

Increasing the selectivity of supported Rh catalysts during the partial oxidation of methane by the addition of N₂O into the feed.

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Introduction

Dynamic processes occurring at the surface of oxide catalysts during oxidation reactions could modify strongly the surface properties of the catalysts. The introduction of N₂O as gas dope into the feed could improve activity and selectivity and/or inhibit side reactions in the oxidative dehydrogenation and the ammoxidation of propane [1, 2]. In line with this, we present new results studying the effects brought about by the introduction of small amounts of N₂O in the feed during the partial oxidation of methane (POM) over supported Rh catalysts.

Experimental

Rh/Al₂O₃ and Rh/MgO (1wt.%) catalysts were prepared by the wet impregnation method with an aqueous solution of (NH₃)₄RhCl₆·3H₂O. Activity tests (CH₄:O₂ = 5:2.5 vol.%; N₂ balance, total flow: 100 ml/min) were performed in a multiple reactor system operated at atmospheric pressure using 0.1g of powdered catalyst. The reaction conditions for the tests carried out in the presence of N₂O were identical to those of the tests in the absence of dope (standard POM), but 300 ppm or 1000 ppm, respectively, of N₂O were added to the POM feed. In order to maintain the same space velocity, the total gas flow was kept constant in all the tests by balancing the flow of N₂ introduced as carrier gas into the reactor. Prior to the reaction, the catalyst was reduced *in situ* under a pure H₂ flow at 600°C for 3 h. Catalysts before and after activity tests were characterized by, BET, H₂ chemisorption, XRD and XPS.

Results/Discussion

The addition of 300 ppm of N₂O leads (Table 1) to: (i) an increase in the selectivity towards H₂, over Rh/Al₂O₃ (21%), which occurs to a lesser extent on Rh/MgO (11%), (ii) a huge increase in the CO selectivity over Rh/MgO (28%), (iii) a modest increase in the CO selectivity on Rh/Al₂O₃ (10%), (iv) a weak increase in the conversion of methane over both catalysts. Further addition of N₂O to the feed (1000 ppm) results in the decrease of activity and selectivity over both catalysts. In fact, catalytic performances in the presence of 1000 ppm of N₂O approach to

those encountered in standard POM conditions (in absence of N₂O, Table 1). An important fact is that when N₂O is removed from the reaction feed, the catalytic performances observed in the absence of dope (standard POM conditions) are slowly re-established.

Table 1. Effect of N₂O addition on CH₄ conversion (XCH₄) and syngas selectivities (SH₂ and SCO) over Rh/Al₂O₃ and Rh/MgO catalysts at 650°C. Values in parenthesis represent the variation of XCH₄, SH₂ and SCO respect to the standard POM conditions (without N₂O in the feed).

Feed composition	XCH ₄		SH ₂		SCO	
	Rh/Al ₂ O ₃	Rh/MgO	Rh/Al ₂ O ₃	Rh/MgO	Rh/Al ₂ O ₃	Rh/MgO
Standard POM	84	71	79	72	85	72
POM + 300 ppm N ₂ O	89 (+7%)	77 (+10%)	96 (+21%)	80 (+11%)	93 (+10%)	93 (+28%)
POM + 1000 ppm N ₂ O	87 (+4%)	74 (+4%)	87 (+11%)	68 (-6%)	87 (+2%)	71 (-3%)

It is clear that the addition of certain amounts of N₂O to the POM feed produces noticeable changes in the catalytic activity, in particular in the selectivity towards syngas (Table 1). The XPS results show that (Table 2), compared with catalysts having worked in absence of dopes, the addition of small amounts of N₂O (300 ppm) promotes the reduction of the catalysts (the XPS Rh3d_{5/2} BE shifts to lower values after the test performed with 300 ppm of N₂O, Table 2), which results in enhancing the selectivity towards syngas. On the contrary, at higher amounts of N₂O co-fed (1000 ppm) the catalysts work under a more oxidised state (increase of the XPS Rh3d_{5/2} BE after the test performed with 1000 ppm of N₂O compared with the catalyst after the test in the presence of 300 ppm, Table 2), which brings about the decrease in selectivity. A small amount of N₂O improves selectivity, which is likely due to: (i) a competitive adsorption of N₂O and O₂ (O₂ adsorption is thus inhibited) and/or (ii) the increase of the reduction rate of supported Rh catalysts. Our results demonstrate that the selectivity during POM reaction can be tuned by adjusting the concentration of N₂O added to the feed.

Table 2. Rh3d_{5/2} XPS binding energy and XPS atomic ratio of Rh/Al₂O₃ and Rh/MgO catalysts.

Sample	XPS at. Ratio · 10 ⁻⁴		Rh3d _{5/2}	
	Rh/Al	Rh/Mg	Rh/Al ₂ O ₃	Rh/MgO
Fresh catalyst	58	93	309.1	308.9
Standard POM	44	116	308.7	308.3
POM + 300 ppm N ₂ O	41	128	308.2	307.5
POM + 1000 ppm N ₂ O	38	129	308.8	308.0

References.

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2. J. Pérez-Ramírez, N. Blangenois, P. Ruíz, *Catal. Letters*, **104**, 163 (2005).