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The Role of Active Oxygen in the AMM-V_xSi-Catalysed Selective Oxidation of Toluene

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The selective catalytic oxidation of toluene with air to benzaldehyde in the gas phase has been studied over amorphous microporous mixed oxide catalysts containing isolated V-centres in microporous silica (AMM-V_xSi). The homogeneous distribution of the vanadium on atomic scale in these catalysts has been proven by XRD, HRTEM/EDX, light microscopy, and FTIR. Benzaldehyde selectivities up to 94% at $X_{\text{toluene}} = 1.7\%$ ($S_{\text{BA}} = 60\%$ at $X_{\text{toluene}} = 6\%$) could be obtained. Experiments under kinetically controlled conditions, i.e., in the absence of pore diffusional or external mass transport limitations, showed that the AMM-V_xSi catalysts are more active than the reference bulk material V_2O_5. The role of active oxygen in this reaction has been elucidated using vacuum transient experiments with labelled $^{18}O_2$ in the TAP reactor. The results revealed that even in the presence of isolated vanadium centres in the silica matrix the active oxygen is lattice oxygen, and the selective oxidation mechanism of toluene is therefore identical to that of bulk V-oxide phases (Mars–van Krevelen type). For the reoxidation of the active site, a new mechanism is proposed on the basis of the mechanistic studies of the present work. © 1999 Academic Press

INTRODUCTION

Selective oxidation reactions with air are of great interest for the chemical industry as well as for basic research. The direct transformation of toluene to benzaldehyde (BA) is often used as a test reaction to investigate the performance of catalysts, e.g., for gas-phase partial oxidation of methyl aromatics. Furthermore, toluene can be subject to electrophilic as well as nucleophilic attack by oxygen and can therefore be applied to investigate different active oxygen species. It is well known that vanadium-oxide-based catalysts are selective in toluene conversion to benzaldehyde as has been reported in a variety of papers (1–3). Benzaldehyde selectivities of $S_{\text{BA}} = 47\%$ ($X_{\text{Toluene}} = 18\%$; $T_{\text{R}} = 723$ K) can be obtained (1). Using appropriate carrier materials, such as SiO_2, and dopants, the benzaldehyde selectivity at similar conversion can be further increased (1). However, conflicting results have been presented in the literature for the same active metal component, i.e., if the vanadium is highly dispersed or embedded in a microporous environment. Whittington and Anderson (4) found total oxidation products to be dominant in the gas-phase oxidation of toluene over V-silicalite, V-ZSM 5, and V-Aerosil 90. Benzaldehyde production in all cases did not exceed a selectivity of 9% ($X_{\text{toluene}} < 20\%$). A possible explanation for the different reaction behaviour is a change in the reaction mechanism due to the different structures of the active sites in the bulk material (domains of V_2O_5) relative to the isolated V-centres in the V-zeolites. In this context the nature of the active oxygen species is of importance. Different forms of active oxygen species may exist on the catalyst surface, leading to the formation of selective oxygenates or total oxidation products (5–7). Lattice oxygen is mainly found to be the active and/or selective species in gas-phase oxidations on vanadium-containing catalysts.

Mars and van Krevelen studied the kinetics of the gas-phase oxidation of benzene, toluene, naphtaline, and anthracene on V_2O_5 catalysts (8). They postulated a two-step reaction mechanism, known as the Mars–van Krevelen mechanism: The reaction of the aromatic hydrocarbon occurs with lattice oxygen only. This first step is followed by reoxidation of the vacancies in the oxide network by gas-phase oxygen. However, there are also indications in the literature that adsorbed oxygen species are active and selective in hydrocarbon oxidation catalysis. In Table 1 some examples are summarised, showing that in vanadium-containing catalysts different forms of oxygen are proposed to be selective. The question of whether lattice or adsorbed oxygen is the selective form in V-containing catalysts is influenced by several parameters in which the distribution of vanadium active sites on the catalyst surface seems to play an important role.

In this paper we present the results of vacuum pulse and stationary flow experiments with $^{18}O_2$ to determine whether the atomically isolated vanadium centres in amorphous microporous mixed oxides (AMM) lead to a change in the reaction mechanism relative to the bulk V_2O_5. The catalysts studied have been prepared by an acid-catalysed sol–gel

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TABLE 1

Proposed Selective Forms of Oxygen in Hydrocarbon Oxidation over Vanadium-Containing Catalysts

Reaction	Catalyst	Oxygen species	Method	Ref.
Methane → formaldehyde	V_2O_5/SiO_2	lattice		(25)
Methane → formaldehyde	V-Carbosil	adsorbed + lattice	TAP	(26)
Methane → formaldehyde	$V_2O_5/SiO_2/V_2O_5/TiO_2$	gas phase	kinetics/TPR	(27)
Ethane → acetic acid	VPO_x/TiO_2	lattice	kinetics	(28)
Propane → propene	V/MgO	adsorbed + lattice	TAP	(29)
Propane → propene	$(VO)_2P_2O_7$	adsorbed + lattice	TAP	(7)
Propane → acrylonitrile	VSb_xO_y	lattice, different sites	TAP	(30)
Butane → maleic anhydride	$(VO)_2P_2O_7$	lattice	TAP	(31–33)
		adsorbed + lattice	TAP	(20)
		adsorbed dioxygen	kinetics	(34)

