

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

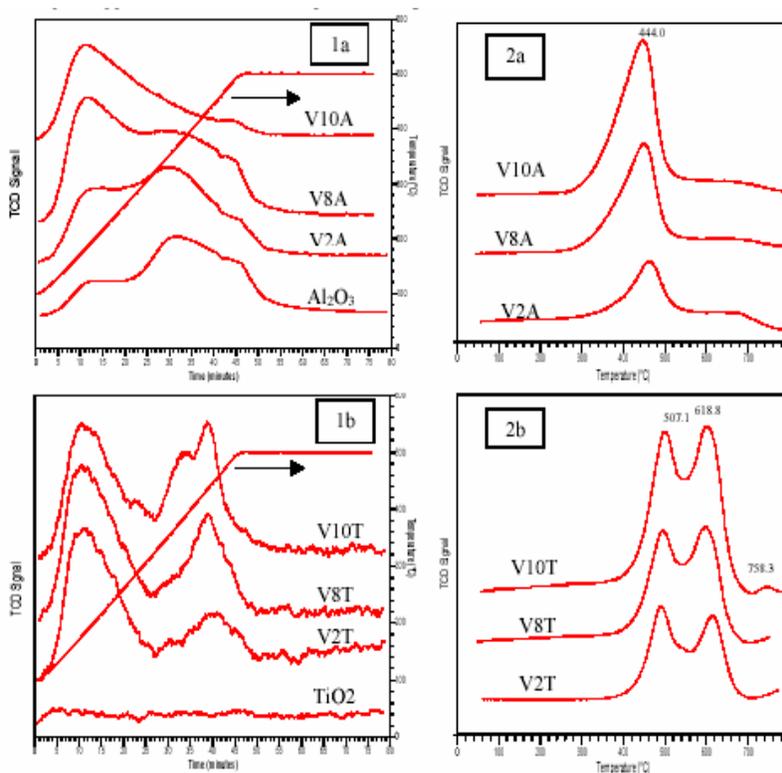


Figure 1. NH_3 TPD of V_xA (a) & V_yT (b)

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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