Pt/V$_2$O$_5$-TiO$_2$ catalysts for VOCs abatement: V$_2$O$_5$ loading effects on the deep oxidation of benzene

Carlos R. Apesteguía$^1$, Tere silica F. Garetto$^1$, Maria S. Avila$^1$, V. Venkat Rao$^2$, Komandur V. R. Chary$^2$

$^1$GICIC (Catalysis Science and Engineering Research Group), INCAPE (UNL CONICET), Santiago del Estero 2654, (5000) Santa Fe (Argentina)

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

*capeste@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/Al$_2$O$_3$ or Pd/TiO$_2$ catalysts the activity for benzene combustion increases. The high activity of Pt/V$_2$O$_5$-TiO$_2$ 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 C$_2$-C$_5$ alkanes [2]. In this work, we study the combustion of benzene over Pt/V$_2$O$_5$-TiO$_2$ catalysts containing different vanadium loadings. The catalysts were thoroughly characterized by several spectroscopic techniques. The aim was to establish the effect of V$_2$O$_5$ loading on Pt dispersion and catalytic activity.

Materials and Methods

V$_2$O$_5$-TiO$_2$ samples (V-T samples) were prepared by wet impregnation of TiO$_2$ (Degussa P-25, surface area 50 m$^2$ g$^{-1}$) with aqueous solutions of ammonium metavanadate to achieve between 1.5 and 6.5 wt% V$_2$O$_5$ loadings. Pt (0.4%) supported on V$_2$O$_5$-TiO$_2$ (Pt(V-T) samples) was obtained by impregnating the supports with aqueous solutions of Pt(NH$_3$)$_2$Cl$_2$. Samples were characterized by XRD, ESR, FTIR and TEM techniques and also by O$_2$ and H$_2$ 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 O$_2$ chemisorption on V-T samples increased with vanadia loading up to 5% of V$_2$O$_5$ and leveled off at higher vanadia loadings, probably because of the formation of V-oxide monolayer on TiO$_2$. These results were in agreement with the information obtained from ESR spectra. FT-IR spectra showed the presence of microcrystalline V$_2$O$_5$ on 8%V/T sample, which was confirmed by XRD diffractograms. At lower vanadia loading no IR band characteristic of V$_2$O$_5$ was observed, suggesting that vanadium oxide was highly dispersed on TiO$_2$ support. The specific surface area of V-T samples sharply decreased with the vanadia content, thereby indicating the blocking of the TiO$_2$ pores by crystallites of vanadia. In the case of Pt(V-T) catalysts, the Pt dispersion (D$_{Pd}$) was measured by H$_2$ chemisorption and the results are shown in Table 1. The D$_{Pd}$ value increased with the vanadia content. The higher Pt dispersion on Pt/V$_2$O$_5$-TiO$_2$ samples of higher V$_2$O$_5$ 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 V$_2$O$_5$ content, indicating that vanadium oxide promotes the oxidation reaction. The value of the temperature at X$_D$ = 50% (T$^*$) decreased from 723 K on 1.5V/T to 663 K on 6.5V/T. The X$_D$ vs. T curves drastically shifted to lower temperatures when Pt was added to V$_2$O$_5$-TiO$_2$ samples, reflecting the high oxidation activity of the metal. In contrast with the results observed in Fig. 1 for V-T samples, the T$^*$ value on Pt/V-T catalysts increased with the V$_2$O$_5$ content (Table 1). Benzene oxidation was also carried out on platinum catalysts by performing X$_D$ 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$_D$ vs time tests, we calculated the reaction rates ($r_D$, mol$h^{-1}g_Pt$) and turnover frequencies (TOF, $h^{-1}$) of benzene combustion. Results are shown in Table 1. In contrast with the results obtained on Pt/V$_2$O$_5$-TiO$_2$ [1], it is observed in Table 1 that the benzene oxidation rate, $r_D$, decreases with the amount of V$_2$O$_5$. Calculations of turnover frequencies confirmed that the TOF values decreased when the % V$_2$O$_5$ 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 large metal particles. The addition of V$_2$O$_5$ to TiO$_2$ favors the dispersion of the metal thereby decreasing the benzene turnover rate.

Significance

The benzene combustion rate increases with vanadia content on V$_2$O$_5$-TiO$_2$ samples. On Pt/V$_2$O$_5$-TiO$_2$, the Pt dispersion increases with the V$_2$O$_5$ content but the activity for benzene oxidation follows an opposite trend because is a structure sensitive reaction preferentially promoted on larger platinum crystallites.

References
