



The influence of chemical transport via vapour phase on the properties of chloride and caesium doped V-Fe mixed oxide catalysts in the oxidation of butadiene to furan

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Abstract

Chloride and caesium doped V-Fe mixed oxides prepared by different methods and calcined under vapour-phase transport-restricted conditions showed a high initial furan yield of up to 40 mol-% in the oxidation of butadiene. However, after only a few hours on stream a significant loss of activity and selectivity was observed. The reason for this undesirable property was investigated using different bulk and surface-sensitive characterisation methods such as x-ray diffraction, x-ray photoelectron spectroscopy, transmission electron microscopy and chemical methods. The data obtained for the structure, morphology, and composition of the fresh and used catalysts were correlated with their activity and selectivity properties. The presence of chloride ions was found to be surprisingly necessary for the origin of furan selectivity even up to 50 %, which was however stable only for a short period of time. Chemical transport via chlorides or bromides was observed to be essential for the formation as well as the maintenance of the activity and selectivity properties of the system. The results obtained are interpreted with an assumption that the formation of volatile halides is necessary to form disperse VO_x species, which act as active and selective centres for the present reaction. Models for the formation and deactivation of these centres are discussed in this work. In addition, the possible roles of caesium and iron oxides in the catalytic system are also described and disputed.

Keywords: V-Fe mixed oxide catalysts, Butadiene oxidation, Furan, Deactivation, Chemical transport, Vapour phase, Catalyst constituents' role

Introduction

The catalytic gas phase oxidation of butadiene to furan in one step is still an unsolved problem in the selective oxidation of hydrocarbons. The reaction is of industrial interest based on the fact that furan is a valuable intermediate, which could easily be hydrogenated to well-demanded tetrahydrofuran. Due to the low selectivity of the known catalysts and/or their insufficient long term stability, this oxidation reaction is not applied in the chemical industry until now. In this study, caesium doped V-Fe mixed oxides were used as promising catalysts for the oxidation of butadiene because of their potentiality to catalyse the selective oxidation of polyaromatic hydrocarbons like fluorene in the gas phase [1]. Yields of furan from 25 to 40 mol-% at a

conversion rate of butadiene between 80 and 90 % were reached on these oxides [2]. To the best of our knowledge, this is the highest furan yield reported so far in the open literature [2, 3]. However, an application of these mixed oxides is limited so far due to their short time-stable catalytic properties. After a few hours time on stream, both the activity and the selectivity of these catalysts are reported to be decreased significantly [2]. Another disadvantage of these catalysts is the problem of insufficiently reproducible catalyst preparations, which led to varying furan yields.

Caesium doped V-Fe mixed oxides catalysts have become the subject of some studies of the selective oxidation of polyaromatics [4-6]. For these reactions, a certain caesium content of the catalysts was observed to be essential for obtaining high selectivity of desired products. Chloride ions, which were present in the catalyst precursors were not de-

ected in the working catalyst. In contrast, in the title reaction in addition to caesium the presence of chloride ions proved to be a necessary prerequisite for good catalytic performance [2].

The role of halides as components of catalysts in selective oxidation reactions has been the subject of only few investigations up to now. In some cases, chloro compounds were dosed along with the reactants to modify the catalyst surface with chloride ions [7, 8]. In other cases, halides were added to the solid catalyst during its preparation [9]. Both, the modification of the catalyst properties by chloride and a participation of atomic chlorine in the gas phase reaction were discussed as reasons for the observed increase of catalytic performance. Thus, in studies by Sugiyama et al. [7, 8] chlorination of magnesia or praseodymium oxide surfaces at temperatures between 723 K and 900 K with tetrachloromethane resulted in an enhancement of the selectivity of ethane in the oxidative dehydrogenation of ethane. At these temperatures, a heterogeneously catalysed reaction on the chlorinated oxide surface was assumed to play a decisive role and chloride ions are thought to influence the active centres. In an other study on the oxidative dimerisation of methane over chloride doped calcium oxide [9], it was proposed that ethane and ethene are formed by the action of the reactant oxygen at the catalyst surface under the participation of atomic chlorine in the gas phase.

Furthermore, chloride and caesium are well-known promoters for alumina-supported silver epoxidation catalysts [10-13]. Extensive studies of the heat of adsorption of oxygen and butadiene on unpromoted and chloride and caesium promoted $\text{Ag}/\text{Al}_2\text{O}_3$ showed an influence of both promoters on the interaction between the reactants and the surface of the silver particles [12, 13]. Different models were proposed to explain the role of the promoters such as: i) modification of the properties of the surface by electronic interactions between the promoters and the surface, ii) influence on the surface structure; iii) formation of Cs-O or Cs-Ag-O compounds and iv) blocking of unselective sites by chloride formation.

An important application of chlorides in solid state chemistry is their use as carriers in chemical transport via vapour phase. This procedure is applied for the synthesis of compounds, the growth of single crystals or the purification of a compound [14, 15]. The effect of physical transport phenomena like diffusion during catalytic processes is well investigated, especially for industrial processes. However, little is known about the influence of chemical transport on the performance of catalysts. The rearrangement of surfaces under the ideal conditions of model catalytic reactions has been one of the main goals of surface science for a long time. Nevertheless, better understanding of such processes under real working conditions is still at the beginning stages until now.

In this communication, we describe how chemical transport can lead to rearrangement processes in caesium and chloride doped V-Fe mixed oxides catalysts during their use and thus controls the catalytic performance of such systems. The objective was also to investigate the role of the

transport processes with an intention to find out whether stable catalytic properties may exist in these mixed oxide catalysts. A detailed analysis of the structure and composition of bulk and surface of the solids should help to get a deeper insight into the dynamic changes of the catalyst during the calcination and the reaction.

