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Catalytic partial oxidation of propane to acrolein

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Abstract

Results are discussed on the direct oxidation of propane to acrolein on Me_xO_y-supported $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_x$ ($Me_xO_y = \gamma$-Al_2O_3, TiO_2, SiO_2) and on $Me_7Bi_5Mo_{12}O_x$ (Me = Mg, Ca, Zn) catalysts. Almost no formation of acrolein was observed over Me_xO_y-supported catalysts although active phases for oxidative dehydrogenation of propane (dispersed VO_x species) and oxygen insertion in propene (scheelite structure) were present. For Me-Bi-Mo-O, selectivities to acrolein and CO_x depended on the nature of the third cation and reaction mixture used. The acrolein selectivities amounted to 34 and 20% (yields of 3.2 and 2.7%) when using $Ca_7Bi_5Mo_{12}O_x$ and $Mg_7Bi_5Mo_{12}O_x$, respectively. Redox properties were found to be an important factor determining the reaction pathways. Tentatively it can be concluded that different types of lattice oxygen are involved in propane dehydrogenation to propene and consecutive reactions towards acrolein and CO_x. Under conditions of effective propane dehydrogenation to propene a competitive reaction between an allylic intermediate and propane forming propene and propyl radical can be assumed as the reason for low acrolein formation in favour to propene. Applying a two layer fixed bed reactor an acrolein yield of 7.4% ($S = 20\%$) was obtained.

Keywords: Partial oxidation; Propane; Acrolein from propane

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1. Introduction

Direct oxidation of propane to acrolein could be an interesting alternative to propene oxidation. The data published on propane oxidation indicate, however, that the reaction still leads to significantly lower selectivities and yields respectively. Maximal yields of 13% as reported by Kim et al. [1] were achieved under conditions where, however, primary gas-phase dehydrogenation of propane occurred [2].

When considering literature data on selectivities of acrolein as a function of propane conversion it can be seen that maximal acrolein selectivities did not exceed 60% even at low propane conversions (Fig. 1). These results can be interpreted in the following manner:

(1) total oxidation occurs as a non-selective side reaction to propene and acrolein formation, and

(2) consecutive total oxidation of acrolein contributes to a loss in acrolein selectivity

Against this background it was the aim of the present study to elucidate some of the factors affecting the partial oxidation of propane. From such results, it is anticipated that eventually catalyst design may profit and reaction conditions can be optimized.

It is widely accepted that propene is an intermediate product in the overall process. It can be

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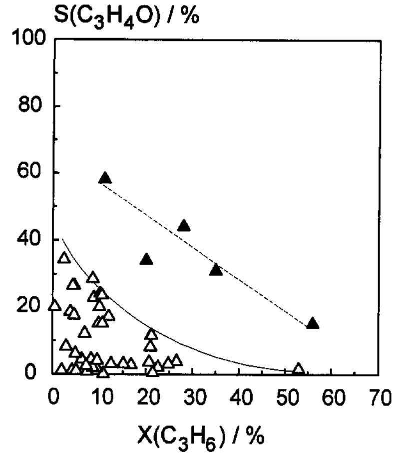

Fig. 1. Dependence of acrolein selectivity on propane conversion (literature data according to [3]: ▲, partly with contribution of gas-phase dehydrogenation of propane [1],[2]).

formed non-catalytically or catalytically. If one catalyst and one reactor is used in the partial oxidation of propane the selective transformation of propene to acrolein has to be carried out at temperatures required for catalytic propane dehydrogenation to propene which are, however, significantly higher than for the propene-to-acrolein reaction; nevertheless, total oxidation has to be avoided. According to these facts a suitable catalyst composition shall consist of cooperatively acting active sites (1) for propane dehydrogenation at lower temperatures than usually applied and (2) for oxygen insertion in propene or some kind of its surface intermediate. For the insertion reaction commonly Bi-Mo-O based catalysts are used in practice; unfortunately, such catalysts do not exhibit any appreciable activity for the required primary oxidative dehydrogenation of propane [4]. Based on this knowledge two types of bifunctional catalytic materials were chosen:

oxygen-insertion catalysts used for propene partial oxidation were supplemented by a dehydrogenation function and

a combination of two catalysts each having one of the functions required.

In the present work Bi-Mo-O type catalysts were modified by coprecipitation of all catalytic compounds along with compounds supporting dehydrogenation activity or by mechanically admixing compounds being active in the oxidative dehydrogenation of propane. Although this study was mainly focussed on the partial oxidation to acrolein some work was also devoted to catalysts (in particular $B_2O_3/\gamma\text{-}Al_2O_3$ and V_2O_5/TiO_2) for oxidative dehydrogenation of propane since this reaction step plays an important role in the overall reaction scheme as outlined above.

2. Experimental

2.1. Catalysts

Two groups of catalysts for oxygen insertion into propene partly already described in literature were differently modified and tested for the partial oxidation of propane.

(1) $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ on different support materials which were to serve as dehydrogenation catalysts;

(2) $Me_7Bi_5Mo_{12}O_x$ (Me = Ca, Mg, Zn), i.e. an additional cation was introduced for supporting dehydrogenation.

$Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$(10 mol%)/$Me_xO_y$ ($Me_xO_y = Al_2O_3$, TiO_2, SiO_2) and $Bi_2O_3 \cdot MoO_3$(10 mol%)/Al_2O_3 as a reference were prepared by coprecipitation of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Bi(NO_3)_3 \cdot 6H_2O$, NH_4VO_3 and $AgNO_3$ at pH 10 from diluted nitric acid solution (1 M) in the presence of Me_xO_y. Water was evaporated; the precursor was dried at 393 K for 12 h and calcined at 823 K for 6 h.

