TUNING THE SELECTIVITY OF MOO_X SUPPORTED CATALYSTS FOR CYCLOHEXANE PHOTO OXIDEHYDROGENATION

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Introduction

Recently, Ciambelli et al. [1] have found that cyclohexane is selectively oxidised to benzene and cyclohexene on MoO_x/TiO_2 catalyst in mild condition (P = 1 atm, T = 308K) under UV illumination. In the present study the photocatalytic properties of sulphated MoO_x/γ-Al_2O_3 catalysts in cyclohexane oxidative dehydrogenation have been determined in a two-dimensional fluidized bed photoreactor.

Experimental

Sulphated (2.4, 4.8, 7.2 wt%) MoO_x/γ-Al_2O_3 (8 wt% MoO_3) were prepared by two-step impregnation with aqueous solution of ammonium heptamolybdate and sulphate. After each step the catalyst was dried at 393 K overnight and calcined in air flow, respectively, at 773 K and 573 K for 3 hours. The catalyst were characterised by TG-MS, N_2 adsorption at 77K, Raman spectroscopy, XPS. Catalytic tests were carried out at 393 K in a fluidized bed reactor fed by 830 (stp)cm^3/min of N_2 containing 1000 ppm cyclohexane, 1500 ppm O_2 and 1600 ppm H_2O. The outlet stream was analysed continuously by on-line quadrupole mass detector and CO-CO_2 NDIR analyser. The reactor was loaded with a physical mixture of 13g ofcatalyst and 58g of α-Al_2O_3 and illuminated by four UV light sources after cyclohexane adsorption on the catalyst surface at T = 393 K.

Results and discussion

Photocatalytic test on sulphated MoO_x/γ-Al_2O_3 at various sulphate contents showed the selective formation of cyclohexene, without production of benzene (as formed with MoO_x/TiO_2 [1]) and CO_x. Cyclohexane conversion increased to about 10 % with increasing sulphate loading to 2.4 wt % and decreased with further increase. Cyclohexane conversion and cyclohexene yield reached 15% with increasing the reaction temperature in the range 300-395 K. Physico-chemical characterisation indicates the presence of either octahedral polymolybdate species on alumina surface as for titania [1] and surface sulphates. Increasing sulphate load, TG test evidenced up to three species of sulphate of different thermal stability. The lower activity observed over 2.4 wt % $SO_4^=$ could be related to polymolybdate decoration by sulphates.

Conclusions

We have found that it is possible to dramatically modulate the selectivity of photocatalytic cyclohexane dehydrogenation in the presence of oxygen. 100% selectivity to cyclohexene has been obtained over sulphated MoO_x/γ-Al_2O_3 catalysts while over sulphated MoO_x/TiO_2 99% selectivity to benzene to benzene or cyclohexene.

References

1 P Ciambelli., D. Sannino, V. Palma, V. Vaiano, Catal Tod., 99 (2005), 143-149.