2. Experimental

The catalyst samples were prepared by two different methods such as i) from aqueous solution (method 1) and ii) by a tribomechanical procedure (method 2) followed by calcination of the precursors obtained. The aqueous preparation of the precursors obtained. Method 1 was carried out by addition of a concentrated aqueous solution of FeCl_3 to a hot (343 K) aqueous solution of NH_4VO_3 and NH_4HCO_3 (for the neutralisation of the formed HCl). For the aging of the formed amorphous brown precipitate, the suspension was stirred for 4h at 343 K. After the addition of the solution of the dopant (either CsCl or Cs_2SO_4), a third of the solvent was separated from the precursor by decantation and, thereafter, the remaining solution was evaporated to dryness in a rotary evaporator. The formed solid was dried at 403 K for 4h. Thus, the atomic ratio of Cl:V or Fe was usually adjusted to two.

For the sake of the simplicity of the method and saving of time, tribomechanical milling (method 2) was chosen to prepare a broad variety of compositions of the catalysts. In this method, a planetary mill (Pulverisette 6, material: agate, Fritsch GmbH, Germany) was used for the comminution of the materials Fe_2O_3 , V_2O_5 , NH_4Cl , and CsCl or Cs_2SO_4 (60 min duration of the milling at rotating velocity rotational frequency of 8.8 s^{-1}).

The standard composition of the precursors applied was V:Fe:Cs:Cl = 1:1:0.06:2 (atomic ratio). In a series of samples, caesium was substituted by lithium, sodium, potassium, and rubidium at constant atomic ratio of the catalyst constituents. Additionally, model catalysts were prepared by doping either vanadium or iron oxides with caesium and ammonium chloride resulting in a composition of the precursors of V:Cs:Cl = 1:0.06:2 and Fe:Cs:Cl = 1:0.06:2, respectively (preparation method 2). The elemental composition of the precursors was used for the designation of the catalyst samples despite the loss of a great part of chlorine during the calcination. No marked changes of the ratios of the other compounds were observed by analyses of the composition of the obtained solids pointing to comparatively small amounts of lost volatile transition metal compounds. The loss of these compounds were within the error margins of the analytical methods used (see below).

After calcination, the obtained fresh standard catalyst 1 from method 1 was designated as "standard sample 1 $\text{V}_1\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ ", whereas the fresh standard catalyst 2 from method 2 was labelled as "standard catalyst sample 2 $\text{V}_1\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ ". The Fe- and V-free model catalysts were designated as $\text{V}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ and $\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ samples, respectively.

To get an active and selective catalyst, the calcination of the precursor materials must be carried out under special-restricted vapour -phase transport-restrictions in a container (crucible with a volume of 20 ml, 20 g loading of solids) closed with a cap. The samples were calcined at 623 K for 6 to 8 h in air. A small leak (diameter: 3mm) in the cap allowed only an inhibited sublimation of the NH_4Cl and of the volatile coloured chlorine containing iron and vanadium compounds (formed by reactions of the oxidic V and Fe compounds in the precursor material with the present NH_4Cl) into the empty space of the surrounding reaction tube which was purged with nitrogen. In the case of the standard samples 2, after the described calcination procedure an additional time of up to 3 h for a deactivation of the samples under reaction conditions proved to be necessary before they attained comparable catalytic properties as the standard samples 1 (see below).

After calcination, the obtained material was homogenised in the planetary mill mentioned above by short milling (900 s) at a low rotational velocity frequency (5.5 s^{-1}), pressed to tablets, crushed, and then sieved to desired particle size. 1 - 4.5 ml of a fraction of granules with a diameter from 0.5 mm to 0.8 mm were used for catalytic and model experiments. The catalytic experiments were performed in a fixed bed tubular glass reactor (I.D.: 11 mm) mostly at a standard residence time of $1.3 \cdot 10^4 \text{ kg}^*/\text{s}/\text{m}^3$ with a feed consisting of 1.1 mol-% butadiene, 3.5 mol-% oxygen, and 95.4 mol-% nitrogen at a reaction temperature of 623 K. The product stream was analysed by on line-GC and on -dispersive infrared photometry. The details of the experimental set-up are described elsewhere [2, 3].

The X-ray photoelectron spectroscopy (XPS) measurements were carried out at a VG ESCALAB 220 iXL with a monochromated $\text{AlK}\alpha$ radiation source ($E = 1486.6 \text{ eV}$). Charging of the samples was compensated with a flood gun. The binding energies were referred to the $\text{C}1\text{s}$ peak at 284.8 eV. To get information about the composition of the near-surface region survey spectra were obtained using a pass energy of 150 eV. For quantitative analysis and determination of the valence states a pass energy of 25 eV were used. In this mode the determined electron binding energy is within a margin of error of $\pm 0.2 \text{ eV}$. The peak areas of these spectra were determined after the subtraction of a Shirley background. The peaks were fitted with Gauss-Lorentz curves. The obtained peak areas were divided by the element-specific Scofield-factor and the analyser-specific transmission function to get the composition in the near-surface region.

The X-ray powder diffraction measurements were carried out on a STOE STADI P automated transmission diffractometer with $\text{CuK}\alpha 1$ radiation. The X-ray powder diffraction pattern was scanned in the 2θ range $5 - 70^\circ$ (step width 0.5° , 100 s per step) and was recorded with a STOE position sensitive detector. The samples were prepared to flat plates. The phase analysis was carried out with the Visual Xpow software package, using the powder diffraction file (PDF) of the International Centre of Diffraction Data.

For the determination of the morphology a CM20 (Philips) transmission electron microscope (TEM) with an energy dispersive X-ray detector (EDAX, PV9900) at 200 kV was used. The samples were mounted without pretreatment on Lacey-carbon coated copper grids. Selected area electron diffraction was carried out with a camera length of 700 mm.

The Fe and V amounts of the catalysts were determined by the inductively coupled plasma emission spectrometer (ICP-OES) iOptima 300 XL (Perkin-Elmer) after dissolution of the samples in nitric acid. Due to its weak signal the Cs amount could not be detected by ICP. Therefore, X-ray fluorescence analysis (Oxford instruments) was used for the estimation of the Cs-amount of selected samples. The chloride content was determined by potentiometric titration. The determination of the specific surface areas was carried out by N_2 adsorption at 77 K according to the BET method.