$Me_7Bi_5Mo_{12}O_x$ (Me = Ca, Mg, Zn) catalysts were prepared by precipitating $Me(NO_3)_2$, $Bi(NO_3)_3 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at pH 5 from diluted nitric acid solution (1 M). After evaporation of water the precursor was dried 393 K for 30 h; the calcination was carried out at 593 K for 5 h and at 723 K for 6 h in two subsequent steps.

$K_4P_2O_7/Ca_7Bi_5Mo_{12}O_x$ was prepared by wet impregnation of $Ca_7Bi_5Mo_{12}O_x$ with a solution of $K_4P_2O_7$. The precursor was dried at 383 K for 24 h and calcined at 723 K for 5 h.

B_2O_3/Al_2O_3 catalysts with boria contents of 15 and 30 wt% on γ-Al_2O_3 were prepared by impregnation of γ-Al_2O_3 (Degussa, 83.8 m^2/g) with boric acid dissolved in warm water. After stirring for 1 h water was evaporated; the solid remainder was dried overnight at 383 K and calcined at 873 K for 14 h. A well characterized V_2O_5(1 wt%)/TiO_2 (EUROCAT, [5]) was used as a reference material for the oxidative dehydrogenation of propane. Mechanical mixtures of $Zn_7Bi_5Mo_{12}O_x$ and B_2O_3 (30 wt%)/Al_2O_3 as well as of γ-Al_2O_3 and $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ were used in the propane oxidation. Additionally, combinations of two catalysts active for dehydrogenation ($Zn_7Bi_5Mo_{12}O_x$ and B_2O_3(30 wt%)/Al_2O_3) and oxygen insertion ($Ca_7Bi_5Mo_{12}O_x$) were examined using a two-layer fixed bed.

2.2. Methods

The 'temporal-analysis-of-products' (TAP) reactor [6] was used for transient experiments under vacuum conditions. Using high-speed beam valves small amounts of gas (10^{15} to 10^{16} molecules/pulse) were passed through a fixed bed of catalyst particles which was located in a vacuum chamber. The time course of the response signal to the pulse was recorded by a QMS at the end of the reactor; the time resolution for analysis was in the submillisecond range. In the TAP system mass transport takes place by diffusion only. Besides these transient studies, steady-state experiments were carried out in the TAP reactor by passing a continuous flow of the reactants through the reactor under reduced pressure ($P_{total} < 10^4$ Pa).

Catalytic experiments were also performed under atmospheric pressure in a plug-flow micro catalytic fixed-bed reactor immersed into a fluidized bed for achieving good temperature control. For product analysis, on-line gas chromatography was used.

The specific surface areas of the catalysts were determined by nitrogen adsorption at 77 K using the 1-point-BET method. All solids were characterized by X-ray diffraction using a Philips PW 1710 diffractometer with Cu K_α radiation. IR-characterization was performed using a Perkin Elmer 1710 FTIR spectrometer equipped with a DRIFT cell (Spectra Tech 003-102). Raman spectra were recorded at ambient pressure with a 1760 FTIR spectrometer using a Nd-Yag laser ($\lambda = 1064$ nm) for excitation. XPS spectra of $Me_7Bi_5Mo_{12}O_x$ (Me = Mg, Ca, Zn) were obtained from a Leybold LHS 10 spectrometer (single-channel detection). For excitation radiation an Al K_α (1486.6 eV) source was used. Atomic ratios for the surface layers were obtained by correcting the intensity ratios with theoretical sensitivity factors [7]. ESR spectra of fresh and discharged $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Al_2O_3$ and $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ were recorded at 10 K, with 9.4362 GHz and 20 mW using a Bruker ER-200-D-SRC device. The sample discharged after partial oxidation of propane at 773 K was kept in argon atmosphere before EPR measurements.

Temperature programmed reduction (H_2-TPR) was performed between 300 and 873 K with a heating rate of 10 K/min. A mixture of 5% H_2 in He was passed through in a continuous flow reactor charged with approx. 0.4 g of catalyst with a total flow rate of 30 ml/min. Water formation was monitored by mass spectroscopy.

3. Results and discussion

3.1. $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$(10 mol%) / Me_xO_y catalysts

3.1.1. Catalytic performance

The silver-doped bismuth vanadomolybdate catalyst as well as the bismuth molybdates described by Kim et al. [1,2] exhibited no activity for the partial oxidation of propane under reduced pressure (cf. Table 1). The modification of this catalyst by coprecipitating the main components (Ag, Bi, Mo, V) in the presence of an additional solid such as Al_2O_3, TiO_2 and SiO_2 led to an increase in activity for the oxidative conversion of propane at fixed contact time as shown in Table 1. The highest propane conversion of 25% was achieved over an Al_2O_3-containing catalyst while a conversion of approximately 13% was obtained on TiO_2- and SiO_2-containing catalysts. The highest yield of acrolein amounted to 1% over the TiO_2-containing catalyst. Besides propene formed with a maximal selectivity of approx. 35%, the carbon oxides were the main products.

For elucidating the influence of gas-phase and adsorbed oxygen on the reaction, pulse experiments in the TAP reactor were carried out using a reaction mixture with and without gas-phase oxygen over $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$(10 mol%)/$Al_2O_3$. The catalyst was pretreated in O_2 at 815 and kept then under vacuum for 10 min in order to remove weakly bonded forms of oxygen. Afterwards propane was pulsed over the catalyst. The degree of catalyst reduction amounted to approximately 0.3% after 200 propane pulses. As shown in Fig. 2, conversions of propane and product yields differ for both reaction mixtures within experimental error only. From this, the participation of adsorbed oxygen from the gas-phase can be ruled out and lattice oxygen only participates in the surface interaction with propane and its consecutive product propene. These results are in good agreement with those obtained from pulse experiments with $^{18}O_2$. No dissociative or molecular adsorption of oxygen was detected as follows from the absence of any oxygen exchange products and from an analysis of the moments of the $^{18}O_2$ and Ne responses performed according to [8].

