The Influence of Structural Properties of γ-Alumina Supported VOx Catalysts on the Reaction Network of Selective Oxidation of Ethane

F. Klose[a,b], **T. Wolff**[a,*], **M. Joshi**[c], **A. Seidel-Morgenstern**[a,c], **Y. Suchorski**[d], **H. Weiss**[d]

[a] *Max-Planck-Institut für Dynamik komplexer technischer Systeme, D-39106 Magdeburg, Germany*
[b] *Otto-von-Guericke-Universität, IFAT, D-39106 Magdeburg, Germany*
[c] *Otto-von-Guericke-Universität, IVT, D-39106 Magdeburg, Germany*
[d] *Otto-von-Guericke-Universität, Chemisches Institut, D-39106 Magdeburg, Germany*
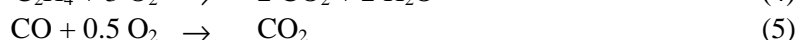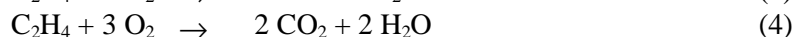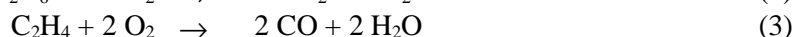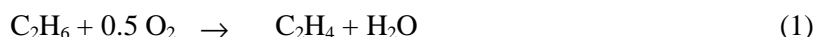
Abstract: Two series of γ-alumina supported VOx catalysts with V loadings between 1 and 15 wt.-% prepared by different techniques were studied due their performance in selective oxidation of ethane. Additionally, experiments on the oxidation of ethylene and CO were performed in order to clarify the contributions of consecutive reactions. The results obtained demonstrate, that at low V loadings, corresponding to a high V dispersion, a higher ethylene selectivity is obtained than at higher loaded catalysts. This is especially due to a higher activity of V_2O_5 for consecutive ethylene oxidation to CO. Additionally, the redox cycles of vanadate and V_2O_5 are different: the first is mainly only between V(IV) and V(III), in contrast to the latter one, which is between V(V) and V(III)

1. Introduction

Selective catalytic oxidation of ethane is of large scientific and industrial interest. Ethylene as its desired product is an important starting material for the synthesis of many valuable chemicals like benzene, styrene, polyethylene, ethanol, acetic acid, etc. Despite of an intensive research catalytic oxidation of ethane is still far from industrial application. Among the possible catalysts supported vanadium oxides are attractive candidates because they are active and quite selective already at moderate temperatures.

It is well accepted that catalytic ethane oxidation occurs via a network of parallel and consecutive reactions with ethylene as intermediate and CO_2 as the thermodynamically favored final product. However, the detailed structure of the reaction network is still under discussion[1-3]. Previously[4] we postulated a network consisting of five partial reactions, the oxidative dehydrogenation of ethane to ethylene (1), the direct oxidation of ethane to CO_2 (2), the consecutive oxidation of ethylene to CO (3) and CO_2 (4) and finally, the oxidation of CO to CO_2.

$$C_2H_6 + 0.5\,O_2 \quad \rightarrow \quad C_2H_4 + H_2O \tag{1}$$
$$C_2H_6 + 3.5\,O_2 \quad \rightarrow \quad 2\,CO_2 + 3\,H_2O \tag{2}$$
$$C_2H_4 + 2\,O_2 \quad \rightarrow \quad 2\,CO + 2\,H_2O \tag{3}$$
$$C_2H_4 + 3\,O_2 \quad \rightarrow \quad 2\,CO_2 + 2\,H_2O \tag{4}$$
$$CO + 0.5\,O_2 \quad \rightarrow \quad CO_2 \tag{5}$$

The scope of study presented is to evaluate the effect of structural properties of the catalyst, like V dopant degree, surface area and the nature of the active phase to the single reactions of the reaction network proposed.

2. Experimental

Two series of catalysts were prepared: by the impregnation of γ-alumina (BET surface area 200 m²/g) either with VO(acac)$_2$ in acetone (series A) or with V_2O_5 in a mixture of ammonia, water and acetone (series B). The impregnated catalysts were dried at 393 K overnight, followed by subsequent calcination under air at 923 K for 8 h. Catalysts were characterized by AAS, XRD, BET/N_2 porosimetry, XPS, thermal analysis and TPR/TPO. In a fully automated laboratory fixed bed reactor plant extensive catalytic tests were performed varying temperature between 673 and 923 K at oxygen to hydrocarbon ratios of 0.5, 1.0 and 30 and GHSV of 23000 and 46000 h^{-1}. Ethylene and CO oxidation were studied under similar conditions to characterize the conversion of these intermediates in the reaction network. To check for reactant product interactions, additional experiments were performed for the oxidation of ethane and ethylene by CO_2.