3. Results

Firstly, the results of the investigations of bulk and surface of the solids before and after calcination are described. Thereafter, a short summary of the measurements of the activity and the selectivity of the catalysts during the oxidation of butadiene is presented. In the last part of this chapter, the influence of this reaction on the composition of the catalysts is shown.

To elucidate the reasons of the observed behaviour of activity and selectivity, the above described off line-analyses by XRD, TEM, ICP-OES, and XPS were carried out because the formation of certain amounts of chloride-containing corrosive deposits during the decisive time interval of the reaction made it difficult to use *in situ*-studies. Therefore, most samples were investigated after 10 - 20 h on stream when no more volatile substances were formed. In the case of the different alkali metal ion (AM)-doped $\text{V}_1\text{Fe}_1\text{AM}_{0.06}\text{Cl}_2\text{O}_x$ samples, the reaction was intentionally stopped at a stage where maximum selectivity was observed and then the composition of the surfaces in these samples was determined by XPS.

3.1. The properties of bulks and surfaces of precursors and catalyst samples before and after calcination

As expected, crystalline phases of NH_4Cl , V_2O_5 , and Fe_2O_3 were found before calcination in the tribomechanically prepared precursors as evidenced by the X-ray diffractograms (fig. 1). The investigation of the morphology of the powdered mixtures by TEM combined with EDX revealed clearly two different kinds of particles such as free vanadia and free iron oxide particles. However, particles containing both these oxides could not be observed (fig. 2). The iron oxide particles were found to be significantly larger than the

due to the lower crystallinity of the samples (fig. 1). In addition to the FeVO_4 main phase, FeCsCl_4 was found as a crys

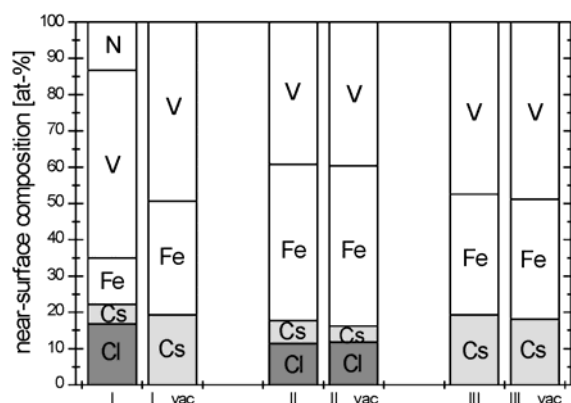


Figure 5: XPS investigation of the influence of a storage of 70 h in vacuum ($p= 2 \cdot 10^{-7}$ Pa) on the composition of the near-surface region of the standard sample 2 $\text{Fe}_1\text{V}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ as precursor (I), fresh (II), and used catalyst (III).

talline phase. For the FeVO_4 phase, a texture was observed indicating a preferred position of the crystallites for this layer-like structure. As a result of this preferred orientation the intensities in the diffractogram are modified.

TEM measurements of the fresh catalysts revealed the formation of polycrystalline particles with a size of a few hundred nanometers as main component (fig. 2). In these particles, the Fe/V ratio was determined by EDX as one. Electron diffraction patterns showed a ring structure indicating a polycrystallinity of the particles and were indexed as FeVO_4 (fig. 2).

The near-surface composition of the solids changed significantly during the calcination. The same Fe/V ratio of one as determined for the bulk was found. As expected no more nitrogen could be detected in the XPS spectra. A slight decrease of the amount of chlorine could be observed. In contrast, the amount of caesium ions did not change significantly (fig. 4). Further, an influence of the calcination on the electronic states especially of iron and caesium was observed. In both cases, the electron binding energies increased (before calcination $\text{Fe}2p_{3/2}$: 710.5 eV, $\text{Cs}3d_{3/2}$: 736.4 eV; after calcination: $\text{Fe}2p_{3/2}$: 711.1 eV, $\text{Cs}3d_{3/2}$: 738.1 eV). These results are hints for changes in the coordination sphere of both elements before and after the calcination.

In contrast to the precursors, the calcined samples proved to be stable in vacuum. Obviously, the volatile chloride of the precursors was transformed into a stable compound by the calcination (fig. 5).

More information about the bonding of the chlorine in the calcined samples was obtained by XPS measurements of iron- or vanadium-free systems (fig. 6). Solids prepared without adding Fe_2O_3 have a near-surface region consisting of vanadia with traces of caesium and chloride. Only negligible quantities of V-Cl or V-Cs-Cl compounds were found in this region after the calcination at 623 K under transport-

restricted conditions. In contrast, in the vanadia-free sample greater amounts of chlorine and caesium could be detected.

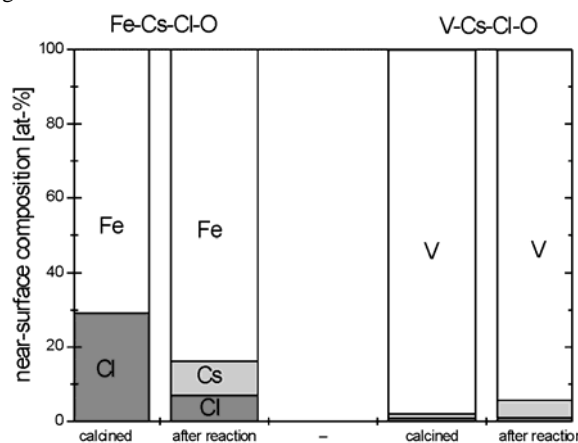


Figure 6: Elemental composition of the near-surface region of the fresh and used Cs and Cl doped iron oxide $\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ (V-free) and vanadium oxide $\text{V}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ (Fe-free) samples.