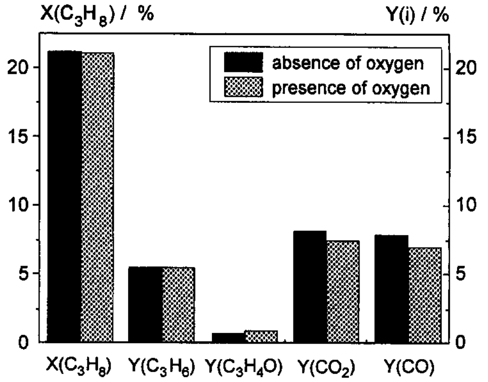

Fig. 2. Propane conversion and product yields when pulsing C_3H_8:O_2:Ne and C_3H_8:He:Ne over oxygen pretreated $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$(10 mol%)/$Al_2O_3$ at 815 K (C_3H_8:O_2(He):Ne = 1:2:2, m_{cat} = 0.2 g, 2.5×10^{15} molecules/pulse).

A significant difference in propane conversion on $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Me_xO_y$ compared to a non-modified catalyst can be first ascribed to an increase in the BET surface area. However, taking into account the low activity ($X(C_3H_8) = 3.6\%$) of a $Bi_2O_3 \cdot MoO_6/Al_2O_3$ catalyst ($S_{BET} = 53.6$ m^2/g) prepared in the same manner as $Ag_{0.01}B_{i0.85}V_{0.54}Mo_{0.45}O_4/Me_xO_y$ another reason for the increased activity of Me_xO_y-containing catalysts can be assumed. There might be, for example, new active sites in

Table 1
Results on catalytic activity of bismuth and molybdenum oxides-based catalysts in the partial oxidation of propane during continuous flow TAP experiments at 850 K and reduced pressure ($P_{total} < 10^4$ Pa, C_3H_8:O_2:Ne = 1:2:2, m_{cat} = 0.25 g, τ_{mod} = 1 g min ml^{-1})

Catalytic components (10 mol%)	Me_xO_y support	S_{BET} (m^2/g)	C_3H_8	C_3H_6		C_3H_4O	
			X (%)	Y (%)	S (%)	Y (%)	S (%)
$Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$		0.7	0				
$Bi_2O_3 \cdot MoO_3$		0.7	0				
$Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$	Al_2O_3	83.7	25.0	8.9	35.6	0.9	3.6
	TiO_2	26.2	12.7	3.3	26.0	1.0	7.9
	SiO_2	104.5	12.6	3.8	29.5	0.4	3.2
$Bi_2O_3 \cdot MoO_3$	Al_2O_3	53.4	3.6	1.1	30.1	traces	n.d.

addition to the sites of bulk Ag-Bi-V-Mo-O and Me_xO_y due to the synthesis conditions of the vanadium containing catalysts.

3.1.2. Effect of preparation method

To examine whether the method of preparation affects the catalytic behavior, the performance of two differently prepared alumina-supported $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Al_2O_3$ catalysts (A and B) as well as Al_2O_3 for comparison was studied in a micro-catalytic fixed-bed reactor at 725 K (cf. Table 2). Sample A represents the catalyst prepared by coprecipitation described in the experimental section while sample B was a mechanical mixture of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ as catalyst for partial propene oxidation and of Al_2O_3 for propane dehydrogenation; the oxides were ball-milled in the presence of water. Sample A is more active than B. For sample A, conversion of propane amounted to ca. 20% while sample B resulted in 5% only (cf. Table 2). Also product distributions differed: over sample B and over Al_2O_3 carbon monoxide was the main product of total oxidations, while over sample A carbon dioxide was mainly formed. The activity and the product distribution of the mechanical mixture was essentially determined by Al_2O_3. The catalytic behavior of the coprecipitated catalyst, however, could serve as an indication that either a new catalytically active phase or active center was formed by the preparation procedure.

3.1.3. Characterization

For $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Me_xO_y$ catalysts, no new phase compared to earlier work (see below) was detected in addition to scheelite-type structure and Me_xO_y by means of XRD as well as by raman spectroscopy. Neither Ag^+ nor the presence of Me_xO_y influenced the lattice parameters of the scheelite structure significantly so that the XRD spectra are in good agreement with those published by Ueda et al. [9] and Kim and Woo [10]. Based on the empirical correlation of Raman stretching frequencies to bond lengths [11,12] the emissions observed in the Raman spectra of the modified $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ (cf. Fig. 3) at approx. 875 and 819 cm^{-1} can be ascribed to Mo–O and V–O vibrations, respectively. While Al_2O_3 and SiO_2 were Raman inactive the additional bands at 638, 512, 438 and 398 cm^{-1} in the spectrum of the TiO_2-containing catalysts can be assigned to anatase and rutile phases.