3. Results and discussion

In the XRD patterns of the fresh catalysts (Fig. 1) the V_2O_5 reflexes appear first at a V loading of 9.5 wt.-% for catalysts from A series, in contrast to B series, where they are present already at a V loading of

5.5 wt.-%. Thus, for the catalysts prepared from $VO(acac)_2$ a higher V dispersion was reached. This agrees with the data from the BET measurements, where the surface drop caused by pore clogging with V_2O_5 is significantly shifted to higher V loadings (Fig. 2). Simultaneously to the appearance of the V_2O_5 phase the crystallinity of the alumina support enhances. For both catalyst series, there were no reflexes which can be attributed to a phase different from γ-alumnina and V_2O_5.

In the TPR experiments, depending on V loading four different reduction peaks can be distinguished, attributable to isolated (473 K) and different polymeric vanadate species (523-623 K) and finally to bulk-like V_2O_5 (>623 K). The H/V ratio measured after repeating several reduction-reoxidation cycles shifts from 1.3 for 1.7-6.1% V to 1.8 for the higher loaded samples. This means that in contrast to V_2O_5, most of the vanadate species do not undergo the full redox cycle between V(V) and V(III), a significant vanadate part remains at +4 under moderate oxidizing conditions. This agrees with the XPS results, where an increase of the average V oxidation state from 4.3 to 4.8 was observed with increased V loading. Also in TPO dispersed vanadite and bulk-like V_2O_3 can be clearly distinguished.

Activity measurements are not finished yet, but at the present state, with oxygen as the oxidant initial ethylene selectivity values between 60 and 80 % were observed and the maximum ethylene yield is higher than 20 % (23000 h^{-1}). These first results indicate that both vanadate and V_2O_5 phases are active at near similar initial selectivitiy, but the latter one is more active especially for the consecutive oxidation of ethylene to CO (reaction 3), so that the maximum possible ethylene yield decreases. Under oxygen shortage conditions further reactions should be added to the network: the oxidation of ethane to ethylene by CO_2 (6), the oxidation of ethylene by CO_2 (7), ethylene pyrolysis yielding soot and finally, the Boudouard equilibrium reactions. For CO_2 as the oxidant ethylene yields can reach similar values, ethylene selectivity is around 80 %.
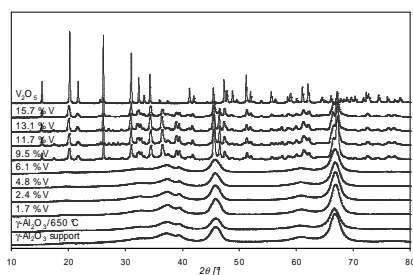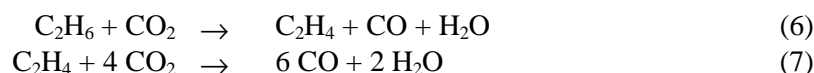
$$C_2H_6 + CO_2 \quad \rightarrow \quad C_2H_4 + CO + H_2O \quad\quad\quad (6)$$
$$C_2H_4 + 4\,CO_2 \quad \rightarrow \quad 6\,CO + 2\,H_2O \quad\quad\quad\quad (7)$$

Fig. 1: XRD patterns from the A series catalysts
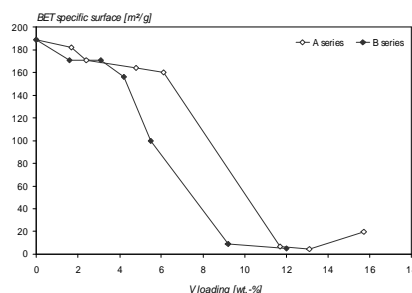
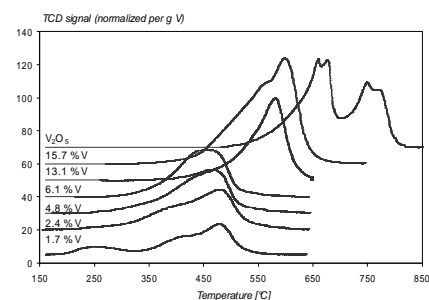**Fig. 2**: Specific surface areas by the BET method

Fig. 3: TPR from the A series catalysts (data from the 3rd reduction-reoxidation cycle)

4. Conclusions

Alumina supported vanadium oxide catalysts are active and selective of catalytic oxidation of ethane to ethylene. Low V loadings corresponding to a high V dispersion are favorable for ethylene formation due to the suppression of ethylene over-oxidation. Vanadia dispersion is significantly influenced by the preparation method. Additionally, the well-dispersed vanadate and the bulk-like V_2O_5 phases show a different redox cycle: vanadate mainly between V(IV) and V(III), V_2O_5 between V(V) and V(III).

References
1) N. F. Chen, K. Oshihara, W. Ueda, *Catal. Today*, **64** (2001), 121.
2) S. T. Oyama, A. M. Middlebrook, G. A. Somorjai, *J. Phys. Chem.*, **94** (1990), 5029.
3) M. P. Casaletto, L. Lisi, G. Mattogno, P. Patrono, G. Ruoppolo, G. Russo, *Appl. Catal. A*, **226** (2002), 41.
4) F. Klose, M. Joshi, C. Hamel, A. Seidel-Morgenstern, *Appl. Catal. A: General*, **260** (2004) 101.

*E-mail: wolff@mpi-magdeburg.mpg.de