3.2. The behaviour of activity and selectivity of the catalysts during the butadiene oxidation

A characteristic property and disadvantage of caesium and chloride doped V-Fe mixed oxides is their loss of catalytic performance during time on stream. A typical dependence of activity and selectivity of a sample prepared by tribomechanical treatment and subsequent calcination for

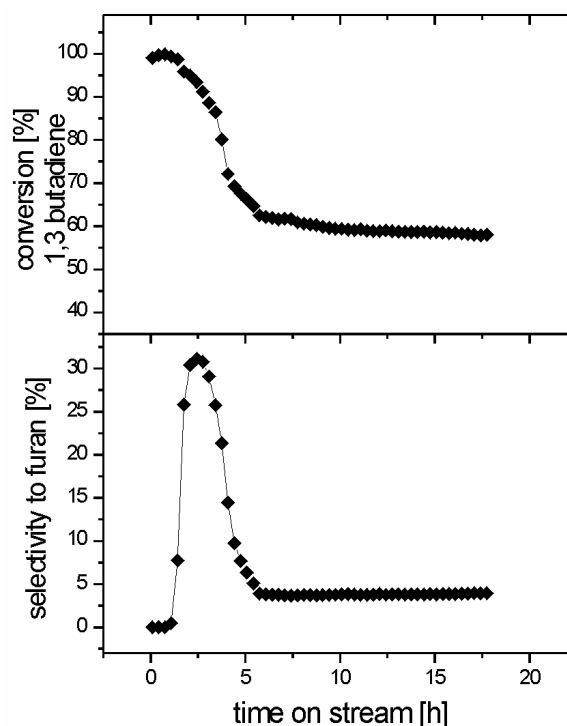


Figure 7: Activity and selectivity of a tribomechanically prepared standard sample 2 $\text{Fe}_1\text{V}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ in dependence of time on stream. Feed: butadiene 1.1 mol-%, O_2 3.5 mol-%, N_2 95.4 mol-%; residence time: $1.3 \cdot 10^4$ $\text{kg}^*\text{s}/\text{m}^3$, linear

velocity of the fed gases: 6.2 mm/s, NPT, reaction temperature: 623 K.

6 h at 623 K (standard sample 2) on the duration of the reaction at $T = 623$ K is shown in fig. 7 (standard modified residence time: $1.3 \cdot 10^4 \text{ kg}\cdot\text{s}/\text{m}^3$, linear velocity of the feed: 6.2 mm/s, NPT, feed: butadiene 1.1 mol-%, O_2 3.5 mol-%, N_2 95.4 mol-%). The conversion of butadiene was 100% at the beginning of the reaction and decreased to 57 % after 17 h under the chosen reaction conditions. In contrast, the selectivity of furan was zero at the start of the reaction but enhanced to a maximum of 35 % at about 95 % conversion of butadiene after 2.5 h on stream. With further decreasing activity, the furan selectivity also dropped and became stable at around 4 %. Separate experiments showed that an increase of the reaction temperature to 643 K led to an acceleration of all described processes. The selectivity maximum was reached one hour faster than at 623 K, and the deactivation of the sample was also accelerated. The maximum furan selectivity was ca. 3% higher than at 623 K. At lower temperatures than 623 K smaller selectivities to furan, e.g., 20 % at 593 K were observed. As expected, both the activity and selectivity decreased at a slower rate.

In contrast to this behaviour, halide-free samples exhibited negligible furan selectivities at the beginning of the reaction, which increased further to 4% with time.

Beside the desired product furan, small amounts of crotonaldehyde, butyraldehyde, acroleine, methyl vinyl ketone, maleic anhydride, acrylic and acetic acid were observed as well as the products of total oxidation.

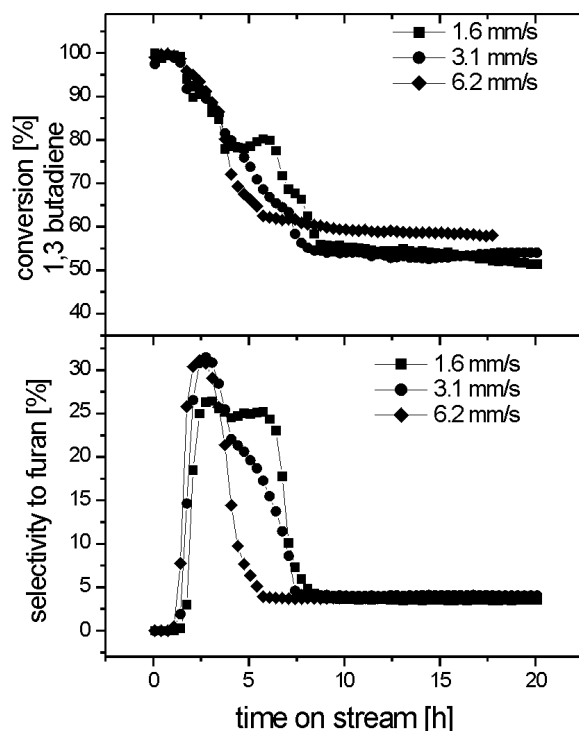


Figure 8: Influence of the linear velocity of the feed on the activity and furan selectivity of the standard sample 2 $\text{Fe}_1\text{V}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ in dependence of time on stream. Feed: butadiene 1.1 mol-%, O_2 3.5 mol-%, N_2 95.4 mol-%; reac-

tion temperature: 623 K, residence time: $1.02 \cdot 10^4 \text{ kg}\cdot\text{s}/\text{m}^3 = \text{const.}$

In further studies, the linear velocities of the fed gases were varied at constant modified residence times and constant composition of the feed. Fig. 8 shows that an increase of the linear velocity led to changes in both selectivity and activity. With increasing linear velocity, higher furan selectivities were reached after shorter times on stream and the catalyst samples deactivated and “deselected” faster, whereas the stationary furan selectivities reached after 10 h proved to be nearly the same in all experiments. Surprisingly, at lower linear velocities than 6.2 mm/s, a formation of shoulders was observed as shown in the graphs. At 3.1 mm/s, weak shoulders reflect reduced velocities of decrease of both activity and selectivity. At 1.6 mm/s, nearly constant activity and furan selectivity were measured from the third until the sixth hour on stream before a renewed and accelerated drop of activity and selectivity took place.