process known to provide AMMs characterised by narrow micropore size distributions and isolated V-centres (no domains). There are already several examples of selective oxidation reactions of hydrocarbons catalysed by AMM-type materials, such as epoxidation of alkenes with TBHP or with organic hydroperoxides (9, 10) and H_2O_2 (11), oxidative coupling of propene with air (12), and oxidation of cyclohexane (13). It has been shown that the gas-phase oxidation of toluene with air provides high benzaldehyde selectivity with the isolated centres of AMM-Mn_xSi-catalysts, whereas with Mn-domains and the pure manganese oxides combustion dominates (14). Even shape-selective properties have been identified for AMM-type catalysts (15). However, there is no information on the source of active oxygen in such AMM-catalytsts. The data on the V-containing zeolites suggest the presence of domains in the case of selective oxidation with AMM-V_xSi, while the presence of isolated V-centres in these materials has been confirmed by EXAFS (13) as well as by DRIFT-studies (16).

The role of lattice oxygen in the selective oxidation with bulk V-oxide can be readily rationalised in accordance with Andersson (17) and Busca *et al.* (18) by the simplified mechanism outlined in Fig. 1b. Here selective oxidation of toluene involves essentially lattice oxygen, assisted by the redox properties of the neighbouring V-centres. Gas-phase oxygen is only required to reoxidise the reduced surface vanadium centres. As long as lattice oxygen can be supplied from the bulk of the surrounding vanadium oxide domain, oxidation may proceed even without gas-phase oxygen and may result in undesired sequential oxidation up to total oxidation for a high average oxidation state of the domain. Such an oxidation must be different on isolated V-centres, where no easy exchange of the lattice oxygen with neighbouring metal atoms is possible. A proposed simplified mechanism for toluene oxidation on an isolated V-centre in silica is outlined in Fig. 1a. Although the first step, oxidative addition of toluene, may proceed as on the bulk vanadia domain (Fig. 1b), the lack of oxidation properties in the neighbouring Si-centres, as well as the lack of oxygen supply from the bulk silica phase, might require that gas-phase oxygen assists the elimination of the benzaldehyde; even so, the oxygen of the benzaldehyde may still originate from the lattice rather than from the gas-phase. These hypotheses suggest that oxidation on isolated centres should be much more selective than oxidation on the surface of bulk vanadia domains. However, this hypotheses is only valid if the nonselective oxidation to CO_x does also occur mainly by lattice oxygen. In fact, as will be shown later in the text, only the smaller part of the CO_x is formed by gas-phase oxygen.

EXPERIMENTAL

Catalyst Preparation

The chemical composition of the sol for the preparation of the AMM-V_xSi catalysts is given by V^V(triisopropoxide oxide) : TEOS : H_2O : HCl : EtOH = $X : (100 - X) : 200 : 35 : 300$, where X is the relative molar amount of the vanadium precursor. The vanadium alkoxide is dissolved in ethanol in a polypropylene beaker. Then the TEOS (tetraethyl orthosilicate) is added while stirring occurs. The gelation process is started by adding water and hydrochloric acid as an 8 N solution while stirring. The beaker is then covered with parafilm. Gelation was obtained after about 3 days. After drying at room temperature, the catalysts are calcined using the following temperature program: from RT at 0.1 K/min to 338 K, kept at 338 K for 180 min, then heated to 673 K at 0.2 K/min and kept there for 180 min, then allowed to cool slowly to RT.

Catalyst Characterisation

Ar adsorption isotherms were obtained at the temperature of liquid Argon with an Omnisorp360 using a static technique for adsorption and desorption. Samples were heated to 250°C and evacuated for 12 h at a pressure of 1×10^{-6} Torr. The micropore distribution was calculated from the isotherm by the method of Horváth and Kawazoe

