

Total oxidation of propane and propene on Pt supported catalysts: Role of the support on catalytic activity

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Introduction

The catalytic oxidation of hydrocarbons on Pt-based catalysts is a key reaction for several industrial chemical processes as well as for automotive emission control. In particular, Pt/Al₂O₃ has been widely investigated in the literature and is described as one of the most efficient catalytic system for the removal of hydrocarbons [1,2]. In this work, we study the role of reducible supports on the total oxidation of propane and propene on Pt-supported catalysts.

Experimental

Al₂O₃ (CK300, Cyanamid Ketjen, 180 m²g⁻¹), CeO₂ (HS5A Rhodia, 230 m²g⁻¹) and TiO₂ (P25, Degussa, 50 m²g⁻¹) were employed as supports. Pt (0.5%) supported on TiO₂ (Pt/Ti), CeO₂ (Pt/Ce) and Al₂O₃ (Pt/A) were obtained by impregnating the supports with aqueous solution of Pt(NH₃)₄(NO₃)₂. N₂ physisorption, XRD, TPR, NH₃ TPD and H₂ chemisorption were employed to characterize the samples. Catalytic activity of Pt catalysts was determined through conversion-temperature (light off curves) and conversion-time (at constant temperature) tests for propane and propene oxidation.

Results/Discussion

The physicochemical properties of the samples are presented in Table 1. The support surface area was not modified by metal impregnation. X-ray diffraction characterization showed that TiO₂ is composed by anatase and rutile and that CeO₂ displays the peaks of a cubic fluorite structure. The density of acid sites was one order of magnitude higher on Pt/Ti than on Pt/A and Pt/Ce. Metal dispersion (D_{Pt}) varied between 32 and 65%.

Table 1. Physicochemical and catalytic properties of Pt-supported catalysts

Sample	S _g (m ² g ⁻¹)	μmolNH ₃ m ⁻²	D _{Pt} (%)	T ⁵⁰ (°C) ^a	TOF(h ⁻¹) ^a	T ⁵⁰ (°C) ^b	TOF(h ⁻¹) ^b
Pt/A	175	0.132	63	395	114	206	102
Pt/Ce	220	0.210	50	332	462	190	351
Pt/Ti	48	1.310	32	332	1052	265	96

^a corresponding to propane oxidation, TOF at 250 °C

^b corresponding to propene oxidation, TOF at 155 °C

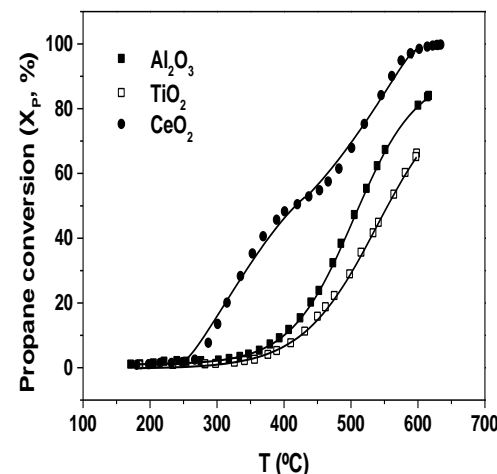


Figure 1. X_P vs T. C₃H₈(0.9):O₂(9.1):N₂(90)

Propane oxidation on Pt catalysts was also carried out at constant temperature (250°C). Conversion-time tests were performed at low conversion (<10%) and the reaction was kinetically controlled. From the conversion-time curves we calculated the reaction rates and then the turnover frequency (TOF) of propane oxidation. The results are presented in Table 1. TOF value on Pt/Ti was about one order of magnitude higher than on Pt/A and two times higher than on Pt/Ce. The superior propane oxidation activity observed for Pt/Ti catalyst could be attributed to the greater support acidity, in agreement with the behaviour observed on Pt/V₂O₅-Al₂O₃ catalysts [2]. The TOF values corresponding to propene oxidation are also given in Table 1. Pt/A and Pt/Ti exhibited similar TOF values, but Pt/Ce was the most active catalyst. The higher activity of Pt/Ce could be attributed to the presence of oxygen vacancies in the support. The results obtained in the propane and propene oxidation show that Pt activity depends on the support. Besides, for a given support the Pt oxidation activity depends on the type of hydrocarbon. For example, Pt/Ti was the most active catalyst for propane oxidation, but oxidized propene at similar rates than Pt/A catalysts. The changes in catalytic behaviour can be attributed to changes in the rate-limiting steps of the oxidation reaction mechanisms.

References

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- [2]. M.S. Avila, C.I. Vignatti, C.R. Apesteguía, V. Venkat Rao, K. Chary, T.F. Garetto, Catal Lett (2010) 134:118–123