

# The effect of acidity on Ni catalyst supported on P modified Al<sub>2</sub>O<sub>3</sub> for the dry reforming of methane

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The dry reforming of methane (DRM) has focused by many researchers due to the growing interest in the regeneration of CO<sub>2</sub>, a global warming gas, and concerns over the depletion of petroleum resources.

This DRM reaction converts greenhouse gases into syngas and it is more suitable for the Fischer-Tropsch process than the steam reforming of methane (SRM) as it produces a lower H<sub>2</sub>/CO syngas. In this respect, supported nickel catalysts have been widely studied, but they are vulnerable to the carbon deposition via CH<sub>4</sub> decomposition and Boudouard reaction (2CO ↔ C + CO<sub>2</sub>), which leads to the deactivation of catalyst for DRM.

It has been reported that the addition of P to alumina support improves the thermal stability and modifies the acid-base surface properties [1]. And some researchers have studied that the basic modifiers, the alkali metal oxides (K<sub>2</sub>O, Na<sub>2</sub>O etc.) or alkaline earth metal oxides (MgO, CaO, etc.), can increase the concentration of Lewis basicity on the support and decrease the carbon deposition [2,3].

Hence, we discussed the effect of P addition on acidity and coke formation of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for DRM. A series of modified Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with various P content (denoted as Ni/xPAI, x = 0, 0.5, 1, 2, 4 and 6 wt.% P) were prepared by an incipient wetness impregnation method using H<sub>3</sub>PO<sub>4</sub> for the support and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The Ni content of Ni/xPAI catalyst was fixed to 10 wt.%. Catalyst characterizations were performed by N<sub>2</sub>-sorption, XRD, XPS, H<sub>2</sub>-chemisorption, temperature-programmed desorption of *iso*-propanol (IPA-TPD) and CO<sub>2</sub>-TPD. The DRM reaction was conducted in flowing a mixture of CH<sub>4</sub>:CO<sub>2</sub>:N<sub>2</sub> = 40:40:20 in vol.% at 750 °C for 20 h after reduction at 750 °C for 1 h.

Table 1 shows the catalytic performance of Ni/xPAI samples at 750 °C for 20 h. Although the initial conversions of CH<sub>4</sub> and CO<sub>2</sub> decreased with the increasing P content, the addition of P to Al<sub>2</sub>O<sub>3</sub> support enhanced the stability of catalysts at an optimum amount. The tendency was well correlated with the maximum peak temperature in IPA-TPD profiles as shown in Fig. 1. It indicates that CO<sub>2</sub> is more easily adsorbed when the base strength on the surface of catalyst increases with the optimum P content. Thus the equilibrium of Boudouard reaction, one of the major causes of catalyst deactivation in DRM reaction, will shift toward left, which may hinder carbon deposition on the surface of catalyst.

Table 1. Catalytic performance of Ni/xP-Al<sub>2</sub>O<sub>3</sub> catalysts for DRM reaction at 750 °C.

Catal. <sup>a</sup>	Conversion (%)				Deactivation rate (%) <sup>b</sup>		H <sub>2</sub> /CO
	CH <sub>4</sub>		CO <sub>2</sub>		CH <sub>4</sub>	CO <sub>2</sub>	
	Initial	20 h	Initial	20 h			
Ni/Al	70.2	54.6	68.4	57.1	22.2	16.5	0.887
Ni/0.5PAI	68.0	62.3	65.0	59.8	8.4	8.0	0.888
Ni/1PAI	66.4	63.2	63.0	60.8	4.9	3.4	0.883
Ni/2PAI	62.5	63.6	60.1	61.3	-1.7	-2.1	0.871
Ni/4PAI	52.6	50.7	51.7	49.8	3.7	3.7	0.836
Ni/6PAI	37.8	32.4	34.9	27.6	14.4	21.0	0.845

<sup>a</sup> Reduced at 750 °C for 1 h before reaction.

<sup>b</sup> Defined as (initial conv. – 20 h conv.) / initial conv. × 100%.

<sup>c</sup> GHSV = 60,000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>, CH<sub>4</sub>:CO<sub>2</sub>:N<sub>2</sub> = 40:40:20 vol% and total flow rate = 100 cm<sup>3</sup> min<sup>-1</sup>.

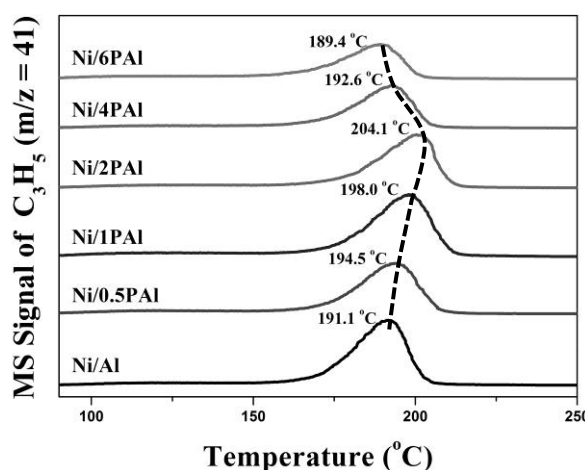


Fig. 1. IPA-TPD profiles of reduced Ni/xP-Al<sub>2</sub>O<sub>3</sub> catalysts.

## REFERENCES

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