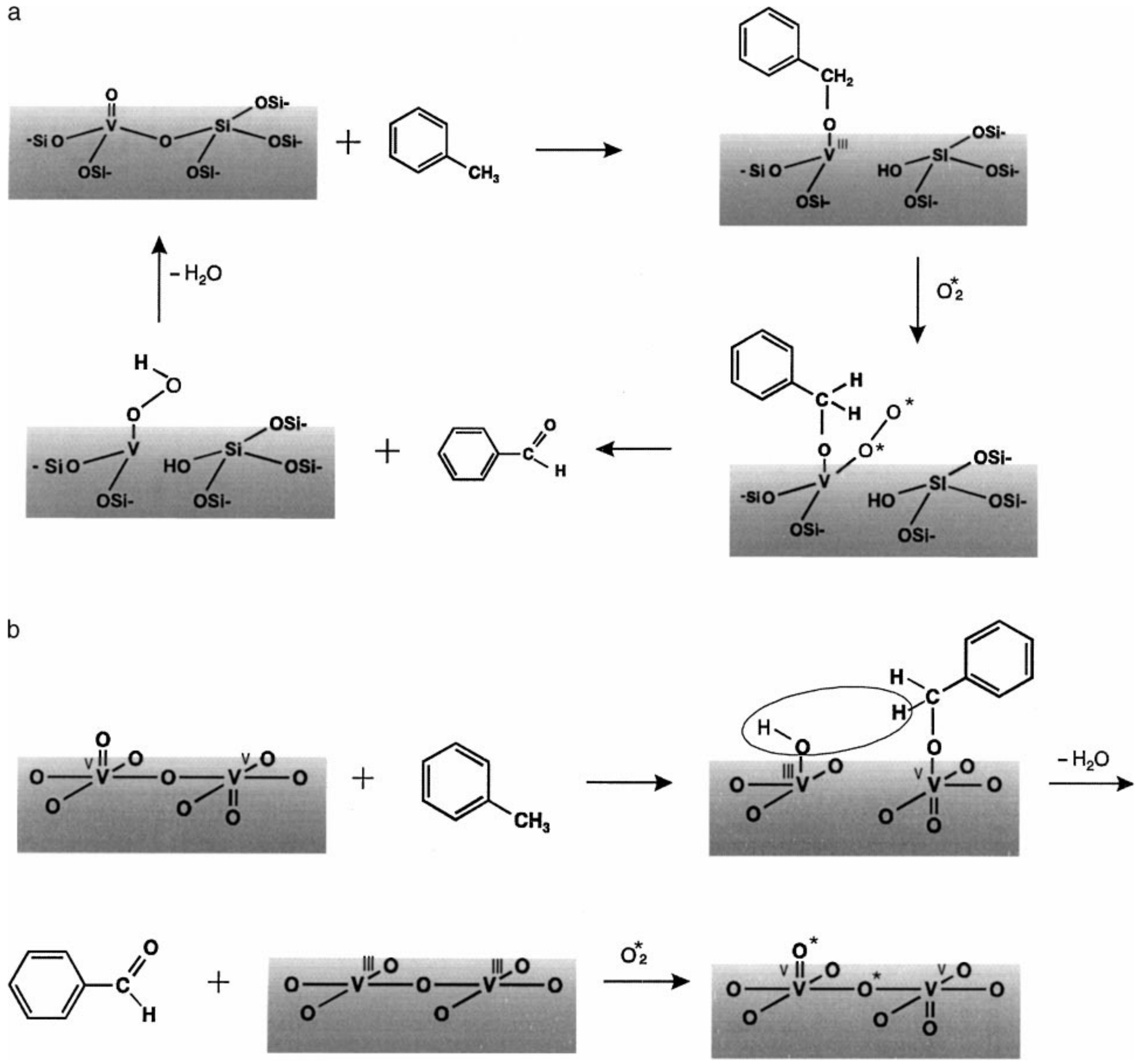

FIG. 1. (a) Mechanistic hypothesis for the selective oxidation of toluene with O_2 on a bulk V-oxide surface. (b) Mechanistic hypothesis for the selective oxidation of toluene with O_2 on an isolated V-centre at the surface of a silica matrix.

(19). The photographs were taken with a Nikon Optiphot-2 light microscope. X-ray powder diffraction patterns (XRD) were obtained with a Stoe Stadi 2/PL powder diffraction system. The AMM catalyst was examined with a high-resolution transmission electron microscopy (HRTEM) on a HITACHI HF 2000 instrument combined with energy dispersive X-ray analysis (EDX). Elemental distribution has been investigated by selected area EDX microanalysis with area sizes varying from 2 nm to several μm. The samples were crushed in an agate mortar in a methanol suspension and transferred to a holey carbon grid (copper, 3-mm diameter). IR-spectra were taken on a Bruker IFS 48 spectrometer using DRIFTS mode.

Steady-State Catalytic Studies at Ambient Pressure

The catalytic activity of the catalysts for the selective oxidation of toluene to benzaldehyde was investigated in a tubular fixed-bed reactor at atmospheric pressure. The reactor, a quartz glass tube (450-mm length, 6-mm diameter), was heated by an electric furnace. The catalyst bed was positioned in the isothermal zone in the middle of the quartz tube fixed with quartz wool. Toluene was added by a syringe to the air as the carrier gas (controlled by a mass flow controller). The low-boiling reaction products were collected for GC-analysis in a cold trap (195 K) after the reactor while the formation of CO_2 was monitored continuously by a gas sensor. The reaction was performed at 410°C at a flow rate of 90 ml $\cdot$ min^{-1} with 100 mg catalyst (particle size 1–2 μm) for most of the investigations. The molar ratio of oxygen to toluene was kept at 9.5. Conversions, yields, and selectivities were calculated for steady-state conditions.

Vacuum Transient Experiments

Vacuum transient experiments were performed in the Temporal-Analysis-of-Products reactor (TAP). A detailed description of the principles of the methods available in this reactor is given elsewhere (20). The operating conditions in the present work are as follows: the amount of catalyst, usually about 22 mg, was placed in the isothermal zone of a stainless steel micro catalytic fixed-bed reactor between two layers of quartz. Gas pulses (10^{15} to 10^{16} molecules/pulse) entered the reactor containing the catalyst sample and were analysed at the reactor outlet by a quadrupole mass spectrometer. Gas transport in the reactor exclusively occurs by diffusion processes under these conditions. Additionally, continuous flows of gas mixtures were passed through the reactor and mass spectra (amu = 1 to 100) were taken sequentially to follow the changes in product composition with time. The average gas flow amounted to 0.4 ml/min (STP). The pressure in the reactor was calculated to <1 kPa under these conditions (no direct measurement possible). Signals at mass numbers belonging to several compounds were deconvoluted by taking into account the fragmentation patterns of the pure substances measured separately using a quartz-filled reactor. Details of the gas mixtures used in the experiments are given in Results and Discussion.