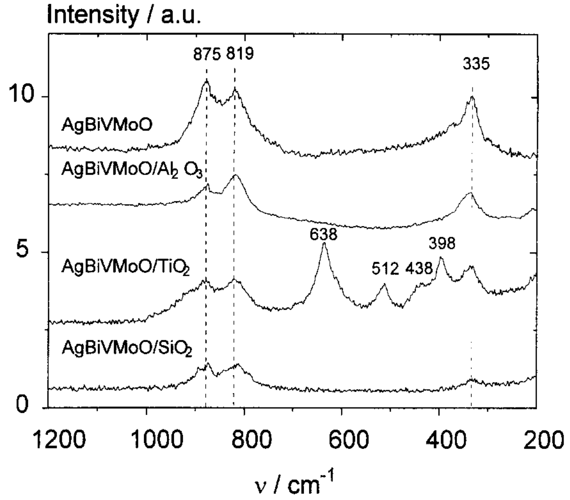

Fig. 3. Raman spectra of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ and $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Me_xO_y$ recorded at 300 K under ambient pressure.

Table 2

Catalytic performance of differently prepared catalysts in a fixed-bed reactor at 725 K and 0.1 MPa (C_3H_8:O_2:N_2 = 1:2:7; m_{cat} = 1.0 g; τ_{mod} = 1 g s ml^{-1}). Sample A: coprecipitation of $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ in the presence of γ-Al_2O_3. Sample B: mechanical mixture of γ-Al_2O_3 and $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$

Catalysts	S_{BET} (m^2 g^{-1})	$X(C_3H_8)$ (%)	$S(C_3H_6)$ (%)	$S(C_3H_4O)$ (%)	$S(CO)$ (%)	$S(CO_2)$ (%)
A	83.7	19.7	31.1	0	16.8	48.9
B	90.5	4.7	33.6	0	45.0	16.7
γ-Al_2O_3	116.6	5.2	32.0	0	41.0	25.8

By means of EPR, dispersed VO_x structures were confirmed on alumina- and titania-supported catalysts prepared by coprecipitation. The catalysts exposed to propane oxidation under atmospheric conditions exhibited the characteristic signal of V^{4+} in a C_{4V} symmetry as shown in Fig. 4 which is in accordance with the spectra and the parameters given in literature [13,14]. The parameters derived from the simulation of the spectra are in accordance with those published for the spectra of VO_x/Al_2O_3 [13]. The EPR spectra of the unsupported $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ were recorded and no formation of V^{4+} in the scheelite phase was detected. It may be, however, assumed that polyvanadate anions were adsorbed on the surface of Al_2O_3 or TiO_2 from the acidic solution before precipitation of the scheelite precursor [15]. Such surface vanadates have been described as active sites for the oxidative dehydrogenation of propane over vanadia-alumina catalysts [13].

To confirm the ability of supported VO_x structures to act as a dehydrogenation catalyst even under vacuum conditions in transient operation of the TAP reactor propane oxidation was studied over well characterized V_2O_5(1 wt%)/TiO_2 (EUROCAT, [5]) consisting of VO_x species attached to the TiO_2 surface. Results of propane conversion and product selectivities on pulsing propane over this catalyst at 766 K are given in Fig. 5. The reaction of propane with the oxidized surface resulted in $X(C_3H_8) = 36\%$; with increasing degree of catalyst-surface reduction conversion decreased coinciding with increasing selectivity to propene.

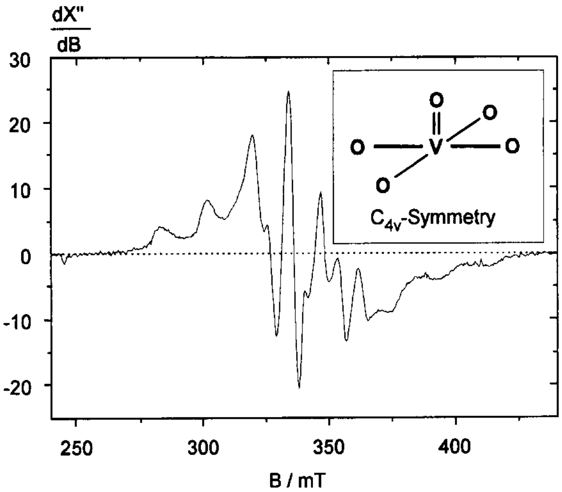

Fig. 4. EPR spectrum of discharged $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Al_2O_3$ ($\nu = 9.4362$ GHz (X-band), $T = 10$ K, $P = 20$ mW) and the proposed C_{4v} structure of the surface V^{4+} species.

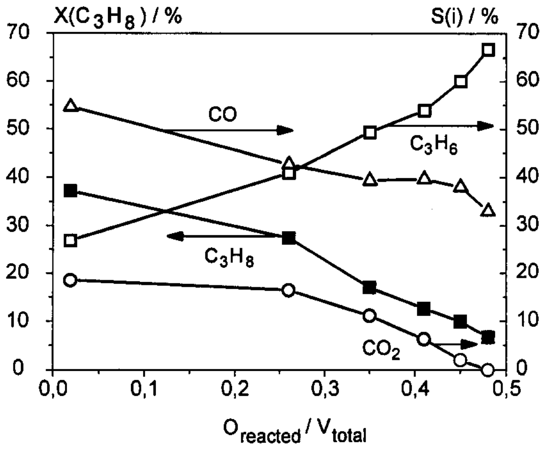

Fig. 5. Dependence of propane conversion and product selectivities on the degree of reduction during pulsing propane over V_2O_5(1 wt%)/TiO_2 in the absence of gas-phase oxygen at 766 K (C_3H_8:Ne = 1:1, $m_{cat} = 0.2$ g, 2.5×10^{15} molecules/pulse).

Although acrolein selectivity amounted to 71% at $X(C_3H_6) = 36\%$ in propene oxidation over $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ at 773 K transient studies in the TAP reactor showed that secondary reactions of propene and acrolein led mainly to total oxidation over $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4/Me_xO_y$ with participation of lattice oxygen.