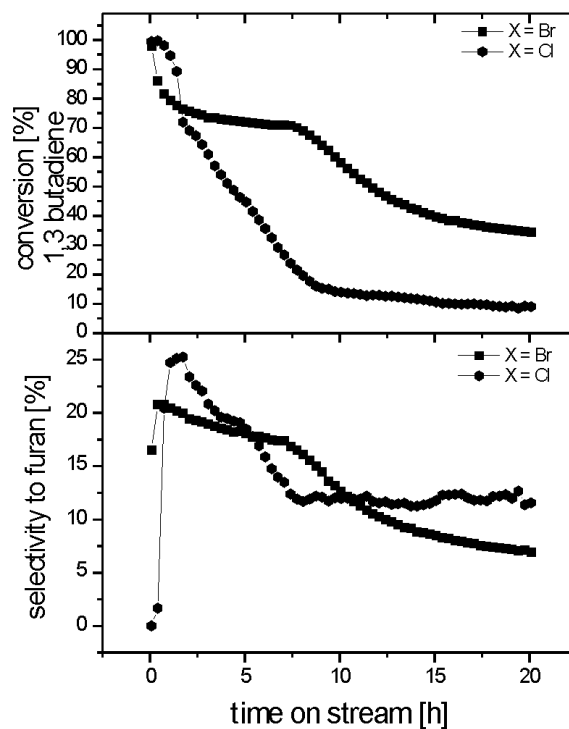


Figure 9: Influence of the nature of the halide ions (X) chloride and bromide on the catalytic performance of the standard catalyst sample 1 $\text{Fe}_1\text{V}_1\text{Cs}_{0.06}\text{X}_2\text{O}_x$. Feed: butadiene 1.1 mol-%, O_2 3.5 mol-%, N_2 95.4 mol-%, linear velocity of the fed gases: 6.2 mm/s, NPT, reaction temperature: 623 K.

A substitution of chloride by bromide anions led to a similar catalytic behaviour of the $\text{Fe}_1\text{V}_1\text{Cs}_{0.06}\text{Br}_2\text{O}_x$ sample. Again, a maximum of the furan selectivity and a deactivation were observed. As shown in fig. 9, the maximum furan selectivity of the bromide sample decreased only by a few per cent in comparison to the chloride sample and the deactivation process was delayed. In this case, the precursors were prepared from aqueous solution according to the method 1. As depicted in fig. 9, both standard samples 1 did not need such a pronounced deactivation period like the

standard samples 2 usually needed. After the calcination procedure, their selectivity was comparable to the selectivity of the samples 2 after about 3 h on stream when the furan selectivity reached its maximum level.

The iron-free Cs and Cl doped vanadia samples deactivated after 20h on stream (fig. 10). This “deactivated” catalyst showed a small furan selectivity of less than 4 %. A similar catalytic behaviour was observed for the halide free $V_1Fe_1Cs_{0.06}O_x$ sample (not depicted) in contrast to the behaviour of the chloride-containing sample “Fe-V-Cs-Cl-O” (Fig.10). The vanadium-free Cs and Cl doped iron oxide deactivated within 3 h. After 45 min on stream, this catalyst exhibited a maximum furan selectivity of 9 % at a butadiene conversion of about 75 %, which dropped quickly to a constant level of 4%.

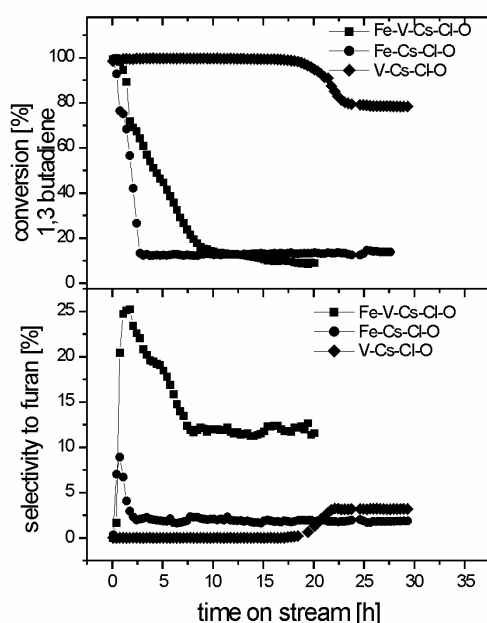


Fig. 10: Activity and furan selectivity of standard sample 2 $Fe_1V_1Cs_{0.06}Cl_2O_x$, $Fe_1Cs_{0.06}Cl_2O_x$ (V-free), and $V_1Cs_{0.06}Cl_2O_x$ (Fe-free) mixed oxides samples in dependence of time on stream. Feed: butadiene 1.1 mol-%, O_2 3.5 mol-%, N_2 95.4 mol-%, linear velocity of the fed gases: 6.2 mm/s, NPT, reaction temperature: 623 K.

Fig. 11 depicts the catalytic properties of the $Fe_1V_1AM_{0.06}Cl_2O_x$ catalysts with different alkali metal dopants. Light alkali metals like lithium and sodium led to catalyst samples with a different activity and selectivity behaviour compared to that of the caesium doped reference system. A comparable catalytic performance with that of the iron-free sample was found for the lithium and sodium doped catalyst samples while the potassium and rubidium doped samples showed similar properties as the caesium doped one.

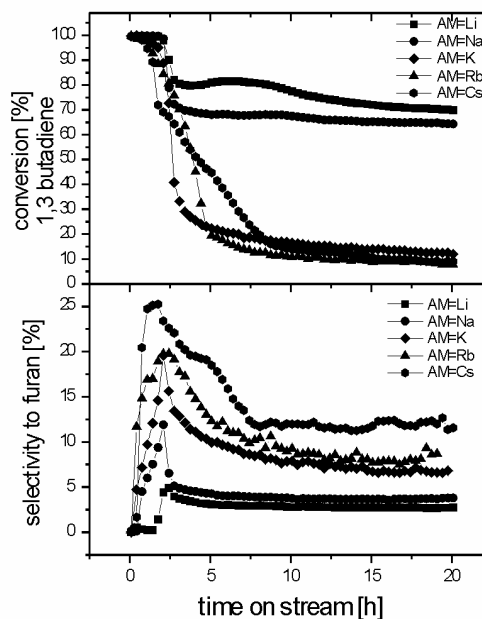


Fig. 11: Influence of the nature of alkali metal ion (AM) dopants on the activity and selectivity of standard sample 2 $Fe_1V_1AM_{0.06}Cl_2O_x$ in dependence of time on stream. Fed gas: butadiene 1.1 mol-%, O_2 3.5 mol-%, N_2 95.4 mol-%, linear velocity of the fed gases: 6.2 mm/s, NPT, reaction temperature: 623 K.