RESULTS AND DISCUSSION

Catalyst Characterisation

Sorption measurements. Figure 2 shows the pore size distribution of AMM-V$_x$Si catalysts with different vanadium contents. Vanadium contents up to 5 mol% have no

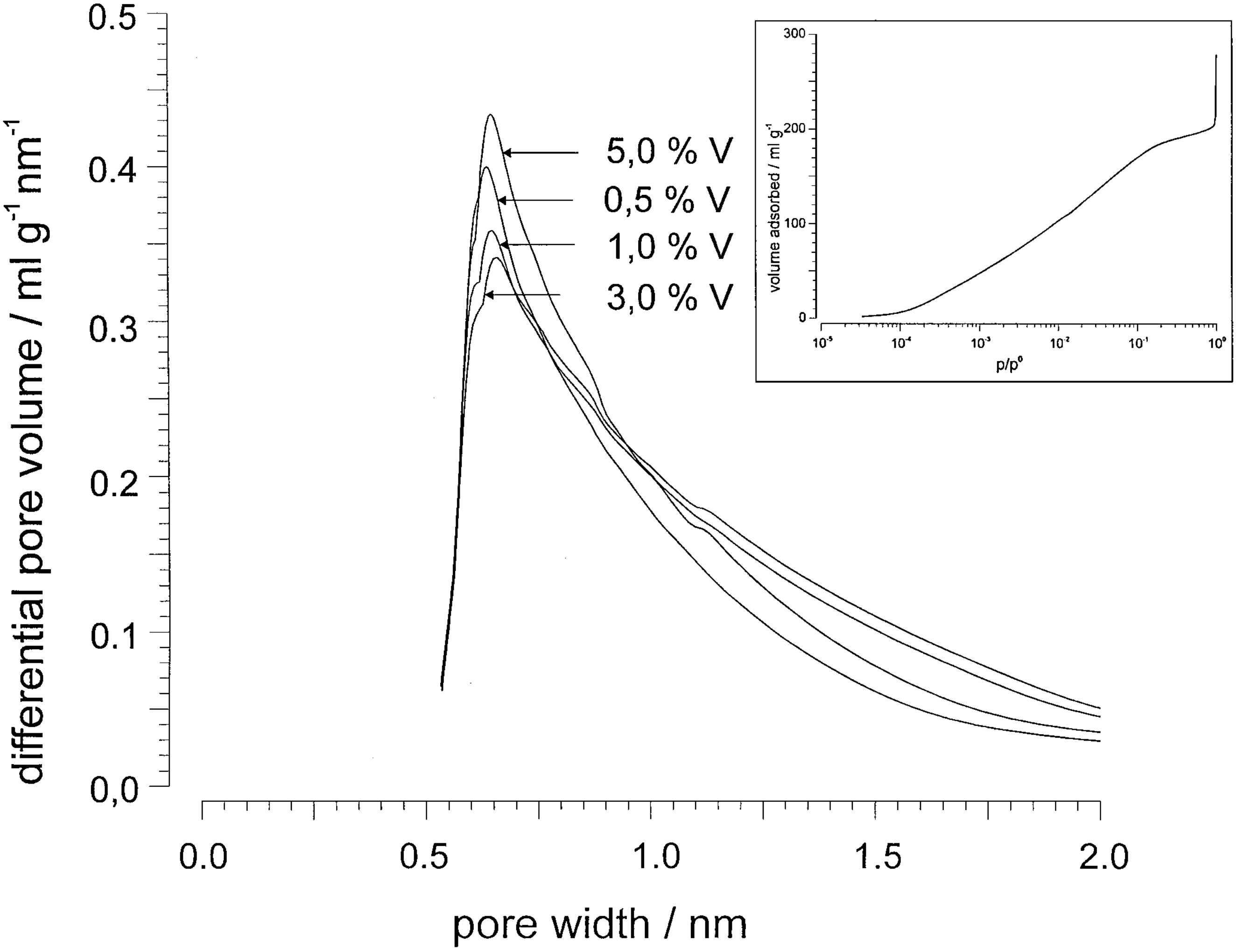

FIG. 2. Micropore size distribution of several AMM-V$_x$Si catalysts and the high resolution Ar-adsorption isotherm of the AMM-V$_5$Si.

TABLE 2

Surface Areas and Mean Pore Diameters of AMM Catalysts with Varying V-Content

Sample	Surface area (m^2/g)	Mean pore diameter (nm)
AMM-$V_{0.5}$Si	473	0.9
AMM-V_1Si	590	1.0
AMM-V_3Si	709	1.1
AMM-V_5Si	559	1.0
V_2O_5	5.4	no micro- or mesopores

significant influence on the maximum in the pore size distribution (0.65 nm pore diameter). Due to the tailing of the pore size distribution to larger diameters the mean pore diameter amounts to 1 ± 0.1 nm (see Table 2). As is typical for sol–gel prepared catalysts, the BET surface areas of all samples are high, from 473 to 709 $m^2 \cdot g^{-1}$. The acid catalysed sol–gel process leads to microporous materials with a narrow pore size distribution.