Summarizing the results on characterization and catalytic activity of Me_xO_y-containing catalysts it follows that in spite of the presence of active phases for oxidative dehydrogenation of propane (dispersed VO_x species) and oxygen insertion in propene (scheelite structure) almost no formation of acrolein was observed. Thus, the simple combination of two active phases in one catalyst was found not to be appropriate for designing a catalyst for the direct oxidation of propane to acrolein.

3.2. *Modifying bismuth molybdate by addition of third cation*

$Ca_7Bi_5Mo_{12}O_x$ has been reported as a rather active catalyst for ammoxidation of propane [16]. From this it was assumed that this material reveals dehydrogenation and insertion functions. Therefore, $Ca_7Bi_5Mo_{12}O_x$ was also tested for the partial oxidation of propane to acrolein; the effect of total substitution of Ca by Mg and Zn as well as of doping with $K_4P_2O_7$ was further studied.

Specific surface areas, XRD results on crystal phase compositions and surface content data from XPS measurements are summarized in Table 3 for Me-Bi-Mo-O (Me = Ca, Mg, Zn) catalysts. For all samples, two phases of bismuth molybdate exist, i.e. γ-Bi_2MoO_6, and α-$Bi_2Mo_3O_{12}$. A third phase was found to be $CaMoO_4$, $MgMoO_4$ or $ZnMoO_4$, respectively. The crystallographic structures of these molybdates are different; calcium molybdate has a scheelite-type structure while zinc and magnesium molybdates have a monoclinic structure. No significant structural changes were detected after catalytic reaction. XPS results showed almost similar surface compositions of Ca- and Mg-containing catalysts. For $Zn_7Bi_5Mo_{12}$, a significant enrichment with Zn was observed while the bismuth and molybdenum contents did not differ much from the other catalysts.

While propane was not converted over pure bismuth molybdates the modification by introducing a third cation resulted in more active catalysts for propane oxidation. The performance of these Me-Bi-Mo-O depended on the third added cation. Oxidative conversion of propane over $Me_7Bi_5Mo_{12}O_x$ catalysts was studied in a wide range of propane and oxygen partial pressures. It was found that propane partial pressure affected significantly propane conversion over a $Ca_7Bi_5Mo_{12}O_x$ catalyst but did not influence conversion in the case of $Mg_7Bi_5Mo_{12}O_x$. The dependencies of propane conversion and products selectivities on propane partial pressure over $Ca_7Bi_5Mo_{12}O_x$ at 823 K and a fixed oxygen partial pressure of 20 kPa are presented in Fig. 6. While for $p^\circ(C_3H_8) = 2$ kPa no detectable propane conversion was observed, conversion increased with increasing $p^\circ(C_3H_8)$. Concomitantly, propene selectivity increased while acrolein selectivity passed through a maximum at $p^\circ(C_3H_8) = 30$ kPa.

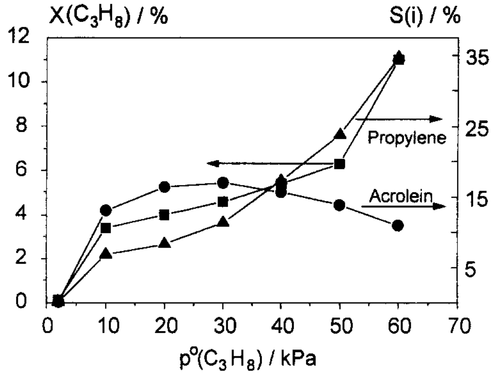

Fig. 6. Influence of propane partial pressure on propane conversion and product selectivities over a $Ca_7Bi_5Mo_{12}O_x$ catalyst at 823 K and $p^\circ(O_2) = 20$ kPa.

Table 3
Characterization results of Me-Bi-Mo-O catalysts

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Crystalline phases	Surface (s) and bulk (b) content (atom%)		
			Me	Bi	Mo
$Ca_7Bi_5Mo_{12}O_x$	1.90	γ-Bi_2MoO_6, α-$Bi_2Mo_3O_{12}$, $CaMoO_4$	6.2 (s)	6.9 (s)	14.6 (s)
$Mg_7Bi_5Mo_{12}O_x$	1.47	γ-Bi_2MoO_6, α-$Bi_2Mo_3O_{12}$, $MgMoO_4$ (poorly crystalline)	6.0 (s)	4.5 (s)	14.7 (s)
$Zn_7Bi_5Mo_{12}O_x$	0.33	γ-Bi_2MoO_6, α-$Bi_2Mo_3O_{12}$(major) $ZnMoO_4$	11.7 (s)	6.0 (s)	14.6 (s)
			9.4 (b)	6.7 (b)	16.1 (b)

The influence of the oxygen partial pressure on propane conversion and product selectivities was studied at a fixed propane partial pressure of 60 kPa; respective dependencies are shown in Fig. 7 for a $Ca_7Bi_5Mo_{12}O_x$ catalyst. An increase of the oxygen content from 10 to 30 kPa resulted in a decrease of acrolein selectivity in favour of CO_x. Maximum acrolein yield obtained on $Ca_7Bi_5Mo_{12}O_x$ amounted to 3.2% at 823 K using a reaction mixture with propane in excess ($p^o(C_3H_8) = 60$ kPa, $p^o(O_2) = 10$ kPa); conversion of propane and oxygen were 9.5 and 99.8%, respectively. It should be noted that an increase of selectivitity to acrolein from 5.9 to 39.7% was obtained over the $Ca_7Bi_5Mo_{12}O_x$ catalyst under oxygen-lean condition ($p^o(C_3H_8) = 60$ kPa, $p^o(O_2) = 10$ kPa) during 5 h time on stream at 803 K.

