

Pt/V₂O₅-TiO₂ catalysts for VOCs abatement: V₂O₅ loading effects on the deep oxidation of benzene

Carlos R. Apesteguía^{1*}, Teresita F. Garetto¹, Maria S. Avila¹, V. Venkat Rao², Komandur V. R. Chary²

¹GICIC (Catalysis Science and Engineering Research Group), INCAPE (UNL-CONICET), Santiago del Estero 2654, (3000) Santa Fe (Argentina)

²Catalysis Division, Indian Institute of Chemical Technology, Hyderabad (India)

*capesteg@fiq.unl.edu.ar

Introduction

Platinum and palladium-based catalysts have been efficiently employed in the abatement of hydrocarbons from gaseous streams. Recently, it has been reported [1] that Pd supported on vanadia-promoted carriers efficiently catalyzes the deep oxidation of benzene. In particular, it was observed that when vanadium is added to Pd/Al₂O₃ or Pd/TiO₂ catalysts the activity for benzene combustion increases. The high activity of Pd/V₂O₅-TiO₂ catalysts was related to the simultaneous presence of two active sites: reducible vanadium sites and oxidized palladium species. In contrast, the oxidation of benzene has not been studied on Pt supported on vanadia-promoted carriers in spite that Pt is more active than Pd for oxidizing aromatic hydrocarbons and C₂-C₄ alkanes [2]. In this work, we study the combustion of benzene over Pt/V₂O₅-TiO₂ catalysts containing different vanadium loadings. The catalysts were thoroughly characterized by several spectroscopic techniques. The aim was to establish the effect of V₂O₅ loading on Pt dispersion and catalyst activity.

Materials and Methods

V₂O₅/TiO₂ samples (V-T samples) were prepared by wet impregnation of TiO₂ (Degussa P-25, surface area 50 m² g⁻¹) with aqueous solutions of ammonium metavanadate to achieve between 1.5 and 6.5 wt % V₂O₅ loadings. Pt (0.4%) supported on V₂O₅/TiO₂ (Pt/V-T samples) was obtained by impregnating the supports with aqueous solutions of Pt(NH₃)₄(NO₃)₂. Samples were characterized by XRD, ESR, FTIR and TEM techniques and also by O₂ and H₂ chemisorptions. The activity for V-T and Pt/V-T samples was determined using both conversion vs temperature (light-off curves) and conversion vs time (at constant temperature) tests.

Results and Discussion

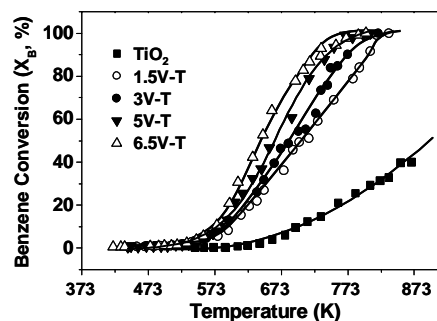
The O₂ chemisorption on V-T samples increased with vanadia loading up to 5% of V₂O₅ and leveled off at higher vanadia loadings, probably because of the formation of V-oxide monolayer on TiO₂. These results were in agreement with the information obtained from ESR spectra. FT-IR spectra showed the presence of microcrystalline V₂O₅ on 8%V/T sample, which was confirmed by XRD diffractograms. At lower vanadia loading no IR band characteristic of V₂O₅ was observed, suggesting that vanadium oxide was highly dispersed on TiO₂ support. The specific surface area of V-T samples sharply decreased with the vanadia content, thereby indicating the blocking of the TiO₂ pores by crystallites of vanadia. In the case of Pt/V-T catalysts, the Pt dispersion (D_{Pt}) was measured by H₂ chemisorption and the results are shown in Table 1. The D_{Pt} value increased with the vanadia content. The higher Pt dispersion on

Pt/V-T samples of higher V₂O₅ loading was confirmed by TEM characterization. Figure 1 shows the light-off curves obtained on V-T samples for the oxidation of benzene. It is observed that the sample activity increased with the V₂O₅ content, indicating that vanadium oxide

promotes the oxidation reaction. The value of the temperature at X_B = 50 % (T⁵⁰) decreased from 723 K on 1.5V/T to 663 K on 6.5V/T. The X_B vs. T curves drastically shifted to lower temperatures when Pt was added to V₂O₅-TiO₂ samples, reflecting the high oxidation activity of the metal. In contrast with the results observed in Fig. 1 for V-T samples, the T⁵⁰ value on Pt/V-T catalysts increased with the V₂O₅ content (Table 1). Benzene oxidation was also carried out on platinum catalysts by performing X_B vs time tests at constant temperature (493 K).

In all the cases, the initial conversion was lower than 10 % and the reaction was kinetically controlled. From the X_B vs time tests, we calculated the reaction rates (r₀, mol/h g Pt) and turnover frequencies (TOF, h⁻¹) of benzene combustion. Results are shown in Table 1. In contrast with the results obtained on Pd/V₂O₅-TiO₂ [1], it is observed in Table 1 that the benzene oxidation rate, r₀, decreases with the amount of V₂O₅. Calculations of turnover frequencies confirmed that the TOF values decreased when the % V₂O₅ in the sample was augmented (Table 1). These results can be interpreted by considering that benzene oxidation on Pt is a structure sensitive reaction that is preferentially promoted on

Figure 1: Light-off curves for benzene combustion



large metal particles. The addition of V₂O₅ to TiO₂ favors the dispersion of the metal thereby decreasing the benzene turnover rate.

Table 1: Benzene combustion activity on Pt/V-T samples

Sample	V ₂ O ₅ (wt %)	D _{Pt} (%)	T ⁵⁰ (K)	r ₀ (mol h ⁻¹ g _{Pt} ⁻¹)	TOF (h ⁻¹)
Pt/TiO ₂	-	13	508	0.223	335
Pt/1.5V-T	1.5	21	533	0.174	162
Pt/3V-T	3.0	39	563	0.162	80
Pt/5V-T	5.0	83	543	0.160	38
Pt/6.5V-T	6.5	77	573	0.124	31

Significance The benzene combustion rate increases with vanadia content on V₂O₅-TiO₂ samples. On Pt/V₂O₅-TiO₂, the Pt dispersion increases with the V₂O₅ content but the activity for benzene oxidation follows an opposite trend because is a structure sensitive reaction preferentially promoted on larger platinum crystallites.

References

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