X-ray diffraction (XRD). XRD spectra (not shown as a figure) were recorded to control the stability of the incorporation of vanadium in the catalysts. The lack of evidence for crystalline SiO_2 or vanadium oxide domains is consistent with the expected amorphous structure of the materials. The XRD patterns of the used catalysts after the gas-phase oxidation of toluene at 410°C still showed no indication of crystalline areas, indicating that the X-ray amorphous microstructure remains stable even at the relatively high temperatures under reaction conditions.

Electron microscopy (HRTEM/EDX). The high-resolution image of the sample AMM-V_5Si confirmed the amorphous character of the catalyst (not shown). Neither the electron diffraction pattern typical for microcrystalline samples nor lattice fringes could be detected. The homogeneous distribution of the vanadium was confirmed by the combination of high-resolution imaging with energy-dispersive X-ray microanalysis (EDX). The Si/V ratios in the thin particles do not depend on the area selected for the point analysis (area range, 2 nm to several μm), confirming the homogeneous elemental distribution of vanadium in the sample. The lack of evidence for the presence of vanadium oxide domains points to isolated V-centres in the microporous silica framework, in perfect agreement with parallel studies on AMM-V_xSi catalysts (13). EXAFS studies had shown that the nature of these isolated V-centres is best described as $O{=}V(O\text{-})_3$ with all three O-atoms exclusively connected to Si-atoms of the surrounding silica framework (13).

IR-spectroscopy (DRIFTS). Figure 3 shows the diffuse reflection IR spectra of the catalysts AMM-V_xSi with a molar vanadium content ranging from 0.5 to 5 mol% and vanadium pentoxide (V_2O_5) as reference material. The main bands of V_2O_5 (at 1025, 980, and 850 cm^{-1}) refer to the $\nu_{as}(V^{5+}{=}O)$ vibration (21, 22), the $\nu_{as}(V^{5+}{=}O,)$ vibration for amorphous or two-dimensional structures (23), and the $\nu_{as}(V\text{–}O\text{–}V)$ vibrations (23), respectively. The band at 980 cm^{-1} has also been ascribed to V^{4+} species (22), which usually remain even in an oxygen-pretreated V_2O_5 sample. None of the signals of the reference material are present in the AMM-derived spectra, confirming the absence of large vanadium pentoxide domains. With increasing vanadium content a slight increase of the band at 935 cm^{-1} can be noted in the spectra of the AMM-materials. This band can be attributed to the presence of pseudotetrahedrally coordinated oxovanadium species connected to the oxide network via three oxygen atoms (24), confirming above-mentioned EXAFS study.

Catalytic Experiments at Ambient Pressure

The selective toluene oxidation with air to benzaldehyde was used to study the catalytic performance of the AMM-V_xSi catalysts. In order to compare the catalytic behaviour of isolated vanadium sites with that of domains of V^V-oxide (bulk V_2O_5), it is important that the reactions are performed in the microkinetic regime. As a consequence, proper reaction conditions were determined, under which external and pore diffusional mass transport limitation could be excluded. For further improvement of the benzaldehyde yields, the vanadium content, residence time, and reaction temperature were varied.

External mass transport limitation. The regime of mass transport limitation was identified by varying the gas flow rate at constant modified residence time $m_{cat}\dot{V}^{-1}$ (410°C, particle size 1–2 μm). The modified residence time was kept constant by a proportional increase of the catalyst mass with increasing gas-phase flow rates. Figure 4 shows that the reaction rate is not limited by external mass transport

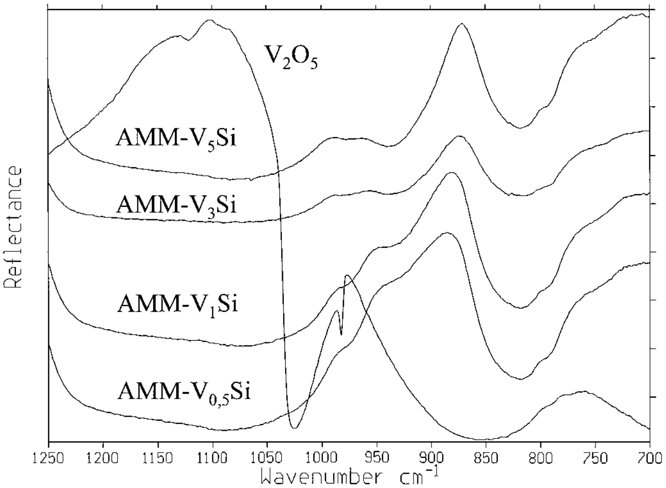

FIG. 3. IR-DRIFTS spectra of AMM-V_xSi ($x = 0, 5, 1, 3,$ and 5) as a function of vanadium content and the reference material V_2O_5.

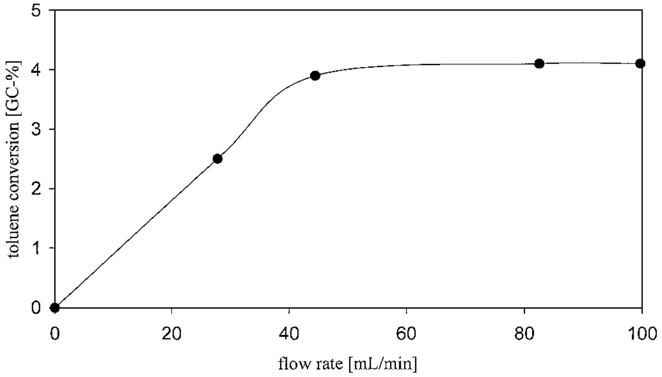

FIG. 4. Dependence of total toluene conversion on the flow rate with catalyst AMM-V_5Si.

for total flow rates larger than 45 ml · min^{-1}. Therefore, in all further experiments a flow rate of 90 ml · min^{-1} was used.