Catalytic results showed rather different behavior of Ca- and Mg-containing samples when increasing oxygen content in the reaction mixture. For $Mg_7Bi_5Mo_{12}O_x$, an increase of oxygen partial pressure from 10 to 30 kPa at a fixed value of $p^o(C_3H_8) = 60$ kPa resulted in an increase of propane conversion, which, contrary to Ca-containing catalyst, coincided with increasing acrolein selectivity from 9 to 20%. Results on catalytic performance of different Me-Bi-Mo-O systems at 803 K, $p^o(C_3H_8) = 60$ kPa and $p^o(O_2) = 30$ kPa are given in Table 4. In contrast to the Mg- and Ca-modified systems where acrolein selectivity exceeded or was close to propene selectivity partial oxidation of propane over Zn-Bi-Mo-O resulted in the formation of propene in excess. The rather different behavior of Zn-Bi-Mo-O can be ascribed to a surface enrichment of Zn; this, however, needs further elucidation. Taking into account almost similar surface composition of Ca- and Mg-containing catalysts the difference in their catalytic activity might be caused by, e.g. different structures of the $MeMoO_4$ phases or their different crystallinity.

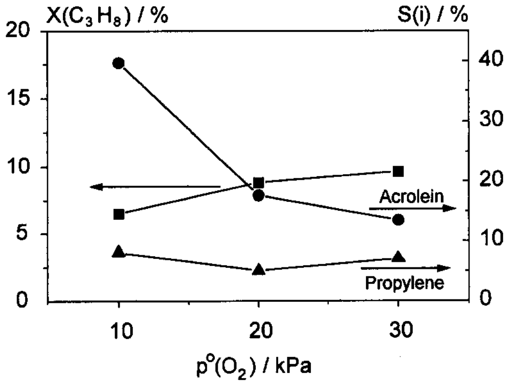

Fig. 7. Influence of oxygen partial pressure on propane conversion and product selectivities over a $Ca_7Bi_5Mo_{12}O_x$ catalyst at 803 K and $p^o(C_3H_8) = 60$ kPa.

Table 4

Catalytic performance of $Me_7Bi_5Mo_{12}O_x$ catalysts at 803 K (C_3H_8:O_2:N_2 = 6:3:1, $\tau_{mod} = 1$ g s ml^{-1})

Catalyst	X (%)		S (%)				
	C_3H_8	O_2	Acr [a]	C_3H_6	CO	CO_2	C_2H_4
$Ca_7Bi_5Mo_{12}O_x$	9.6	67.9	13.5	7.0	42.7	36.8	
$Mg_7Bi_5Mo_{12}O_x$	13.5	55.6	20.0	24.3	27.6	19.8	8.3
$Zn_7Bi_5Mo_{12}O_x$	5.6	8.6	6.3	71.4	10.4	6.0	5.9

[a] Acr, acrolein.

From the product distribution on Ca- and Mg-containing catalysts for close values of propane conversion (cf. Table 4) it is obvious that significantly less CO_x formation occurred in the case of Mg. Also, as mentioned above, the formation of acrolein on these two catalysts depends differently on increasing oxygen partial pressure. These findings could be correlated with the redox properties of both catalysts. Results of H_2-TPR experiments presented in Fig. 8 showed that $Ca_7Bi_5Mo_{12}O_x$ is more easily reduced than $Mg_7Bi_5Mo_{12}O_x$. Therefore, it can be assumed that the different product distributions obtained on these two catalysts, especially the different dependencies on increasing oxygen partial pressures, are determined by the different reducibilities of these solids. For easily reduced Ca-Bi-Mo-O the increase in acrolein formation was observed only at a low oxygen content (10 kPa) under conditions of complete oxygen conversion. In the case of the Mg-containing catalyst the suppression of total oxidation when using a reaction mixture with higher oxygen content (30 kPa) can be assigned to more strongly bonded forms of lattice oxygen on this catalyst. Another catalyst containing strongly bonded forms of lattice oxygen was obtained by modifying Ca-Bi-Mo-O with 2 wt% $K_4P_2O_7$ (cf. Fig. 8) since doping led to significant less reducibility of Ca-Bi-Mo-O. This affected significantly the catalytic properties although no extra crystalline phase could be derived from XRD patterns in the doped system compared to the Ca-Bi-Mo-O. Surface composition from XPS showed that the K/P ratio did not correspond to pyrophosphate and amounted to approximately 2.4 and 3.5 for 2 wt% and 6 wt% $K_4P_2O_7$-doped catalyst, respectively. No changes were detected in the K/P ratio after catalytic reaction. From the above data it can be concluded that the change in the redox properties of Ca-Bi-Mo-O catalyst by doping with K and P cannot be ascribed to the formation of $K_4P_2O_7$-phase.