3.3. The influence of the reaction conditions on the bulk and surface compositions of the catalysts

The characterisation results illustrate that the reaction conditions strongly influence the formation and concentration of several components in the bulk and at the surface of the samples. So, the diffraction patterns of the “stable” samples reveal that the reaction led to an improvement of the crystallinity. Triclinic $FeVO_4$ and Fe_2O_3 were found as main phases (fig. 1). A strong loss of chloride ions was detected by potentiometric titration. The study of the morphology of the used catalysts by TEM showed that the particle size of $FeVO_4$ was larger than that in the fresh samples. A broad range of the Fe/V ratios from 1:1 to 1:3 was detected with EDX in particles of the used samples in contrast to the fresh samples, which exhibit a uniform Fe/V ratio of 1:1. Electron diffraction patterns confirm the presence of $FeVO_4$ in larger and of $Fe_2V_4O_{13}$ in smaller particles (fig.12). In contrast, the calcined samples show ring patterns due to polycrystallinity. A dramatic increase of crystal size of the Fe_2O_3 particles was also observed to occur during the course of reaction. These very large particles were found in TEM only after crushing the samples in an agate mortar to reduce the particles size and, thus, allow the debris to stick on the grid.

The changes in the composition of the near-surface region during the reaction were also significant (fig. 4). The chloride ions vanished, while the amount of caesium ions increased. Likewise, a slight loss of the amount of iron spe

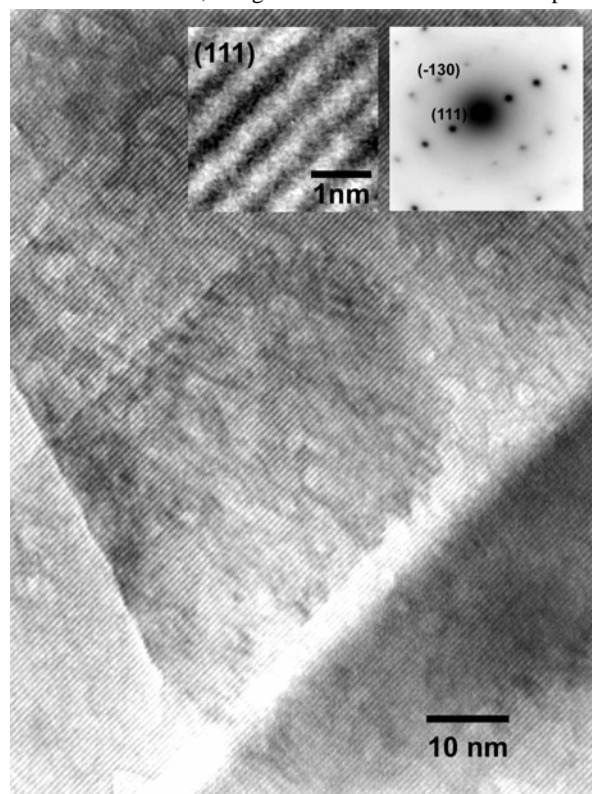


Fig. 12: TEM image of a $\text{Fe}_2\text{V}_4\text{O}_{13}$ single crystal. Left inset: lattice plane, right inset: diffraction pattern.

cies was observed. The determination of the surface compositions of the catalyst samples before and after reaction and at the moment of the maximum furan selectivity gave no hints for steplike changes, so that a continuous development of the composition of the surface region during the reaction can be concluded (fig. 4). The valence states of the catalyst components also did not markedly alter. This is possibly due to the contact of the samples with oxygen during transport to the spectrometer chamber leading to an oxidation of the vanadium and iron ions in the surface region. This could mask the probable decrease of their oxidation numbers which should be lowered by the influence of the reaction gases. In the case of the chloride ions, an alteration of the binding energies of the Cl 2p electrons from 198.8 eV to 198.3 eV was observed, which can be explained by a variation of the surroundings of these ions. It should be noted that these chloride compounds are stable under ultrahigh vacuum conditions. No coke deposition on the catalysts was found during the reaction.

Deposition of different solids was observed during the course of reaction on the walls of the quartz reaction tube. Only NH_4Cl was determined in the X-ray diffraction patterns of these deposits. However, XPS measurements of the deposits showed the presence of iron, vanadium, and oxygen

as components in addition to nitrogen and chlorine. The NH_4Cl content was surprising at first sight because no more nitrogen was detected by XPS investigation of the calcined samples. However, chemical bulk analysis showed the existence of certain amounts of nitrogen (probably as ammonium ions), which proved to be not stable enough at the surface in the UHV for a few minutes. The Fe/V ratio measured by ICP was equal to two, whereas this ratio as detected with XPS for the near-surface region of these deposits was equal to ten. Therefore, it must be concluded that not only NH_4Cl sublimates during the reaction, but also iron- and vanadium-containing compounds. This comparatively weak sublimation during the reaction, however, has only a small influence on the Fe/V bulk ratio of the catalyst samples.

The iron-free fresh Cs and Cl doped vanadia model catalyst showed only small changes in the composition of the near-surface region caused by the reaction. The amount of caesium ions increased, whereas chloride anions were found by XPS only in negligible quantities before and after the reaction. In contrast, the composition of the surface of the vanadium-free fresh Cs and Cl doped iron oxide sample changed significantly during the reaction. Similar to all other investigated samples, caesium enriched during the reaction, whereas chloride anions disappeared from the near-surface region.