Pore diffusional limitations. Microporous catalysts such as zeolites or the AMM-catalysts are prone to pore diffusional limitations affecting the product formation and selectivity. The potential effect of pore diffusion on toluene conversion and benzaldehyde yield was investigated by varying the catalyst particle size under constant reaction conditions (410°C, 90 ml · min^{-1} total flow rate, 30 mg catalyst). This type of experiment can be applied when the pore structure and the distribution of the active sites in the catalyst particle are homogeneous, as already shown above in the characterisation of the AMM-materials. The different particle size fractions were obtained from milled catalysts by microsieving. Special care was taken to assure the absence of smaller catalyst particles in the larger sieve fractions. Sample 1 (AMM-V_5Si) was crushed manually in a mortar and then separated by microsieving; sample 2 was milled in a ball mill without further sieving (particle size <1–2 μm). Light microscopy was used to confirm the particle sizes in the sieving fractions, as well as to confirm the absence of impurities due to electrostatically attached smaller particles. Figure 5 shows the effect of particle size on toluene conversion under identical reaction conditions. At particle sizes smaller than 50 μm the conversion is constant, confirming the reaction rate control and the absence of pore diffusional limitations within the fraction of pores available for catalysis. In all further experiments a catalyst particle size <1–2 μm was used.

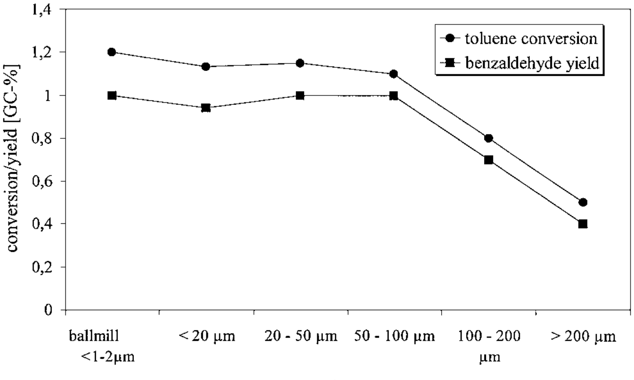

FIG. 5. Dependence of toluene conversion and benzaldehyde yield on the catalyst particle size.

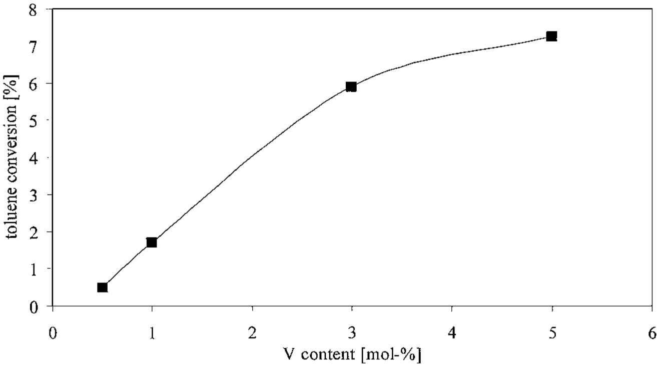

FIG. 6. Dependence of toluene conversion on the vanadium content of the AMM-catalysts.

Influence of vanadium content. The influence of the vanadium content on the conversion was examined in order to optimise the benzaldehyde yield. As shown by the physisorption measurements there is no influence of the vanadium content on the pore structure up to 5 mol%. So the catalytic activity is just influenced by the higher amount of isolated active centres. A catalyst mass of 100 mg was used at a temperature of 410°C (flow rate 90 ml · min^{-1}, particle size 1–2 μm). Figure 6 shows a linear increase in toluene conversion with increasing vanadium content up to 3 mol%, confirming first-order reaction rate in vanadium concentration. A vanadium content higher than 5 mol% does not lead to a further increase in toluene conversion under the reaction conditions chosen.

Influence of modified residence time ($m_{cat} \cdot \dot{V}^{-1}$). The residence time of the reaction components in the catalyst bed is a very sensitive parameter affecting conversion and yield. This influence was studied by varying the catalyst mass (m_{cat}) between 25 and 150 mg at a constant flow rate ($\dot{V}$) of 90 ml/min (AMM-V_5Si, 410°C, particle size <1–2 μm). Figure 7 shows a first-order dependence of toluene conversion and benzaldehyde yield on residence time. However, benzaldehyde selectivity decreases with increasing modified residence time, indicating consecutive degradation reactions. Interpolation to residence time 0 shows that there is nearly no background activity attributable to autoxidation at the reaction temperature of 410°C.

