In-situ UV/Vis spectroscopy for analysis of dynamics of surface processes: Kinetics of reduction and oxidation of VO_x in the oxidative dehydrogenation of propane over VO_x/Ti-Si-MCM-41 with O_2 and N_2O

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Introduction

UV-Vis spectroscopy nowadays is one of a very few methods, which allows to characterize heterogeneous catalysts under real working conditions [1-2]. However, in-situ UV/Vis spectroscopy is not often applied for analyzing kinetic processes occurring on the catalyst surface [3-4]. In the present contribution, we demonstrate the potential of in-situ UV/Vis spectroscopy operating under transient and steady-state conditions for deriving kinetic parameters of reduction (with C_3H_8) and reoxidation (with O_2 and N_2O) of highly dispersed VO_x species over Ti-Si-MCM-41 (Ti/Si=0-1.5) materials as well as for analyzing their reduction degree under conditions of the oxidative dehydrogenation of propane (ODP).

Materials and Methods

A series of VO_x/Ti-Si-MCM-41 materials with a total vanadium loading of 3.7 wt.% was prepared by impregnating the support with vanadyl acetyl acetate, dissolved in toluene. The mesoporous support materials with a Ti/Si ratio varying from 0 to 1.5 were prepared by the procedures given in the literature [5]. Resulting catalysts were characterized by ICP, XRD, EPR, H_2-TPR, Laser Raman spectroscopy and UV/Vis spectroscopy combined with mass-spectroscopic analysis. For characterizing the performance of the catalytic materials in the ODP reaction, continuous flow tests were performed at atmospheric pressure and 773 K using oxygen and nitrous oxide as oxidizing agents.

Results and Discussion

Based on kinetic evaluation of transient UV/Vis experiments, kinetic constants of reduction and reoxidation of surface VO_x species by C_3H_8 and $O_2(N_2O)$, respectively, were determined for the VO_x(3.7)/Ti-Si-MCM-41 catalysts at 773 K. Three effects of titania on redox properties of VO_x species were identified: 1) the constant of reduction by C_3H_8 increases significantly, ii) the constant of oxidation by O_2 decreases; and iii) the constant of oxidation by N_2O increases. Moreover, this kinetic analysis revealed also that there exist at least two types of differently reducible and oxidizable VO_x species in the samples with titania. These results correlate well with the results of H_2-TPR analysis.

Table 1 compares the ratio of constant of reduction by C_3H_8 ($K'_1(C_3H_8)$) to the constant of oxidation by O_2 ($K'_1(O_2)$) and the $K'_1(O_2)$ to $K'_1(N_2O)$ as function of Ti content in the support. The first ratio determines the reduction degree of the catalysts in the reaction; the higher the ratio the higher the reduction degree. The second ratio determines the difference in the reduction degree under ODP condition with O_2 and N_2O; the higher the ratio the higher the difference. The reduction degree of VO_x/Ti-Si-MCM-41 catalysts in the ODP reaction can be tuned by the ratio of Ti/Si and by the oxidizing agents (O_2, and N_2O).

Table 1. The ratio of the $K'_1(C_3H_8)$ to the $K'_1(O_2)$ and the $K'_1(O_2)$ to the $K'_1(N_2O)$ as function of Ti/Si ratio.

Ti/Si	0	0.12	0.64	1.5
$K'_1(C_3H_8)/ K'_1(O_2)$	0.024	0.20	0.33	1.52
$K'_1(O_2)/ K'_1(N_2O)$	37	18	11	6.6

These kinetic results correlate well with UV/Vis measurements under steady-state ODP conditions and with catalytic performance of the catalysts in the ODP reaction with O_2 and N_2O as oxidants. Propene selectivity is significantly influenced by the ratio of Ti/Si in the catalysts and by the oxidizing agents (O_2, and N_2O). The presence of Ti influences also the turnover frequencies in the ODP reaction. The ODP activity increases linear with an increase in the constant of reduction of VO_x species by C_3H_8 (Figure 1).

Significance

The present contribution highlights the applicability of in-situ UV/Vis technique for analyzing the reduction degree of highly dispersed transition metal oxide aggregates as well as for deriving kinetic parameters of their reduction and oxidation.

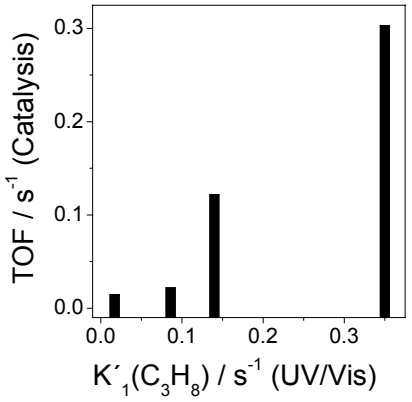

Figure 1. Comparison of the constant of reduction of VO_x species by C_3H_8 ($K'_1(C_3H_8)$) from UV/Vis measurements with the TOF values of propane conversion obtained in the catalytic ODP experiments at 773 K using $C_3H_8/O_2/Ne$=40/20/40.

References

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