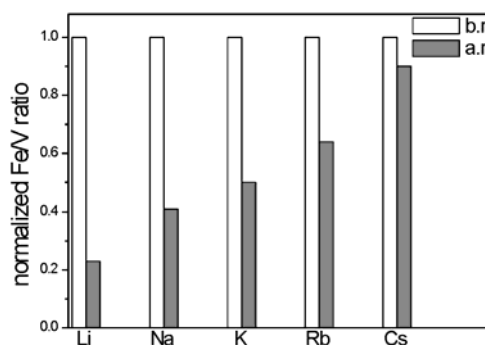


Fig. 13: Change of the Fe/V-ratio of various alkali doped $\text{Fe}_1\text{V}_1\text{AM}_{0.06}\text{Cl}_2\text{O}_x$ before (b.r.) and after reaction (a.r.), Fe/V-ratio normalized for each freshly calcined sample.

It is evident from fig. 13 that the nature of the alkali metal dopant has a considerable influence on the stability of the iron content in the surface region. In the case of the light alkali metals a significant decrease of the Fe/V ratios was observed. The heavier alkali metals, especially caesium, were found to have a stabilising effect: for caesium only a weak change of the Fe/V ratio was found in the used sample.

4. Discussion

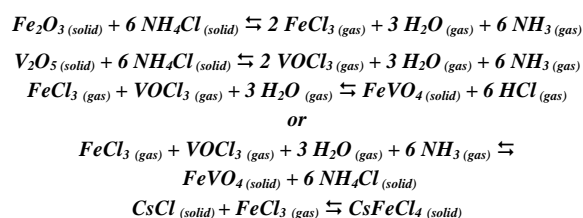
The results allow us to develop the following model describing the role of components of the catalyst during the transport-restricted calcination and the oxidation of butadi-

ene to furan. This provides us an opportunity to explain the activation and deactivation processes on the basis of structure-reactivity relationships.

4.1. Influence of calcination

As mentioned above during calcination the new phases FeVO_4 and CsFeCl_4 are formed. At the same time, in the near-surface region nitrogen containing components disappear and the amount of iron ions increases. A part of chloride containing compounds sublimates during calcination. However, for the larger part of chlorine, it was found that the nature of the chloride containing compounds alters during the calcination from chloride compounds instable under ultrahigh vacuum conditions (probably NH_4Cl) to chloride compounds stable under these conditions.

It is well known that chlorides can be used as carriers for chemical transport [14,15]. Therefore, the following simplified model reactions are proposed between NH_4Cl and other components of the system during the calcination at 623 K resulting in the formation of new compounds:



No indication of a reaction between caesium chloride and vanadium containing compounds was observed leading to Cs-V-Cl-O components. Even for the Cs and Cl doped vanadia sample without iron a nearly pure vanadia surface was found with XPS. A condensation of FeCl_3 on the surface of the solids in the nearly sealed crucible during cooling after the calcination procedure cannot be excluded, whereas the volatility of VOCl_3 seems to be too high for depositing of a significant amount of this compound on the solids. Probably a part of the formed VOCl_3 reacts with OH groups on the surface of the solids to HV_xO_y particles, which are too small or too little crystalline to be detectable with X-ray diffraction. An analogous process for FeCl_3 leading to Fe_xO_y containing particles seems also to be possible.

After calcination under transport-non-restricted conditions a complete loss of chloride ions was observed in the prepared fresh samples as reported in the literature [4-6]. Obviously, the formed volatile chloride containing compounds were transported completely away from the samples. This was also proven by the finding, that deposits formed during the reaction on the reactor walls contained chloride ions besides nitrogen, iron, and vanadium.

For the further discussion it must be stressed again that a defined transport-restricted calcination is necessary to get a selective catalyst. However, the samples obtained by the tribomechanical method proved to be frequently very

active at the beginning of the butadiene oxidation and therefore showed no selectivity for furan for a certain time on stream during the deactivation period.

4.2. The active and selective catalyst

In the following chapter, processes which are thought to lead to the formation and destruction of the active sites will be discussed. Fig. 4 illustrates that for the formation of the active and selective catalyst the presence of all four components iron, vanadium, caesium, and chlorine is essential. Whereas the oxides of vanadium as well as iron were clearly identified as active species in a variety of oxidation catalysts [4], it is necessary to discuss in detail the role of caesium and chloride ions for a deeper understanding of the mode of action of the investigated $\text{Fe}_1\text{V}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ catalyst.

The role of caesium

After calcination, the standard sample 2 showed similar catalytic properties as the caesium and chloride doped fresh iron-free vanadia catalyst at the beginning of the reaction: a high activity, but no selectivity to furan. In the case of iron-free vanadia catalyst a low furan selectivity of a few per cent developed after a deactivation period accompanied by a marked surface enrichment of caesium. A similar enrichment of caesium was found for the $\text{V}_1\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ catalyst. Therefore, the question arises to what extent the enrichment of caesium is responsible for the increase of selectivity and decrease of activity.

At first sight, simple correlations seem to explain the observed findings. It is very likely that the enrichment of caesium reduces the surface acidity and increases the surface basicity. This effect should support the desorption of oxygenate(s) having basic properties such as the desired furan and prevent the formation of maleic anhydride the undesired product of consecutive oxidation. On the other hand, the basification of the surface should inhibit the adsorption of the basic butadiene molecule, thus reducing the catalytic activity.

Another possible effect of caesium which was discussed by Brückner et al. for the aforementioned Cs doped Fe-V mixed oxide catalyst in the selective oxidation of polyaromatics [4] seems to be not valid for the butadiene oxidation. In this catalytic system caesium is thought to stabilize oxygen defects that are proposed as active sites in the present selective oxidation. However, in contrast to the catalytic system presented in this article, the catalysts for the oxidation of polyaromatics were chloride-free and this difference is decisive for the following discussion on the role of chloride in the $\text{V}_1\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ system.