Influence of reaction temperature. The influence of the reaction temperature on toluene conversion and benzaldehyde yield was studied in the temperature range between 370 and 430°C. Control experiments without catalyst

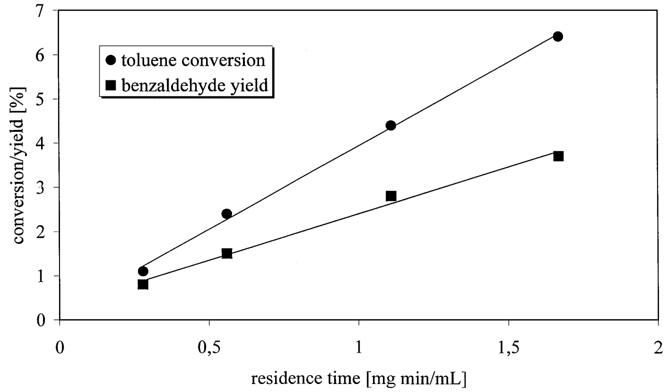

FIG. 7. Dependence of toluene conversion and benzaldehyde yield on the modified residence time (AMM-V_5Si).

showed that combustion of toluene by autoxidation starts at temperatures above 430°C. For the experiments, a catalyst mass of 100 mg was used (AMM-V_5Si, particle size <1–2 μm, flow rate 90 ml · min^{-1}). Figure 8 shows that conversion and yield increase and selectivity decreases with temperature. With consecutive stepwise (10°C) increase and decrease in the reaction temperature from 370 to 430°C and back in single experiments, a slight decrease in activity was observed. This decrease in activity is attributed to coking, since the initial activity of the catalysts could always be fully regenerated after catalyst treatment in air at 410°C for 3 h.

Comparison with reference catalyst. In Table 3 the results of the gas-phase oxidation of toluene to benzaldehyde under optimised conditions are summarised. The experiments were repeated with V_2O_5 under identical reaction conditions (same catalyst mass, same molar amount of the active metal compound). The vanadium pentoxide (nonporous) was milled in a ball mill before the reaction (particle size <1–2 μm, nonporous, only outer surface area of 5.4 m^2/g). Table 3 shows a high benzaldehyde selectivity at low conversion for the AMM-materials. Under identical reaction conditions the reference material V_2O_5 shows a different behaviour. Using the same catalyst mass (same modified residence time) leads to much higher conversions and much lower selectivities (combustion is dominating). This behaviour can be explained by the higher molar amount of vanadium, which favours the total oxidation of toluene to carbon dioxide. Using the same molar amount of active metal compared to the AMM catalyst (V_5Si), no significant conversion was achieved. This can be attributed to the much higher V-oxide-surface in the AMM-material (5 mol% corresponding to about 25 m^2/g as an estimate) relative to the negligible total surface area of the 14 mg V_2O_5. The higher activity for combustion of the 100-mg sample of V_2O_5, however, cannot be attributed to the surface area, since even here the total V-oxide surface is much smaller than 1 m^2 and thus much smaller than that of the AMM-catalyst. Before the steady state is reached, the CO_2 formation over V_2O_5 decreases with time until it approaches a constant value. This effect may be explained by assuming a reaction mechanism utilising lattice oxygen (see the next section). On the fresh catalyst an excess of reactive lattice oxygen is probably responsible for the strong total oxidation. With increasing reaction time, however, the number of available active oxygens on the surface decreases due to the difference in the conversion rate of toluene (reduction) and the reoxidation rate of the oxide lattice defects by gas-phase oxygen.

TABLE 3

Comparison of the Catalytic Performances of the AMM Catalysts and V_2O_5

Catalyst	X(toluene) (%)	S(benzaldehyde) (%)
AMM-V_1Si (100 mg = 0.015 mmol V)	1.7	94
AMM-V_5Si (100 mg = 0.077 mmol V)	6.0	60
V_2O_5 (14 mg = 0.077 mmol V)	0	0
V_2O_5 (100 mg = 0.55 mmol V)	26.9	14

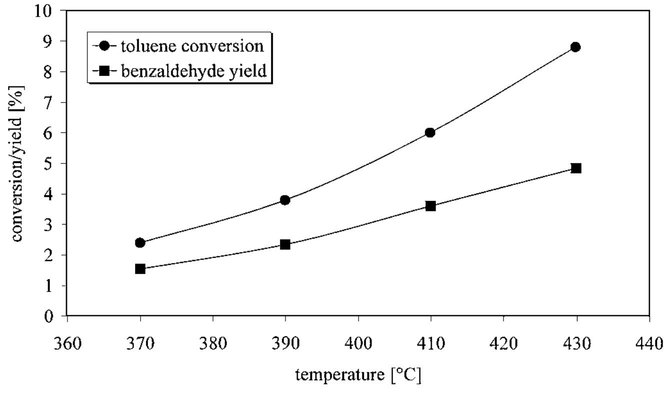

FIG. 8. Dependence of toluene conversion and benzaldehyde yield on the reaction temperature (AMM-V_5Si).