As shown in Fig. 9, doping $Ca_7Bi_5Mo_{12}O_x$ with $K_4P_2O_7$ diminished CO_x and acrolein selectivities. When adding 2 wt% of $K_4P_2O_7$ a decrease in acrolein selectivity from 33.4 to 1.7% was observed while C_3H_6 selectivity increased from 38.9 to 76% when using a reaction mixture with $p^o(C_3H_8) = 60$ kPa, $p^o(O_2) = 10$ kPa (cf. Fig. 9). Although product distribution was significantly affected no change in propane conversion was observed. Thus, the oxygen sites involved in the oxidative dehydrogenation of propane, which, however, do not facilitate the formation of acrolein, are not eliminated by K–P–O doping. Under conditions where gas-phase homogeneous reactions could be neglected ($X(C_3H_8) < 3\%$ in the absence of catalyst) the maximal yield of propene amounted to 14.1% ($S = 73.4\%$) over $K_4P_2O_7$(2 wt%)/$Ca_7Bi_5Mo_{12}O_x$ at 823 K upon applying a reaction mixture with $p^o(C_3H_8) = 60$ kPa and $p^o(O_2) = 30$ kPa. It may be assumed that $K_4P_2O_7$ doping led to the elimination of weakly bonded oxygen which may easily oxidize reaction intermediates. This was confirmed by experiments on propene oxidation. A significant difference between undoped and K–P–O-doped $Ca_7Bi_5Mo_{12}O_x$ catalysts towards propene oxidation (2% C_3H_6 in air, $T_R = 773$ K, $\tau_{mod} = 1$ g s/ml) was observed: much lower conversion of propene ($X(C_3H_6) = 15\%$, $S(C_3H_4O) = 44\%$) on $K_4P_2O_7$ (6 wt%)/$Ca_7Bi_5Mo_{12}O_x$ compared to the undoped one ($X(C_3H_6) = 93\%$, $S(C_3H_4O) = 56.1\%$) confirmed that oxygen involved in the acrolein and CO_x formation from propene is eliminated by doping with $K_4P_2O_7$. Thus, due to a significant suppression of surface-induced oxidation the selective formation of propene becomes possible. From the above results it can be proposed that different types of oxygen are involved in propane dehydrogena-

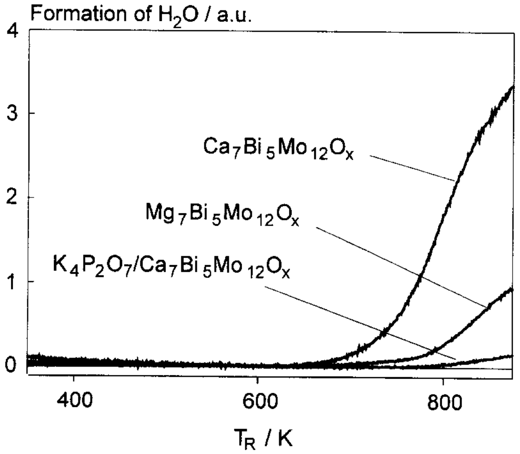

Fig. 8. Results on water formation during H_2-TPR experiments on different catalysts.

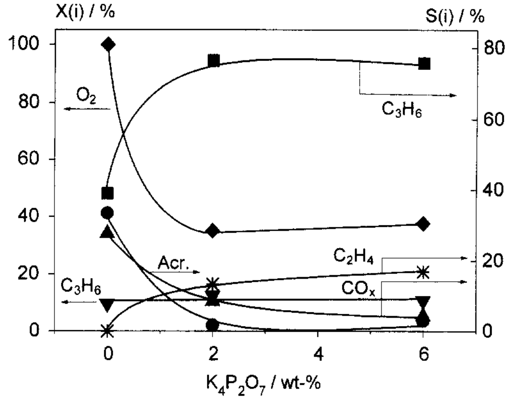

Fig. 9. Dependence of propane conversion and product selectivities on the amount of $K_4P_2O_7$ addition to $Ca_7Bi_5Mo_{12}O_x$ (T_R = 823 K, $C_3H_8:O_2:N_2 = 6:3:1$, $\tau_{mod} = 2$ g s/ml).

tion and secondary reactions of propene leading to the formation of acrolein and CO_x.

3.3. Concomitant use of catalysts for oxidative dehydrogenation and oxygen insertion

Based on the approach to combine materials being active in the oxidative dehydrogenation of propane and in the partial oxidation of propene a criterium was used for the selection of a catalyst for propane dehydrogenation which was defined by high yields of propene under incomplete conversion of oxygen in order to provide oxygen for the secondary reaction step towards acrolein. Among the tested catalysts B_2O_3/γ-Al_2O_3 was found to be most suitable; results on the oxidative dehydrogenation on these catalysts are given in Table 5. A propene yield of 18% (S = 44.6%) was obtained on B_2O_3(30 wt%)/γ-Al_2O_3 using a reaction mixture with $C_3H_8/O_2 = 1/2$ ($X(O_2) = 35.1\%$) (cf. Table 5). These catalyst compositions were reported in the literature for the oxidation of ethane [17] but, however, were not reported for the oxidative dehydrogenation of propane before.

A mechanical mixture (3:1) of B_2O_3(30 wt%)/γ-Al_2O_3 and $Zn_7Bi_5Mo_{12}O_x$ catalysts was tested in the propane oxidation. The latter had shown rather high selectivity with respect to acrolein formation ($S(C_3H_4O)$ = 75%; $X(C_3H_6) = 51.4\%$) in the oxidation of propene (2% C_3H_6 in air, $T_R = 773$ K, $\tau_{mod} = 1$ g s/ml). Catalytic results when using a mechanical mixture showed that along with some increase in the yield of acrolein, which was expected, an increase in propane conversion and propene yield was observed. These observations led to the assumption that the interaction of intermediate allylic radicals with propane forming propene competes at high temperature with oxygen insertion. In order to clarify this effect propane conversion on a $Zn_7Bi_5Mo_{12}O_x$ catalyst was studied at 823 K in the presence of different amounts of propene in the reaction mixture. Results are given in Fig. 10. Increasing propene partial pressure resulted in a significant increase of propane conversion. It was not possible to determine correctly which products were formed from propane since propene being present in the feed gas was also converted into acrolein and CO_x. However, propene concentration in product gas during oxidation of propane/propene

