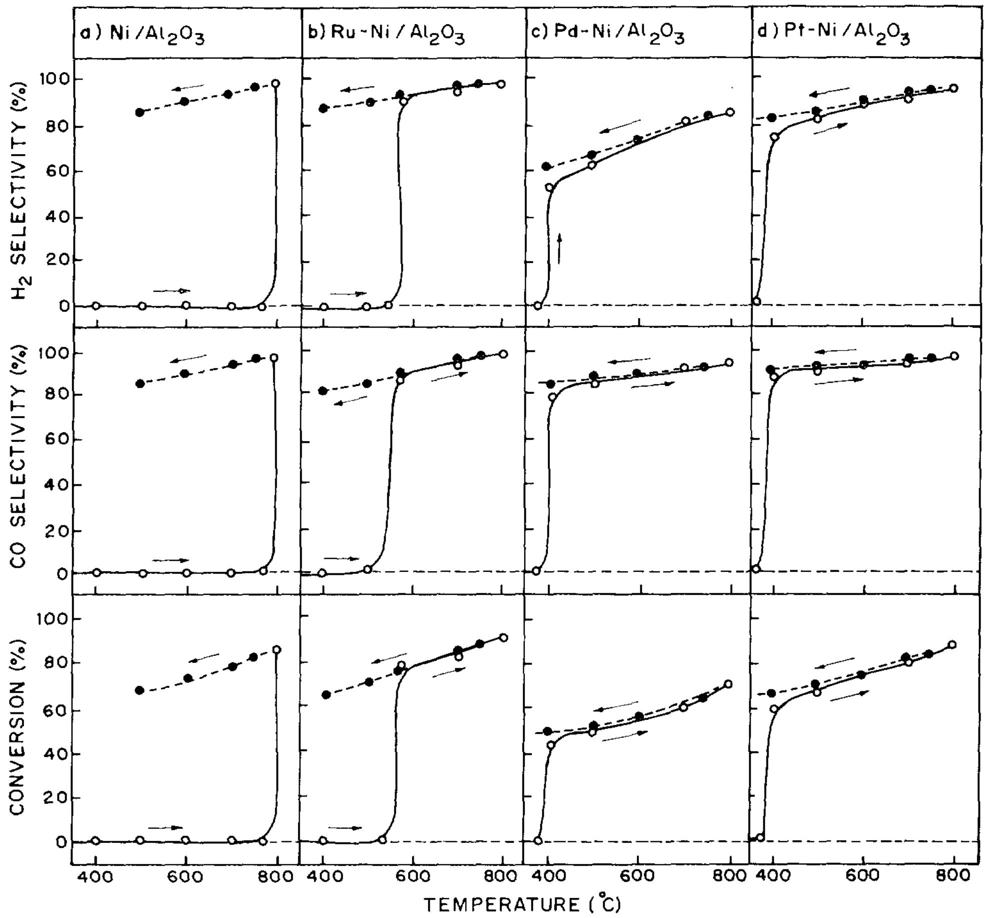

FIG. 1. Temperature dependence of activity/selectivity of Ni/Al_2O_3 (18.7 wt%Ni) catalyst (in calcined form) with or without noble metal (2.5 wt%) in oxidative conversion of methane to syngas. ((○) increasing and (●) decreasing temperature).

TABLE 2

Hydrogen Chemisorption and Dispersion of Noble Metal on the Catalysts

Catalyst	H_2 chemisorbed[a] (at 30°C) ($\mu mol \cdot g^{-1}$)	Dispersion of noble metal (%)
Pt/Al_2O_3	1.23	1.9
$Pt-Ni/Al_2O_3$	1.05	1.6
Ru/Al_2O_3	4.53	3.7
$Ru-Ni/Al_2O_3$	2.17	1.8
Pd/Al_2O_3	8.95	7.6
$Pd-Ni/Al_2O_3$	1.24	1.1

[a] For noble metal-Ni/Al_2O_3 catalysts, the H_2 chemisorption data reflect subtraction of the data for Ni/Al_2O_3.

of the noble metal are decreased due to the presence of nickel in the catalyst. Preliminary SEM-EDX analysis of $Pt-Ni/Al_2O_3$ catalyst indicated that Pt is concentrated in the catalyst particles containing a high concentration of nickel; however, the Pt/Ni ratio in all the particles is found to be nearly the same. This suggests that the noble metal is in close association with nickel in the catalyst. The improved performance of the Pt- or Ru-added Ni/Al_2O_3 seems to be due to a synergetic effect of the two metals in the catalyst.

The decrease in T_S caused by the addition of noble metal is mostly due to the following reasons. The T_S for the noble metal/Al_2O_3 catalysts is low. Hence, in the presence of noble metal, the reduction rate of $NiAl_2O_4$ is expected to be greatly enhanced due to the formation of H_2 in the reaction over the noble metal at a low temperature and also due to the spillover of atomic hydrogen (which is very active), which is formed on the noble metal, to $NiAl_2O_4$. However, for a complete understanding, a further investigation is necessary.

This investigation leads to the conclusion that the addition of noble metal (Pt, Pd, or Ru) to Ni/Al_2O_3 catalyst results in a large decrease in the reaction start temperature (from about 790°C to as low as 400°C) in the oxidative conversion of methane to syngas over the unreduced catalyst and also causes an improvement in the catalytic activity/selectivity, depending upon the noble metal and its concentration in the catalyst.

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