

Characterization of Vanadia Catalysts Supported On Different Carriers by TPD, TPR

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Introduction

Since V_2O_5/TiO_2 catalysts were successful in the oxidation of oxylene, vanadium-containing catalysts were widely used in the oxidation of other aromatic and paraffinic hydrocarbons [1]. The characterization of these catalysts has been investigated by a great number of physical and chemical methods in many laboratories. But their redox property is not without controversy. TPR (Temperature-programmed Reduction) and NH_3 TPD (Temperature-Programmed Desorption) are powerful methods to characterize the redox property and the surface acidity of solid catalysts [2,3]. In this article, the influence of different supports on the redox property and the acidity of V_2O_5 catalysts will be clarified by TPR and NH_3 TPD.



Experimental

1. Catalyst preparation. Two systems of catalysts were prepared by the wet impregnation. They were indicated as VxA (for V_2O_5/Al_2O_3) and VyT (for V_2O_5/TiO_2), where x and y are the loadings of vanadium expressed in wt. %. Alumina (BET surface area = $195\text{ m}^2/\text{g}$) and Titania (BET surface area = $55\text{ m}^2/\text{g}$) were impregnated with vanadium oxalate aqueous solution, followed by drying at $110\text{ }^\circ\text{C}$ for 14h and calcination at $650\text{ }^\circ\text{C}$ and at $450\text{ }^\circ\text{C}$ (for VxA and VyT, respectively) for 3h.

Table 1. T_{\max} in NH_3 _TPD and TPR of VxA and VyT

| Sample | Support | % wt. V_2O_5 | Theoretical monolayer coverage ^(a) | T_{\max} (NH_3 _TPD) | | | T_{\max} (TPR) | | |
|--------|-----------|----------------|---|---------------------------|--------|--------|------------------|---------------|---------------|
| | | | | Weak | Medium | Strong | Mono-vanadate | Poly-vanadate | V_2O_5 bulk |
| | Al_2O_3 | 0 | | 192.1 | 369.1 | | | | |
| V2A | Al_2O_3 | 2 | 0.07 | 191.8 | 368.8 | | 458 | | |
| V8A | Al_2O_3 | 8 | 0.28 | 173.7 | 379.0 | | 446.0 | | |
| V10A | Al_2O_3 | 10 | 0.35 | 184.2 | | | 444.0 | | |
| | TiO_2 | 0 | | | - | | - | | - |
| V2T | TiO_2 | 2 | 0.25 | 172.6 | | 443.0 | 493.5 | 629.6 | |
| V8T | TiO_2 | 8 | 1.00 | 166.4 | | 418.0 | 506.7 | 618.2 | |
| V10T | TiO_2 | 10 | 1.25 | 168.8 | 356.4 | 417.5 | 507.1 | 618.8 | 758.3 |

^(a) Theoretical Monolayer Coverage of V_2O_5 equals $0.145\%V_2O_5/m^2$ [1,4]

2. Characterization of catalysts. Temperature-Programmed Reduction (TPR) with hydrogen and Temperature-Programmed Desorption (TPD) of NH_3 were carried out in a Micromeritics AutoChem II 2920 analyzer.

In the TPR experiments, the sample without pretreatment was reduced with a 10% H_2/Ar mixture (25 ml/min) by heating at $10^\circ\text{C}/\text{min}$ to 800°C . In the TPD experiments, the sample, after decontaminating at 300°C , was saturated with 10% NH_3/He (15 ml/min) at 100°C for 1h, and then was purged with pure He for 1h. For the desorption, it was heated ($10^\circ\text{C}/\text{min}$) to 500°C in flowing He (25 ml/min).

Results and Discussion

NH_3 TPD of V_xA contrasted with that of V_yT . When the loadings of vanadia rose, the NH_3 TPD profiles of V_xA shifted to low temperature, showing that the amount of weak acid sites increased and the amount of medium and strong acid sites decreased. Contrarily, on NH_3 TPD profiles of V_yT , the strong acid sites increased as loadings of vanadia increased. Above monolayer (V_{10}T), a third peak appeared at the middle temperature range.

The TPR of $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ showed only one peak at lower temperature. It was attributed to the reduction of the monovanadate species. There are two reduction peaks in the TPR

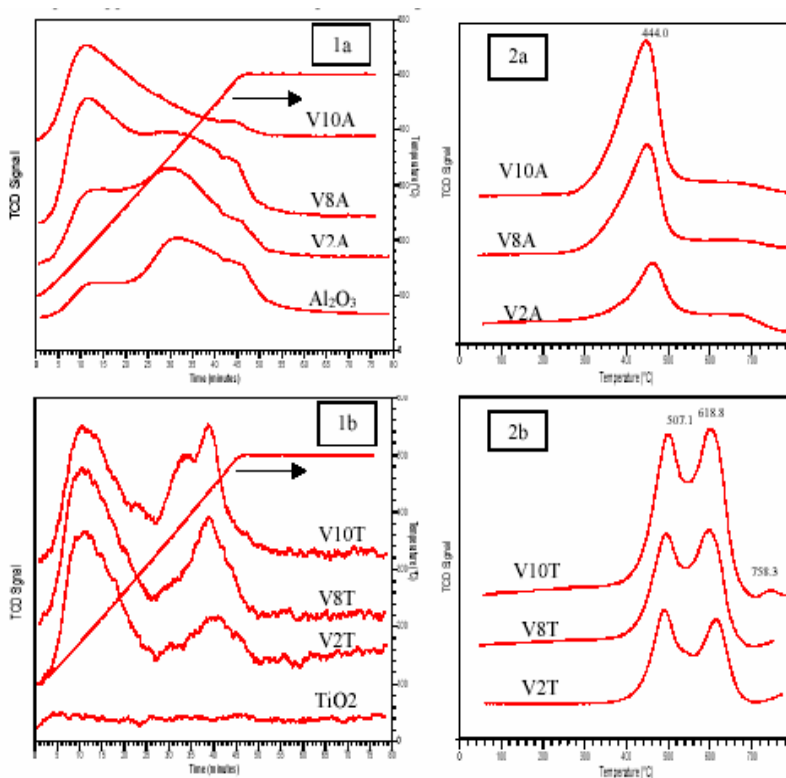


Figure 1. NH_3 TPD of V_xA (a) & V_yT (b)

Figure 2. TPR of V_xA (a) & V_yT (b)

profiles of $\text{V}_2\text{O}_5/\text{TiO}_2$ under monolayer coverage (V_{2}T and V_{8}T): they were attributed to the reduction of mono- and poly-vanadate species. When the coverage was over the monolayer (V_{10}T), a third peak appeared at higher temperature, it might be the reduction of V_2O_5 crystallites.

Conclusions

1. When the loadings of vanadia rose, the amount of weak acid sites on V_xA increased whereas, the quantity of strong acid sites on V_yT increased.

2. V_2O_5 supported on Al_2O_3 was reduced more easily than on TiO_2 because its theoretical monolayer coverage was lower.

References

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