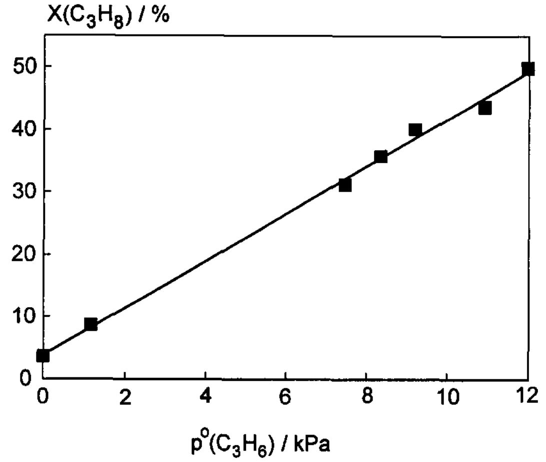

Fig. 10. Effect of propene partial pressure in a propane/oxygen mixture on propane conversion over a $Zn_7Bi_5Mo_{12}O_x$ catalyst ($T_R = 823$ K, $p(C_3H_8) = 5$ kPa, $p(O_2) = 50$ kPa, $\tau_{mod} = 4$ g s/ml).

Table 5
Catalytic performance of B_2O_3/Al_2O_3 catalysts in the oxidative dehydrogenation of propane at 823 K

	p° (kPa)		τ_{mod}	X (%)		S (%)				
	O_2	C_3H_8	(g s/ml)	O_2	C_3H_8	C_3H_6	Acr	C_2H_4	CO	CO_2
B_2O_3 (15 wt%)/Al_2O_3	20	10	2	15.8	15.6	56.2	trace	11.5	19.3	13.0
B_2O_3 (30 wt%)/Al_2O_3	20	10	4	20.2	21.1	47.8	0.5	13.7	21.0	17.0
	50	25	4	35.1	40.4	44.6	4.3	13.2	28.9	9.0

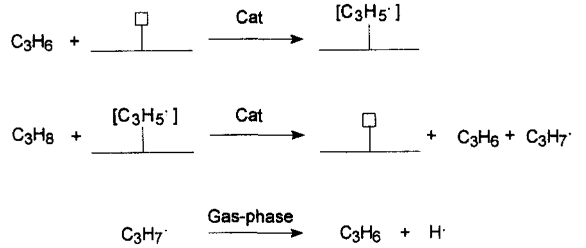

Fig. 11. Reactions proposed for the oxidation of propane/propene mixtures over Zn-Bi-Mo-O catalyst.

mixture was higher than that during oxidation of propene. It can be assumed that the additional amount of propene formed during oxidation of the propane/propene mixture can be due to the reaction of propane with allylic radicals resulting in propene, propyl radicals and reduced oxidation sites according to following reactions (cf. Fig. 11).

A recent study of Hayashi et al. [18] on the formation of propene oxide by homogeneous gas-phase reaction of propane and propene with oxygen showed that the rate and selectivity to propene oxide were markedly enhanced by mixing propane and propene. The nature of this phenomena was not completely clarified. Present results showed that an addition of propene in the propane/oxygen mixture enhanced markedly the conversion of propane over Zn-Bi-Mo-O catalyst at 823 K. Also, this propane–propene interaction which led to the formation of an additional amount of propene might be considered as a competitive reaction compared to oxygen insertion into propene since allylic intermediate does not transform to acrolein but to propene and propyl radical.

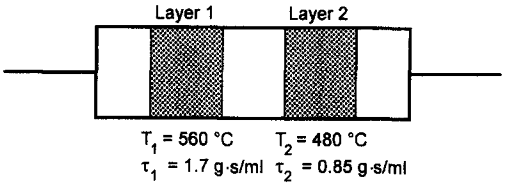

Fig. 12. Structured catalyst bed for the partial oxidation of propane to acrolein. Layer 1: B_2O_3(30 wt%)/Al_2O_3/$Zn_7Bi_5Mo_{12}O_x$ (1:0.3). Layer 2: $Ca_7Bi_5Mo_{12}O_x$.

Table 6
Results on propane oxidation in a two-layer fixed-bed reactor at $p^0(C_3H_8) = 7.3$ kPa, $p^0(O_2) = 21$ kPa, for reaction conditions see also Fig. 12

X (%)	S (%)				Y_{Acrolein}
C_3H_8	C_3H_6	Acrolein	CO	CO_2	(%)
36.6	2.6	20.0	50.4	25.9	7.4

To diminish the above-mentioned reactions between propane and propene which contribute to the reaction pathways mostly at high temperatures a two layer fixed bed each layer operating at an optimal temperature can lead to an improvement of the acrolein yield. Applying such type of reactor (cf. Fig. 12) an acrolein yield of 7.4% (cf. Table 6) was obtained without contribution of gas-phase propane dehydrogenation.

4. Conclusions

The catalyst design approach applied for the oxidation of propane to acrolein, i.e. combining two active phases (precipitation or mechanical mixture) has severe shortcomings since the two active phases do not act cooperatively to any large extent. Redox properties were found to be an important factor determining the reaction pathways. Tentatively it can be concluded that different types of lattice oxygen are involved in propane dehydrogenation to propene and consecutive reactions towards acrolein and CO_x. Under conditions of effective propane dehydrogenation to propene a competitive reaction between an allylic intermediate and propane forming propene and propyl radical can be assumed as the reason for low acrolein formation over catalysts used. For catalyst improvement a complex active center forming acrolein by a 'one-step' surface process from propane appears necessary or dehydrogenation and oxygen insertion should be totally separated (two-reactors concept).

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