The role of chloride

Chloride ions are assumed to play different roles in catalysed oxidation reactions such as: (i) incorporation in the surface of the catalyst, thus modifying the properties of the surface or as component of the catalytic centres as described in the case of the oxidative dehydrogenation of ethane over chloride-doped magnesia or praseodymium oxide surfaces [7, 8]; (ii) oxidation to chlorine and then acting as reactant near the surface as discussed in case of the oxidative dimerisation of methane [9]; (iii) added together with an oxygen species to one of the double bonds of butadiene resulting in a structure similar to that of chlorohydrin, which could form the 1,2-epoxide able to isomerise to dihydrofuran; (iv) as carrier for components necessary for the formation of the active and selective sites by chemical transport without playing an active role as a partner in the reaction.

Among all those effects, role (iv) is preferred by us due to the necessity of the presence of halide ions in the preparation procedure and in the catalysts formed and, especially, by the results of the change-of-linear-velocity experiments. Due to the finding that a substitution of NH_4Cl by NH_4Br in the preparation procedure did not change markedly the catalytic properties a direct participation of the halides in the catalytic system as components of the active sites or as reactants is unlikely. The hypothesis on the role of the halides as carriers is further discussed in the following section.

4.3. The development of the selectivity of the catalyst

Two types of transport processes via halides should be possible to form the active and selective sites of $\text{V}_1\text{Fe}_1\text{Cs}_{0.06}\text{Cl}_2\text{O}_x$ catalysts:

- A) transport of halide-containing compounds, which could be converted into catalytically active components or
- B) get rid of unwanted compounds to generate new active and selective sites on the remaining surface.

Under transport-restricted conditions, the transport of the catalytically active compounds during calcination may occur by diffusion or convection. These processes are thought to lead to the formation of centres which are too active and, therefore, act as non selective sites during the initial stage of reaction. According to the "principle of site isolation" [16] the reactive lattice oxygen containing centres are assumed to be not isolated enough. A better isolation of these centres from each other is postulated to be the reason for the increase in selectivity at the beginning of the reaction. This process of isolation could occur by chemical conversion or by gas phase transport, which is assumed to be necessary for a repeated formation of the active sites. Indeed, a prolongation of the calcination procedure can lead to the same result as performing the catalytic reaction. As revealed, in the changing-of-the-linear-velocity experiments the residence times for which the volatile active components

can react with other parts of the catalyst layer determine their concentration and location on the surface of the catalyst particles. Consequently, the renewed catalytic properties of the solid are determined by the residence times of the flowing gases.

Alternatively, components at the catalyst's surface, which hinder the formation of active sites could also be transported via vapour phase from the sample away.

Both, this process and the transport reaction of catalytically active components can explain the observed formation of vanadium-rich particles with V/Fe-ratios from 1 to 3 from polycrystalline FeVO_4 particles: iron ions can be taken away as volatile chlorides or VO_x can be deposited on FeVO_4 crystals. However, the described increase of the linear velocity of the feed led only to a little acceleration of the increase of selectivity of the samples in the deactivation period especially if the furan selectivities observed at the linear velocities 3.1 mm/s and 6.2 mm/s are compared. This can not be satisfyingly explained by the second assumption whereas the temporary regeneration of catalytic performance at the lower linear velocity of 1.6 mm/s speaks clearly in favour of the first assumption.

The results of the analysis of the deposits allow a further insight into the processes during the reaction and support the working hypothesis. Besides NH_4Cl as main component, iron and vanadium were found in the deposit by ICP. A Fe/V-ratio of two was found and no large V_2O_5 particles could be detected with TEM or XRD. This finding is thought to be caused by the higher volatility of formed VOCl_x compared to the less volatile FeCl_x . This highly volatile VOCl_x needs a certain time to react with hydroxyl groups at the catalyst surface and/or water formed by the reaction. Therefore, too high linear velocities lead to a fast carrying away of vanadium while lower velocities provide time enough for the formation of deposits of VO_x in the direction to the end of the catalyst layer. This reiterative formation of active sites by chemical vapour deposition ends with the full consumption of chloride (or bromide) ions as the necessary carriers.

4.4. The „deselection“ of the catalysts

As described, the catalyst loses its function in the furan formation with increasing time on stream. The possible reasons could be due to the formation of stable unselective VO_x structures or new compounds from the assumed disperse VO_x particles. One of these new compounds might be the detected $\text{Fe}_2\text{V}_4\text{O}_{13}$. In addition, the enrichment of caesium in the near-surface layers must be taken into consideration. It could result in the formation of non selective caesium containing compounds such as, e.g., CsVO_3 . Also the formation of Cs_2CO_3 could be one of the driving forces of the caesium enrichment at the surface. On the other hand, the XPS results reveal a stabilisation of the Fe/V-ratio in the near-surface region by caesium occurring during the reaction, which was not observed in case of the light alkali metals as dopants. i.e., caesium seems to hinder the formation of iron-poor vanadia-like active sites with bulky structure,

which are not selective as observed for the lithium and sodium doped Fe-V mixed oxide catalysts. This selectivity stabilising effect of caesium can be explained by the formation of Cs-Fe-Cl compounds, which are more stable than pure Fe-Cl compounds.

5. Conclusions

The obtained experimental results allow to establish a working hypothesis with respect to the nature of the active sites and the processes of their formation and depletion occurring during the life cycle of the Cs and Cl doped V-Fe mixed oxide catalyst. During both processes, the activation and the deactivation, transport processes via chlorides play a fundamental role. These transport reactions are thought to lead to disperse VO_x species with a limited life time. Both, an aggregation or a chemical conversion of these species could be responsible for their short life time. Eventually, the final state of the catalyst is a stable but less selective and active one due to the conversion of the active sites to bulky oxide sites having poor catalytic properties. As expected, the lifetime of the catalyst may be prolonged by adding small

amounts of HCl to the feed and spent catalysts can also be regenerated by a repeated calcination in the presence of NH_4Cl as shown elsewhere [2, 3]. However, taking into consideration the results of tests of a great variety of VPO catalysts in the oxidation of butadiene to furan [17], there is no potentiality for the development of stable active and selective catalysts on the basis of bulky oxides for this reaction.

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