Vacuum Transient Experiments

Vacuum pulse experiments in the presence and absence of oxygen. Sequential pulse experiments were performed in the presence and absence of unlabled $^{16}O_2$ and isotopically labeled oxygen $^{18}O_2$ to obtain information about mechanistic details of the toluene oxidation over V_2O_5 and the AMM catalysts, focussing on the participation of lattice and adsorbed oxygen in the reaction. Figures 9a and 9b show the response signals obtained after the sequential pulses of the two gas mixtures, (a) toluene : Ne (1 : 20) and (b) O_2 : Ne (1 : 2.5), with time differences of $\Delta t = 1$ and 0.5 s over AMM-V_5Si and V_2O_5, respectively. The average residence time for the inert gas neon remained always between 0.05 and 0.15 s, depending mainly on the particle size of the

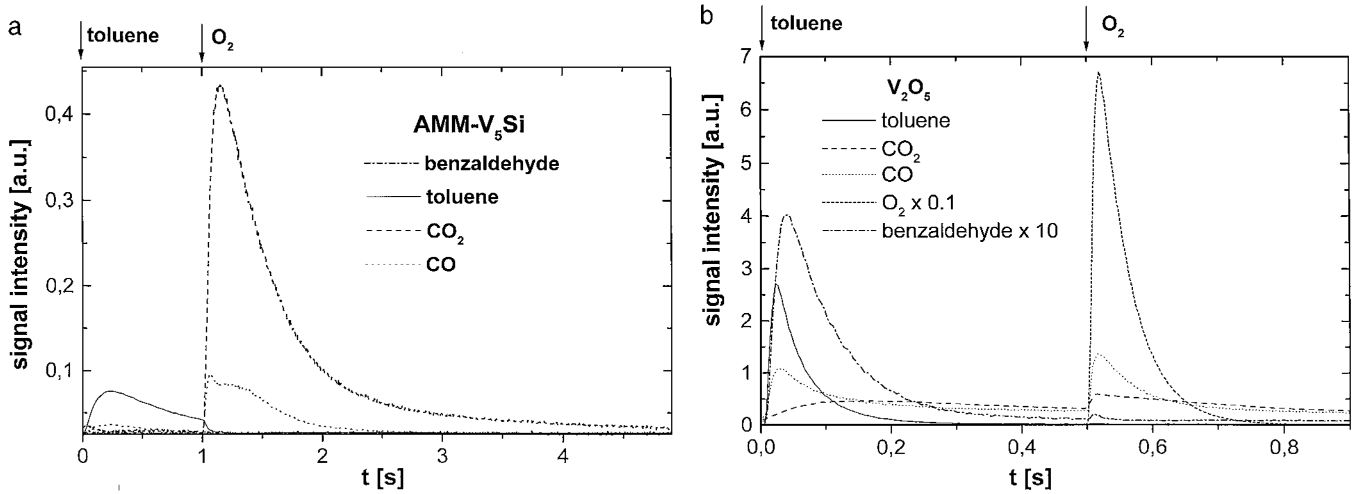

FIG. 9. (a) Response signals of masses 105 (benzaldehyde), 91 (toluene), 44 (CO_2), and 28 (CO) at alternating pulses of toluene/Ne at $t = 0$ s and O_2/Ne at $t = 1$ s on AMM-V_5Si. (b) Response signals of masses 105 (benzaldehyde), 91 (toluene), 44 (CO_2), 32 (O_2), and 28 (CO) at alternating pulses of toluene/Ne at $t = 0$ s and O_2/Ne at $t = 0.5$ s on V_2O_5.

catalyst. Formation of benzaldehyde, CO, and CO_2 is observed in the response signal of the toluene/Ne mixture over V_2O_5, whereas no products are observed over AMM-V_5Si. In the response signal of the oxygen/Ne mixture, CO and CO_2 were observed for both the AMM-V_5Si catalyst and the V_2O_5. The benzaldehyde formation on V_2O_5 in the absence of gas-phase oxygen points to lattice oxygen as the reactive form of oxygen, in agreement with the earlier results of Mars and van Krevelen (8) for V_2O_5 and of Busca *et al.* (18) for vanadium supported on titania. In contrast, the formation of CO and CO_2 for both catalysts in the response of the oxygen pulse indicates that adsorbed oxygen from the gas-phase is the active total oxidation species which reacts with remaining carbon ad-species strongly adsorbed on the catalyst during the toluene pulse. On V_2O_5 both lattice and adsorbed oxygen species seem to catalyse the total oxidation.

No significant amount of products are observed over the AMM-V_5Si catalyst in the absence of gas-phase oxygen. Furthermore, the response signal for toluene has a much lower intensity than expected for a solely reversible interaction. This indicates that either toluene or its reaction products are strongly adsorbed on the AMM catalyst, which is not observed for V_2O_5. Control experiments using pure amorphous microporous silica without the active vanadium compound showed a delayed response signal for toluene due to slow diffusion in the micropores. However, the response signal exhibits a high intensity, and quantification of the signal area showed that the interaction of toluene with the silica matrix is reversible. It was therefore concluded that the missing part of the toluene signal over the AMM-V_5Si catalyst must be due to strong adsorption of toluene or its partial oxidation product, i.e., benzaldehyde, on the isolated vanadium sites. The strong adsorption was confirmed by a control experiment passing 2000 pulses of the toluene/Ne mixture (1 : 20) over the AMM catalyst. After 1 h in vacuum at 410°C an O_2/Ne mixture was sent over the catalyst. CO_2 formation occurred in the response of the oxygen pulses, decreasing in intensity with an increasing number of oxygen pulses (see Fig. 10). The CO_2 formation indicates that strongly bound carbon-containing substances, most probably products originating from the oxidation of toluene with the AMM catalyst, remain on the catalyst surface even under vacuum conditions.

A strong interaction of toluene with vanadium monolayer supported catalysts has been reported by Miyata *et al.* (21) from FTIR investigations on the adsorption and reaction of aromatic hydrocarbons on V/Zr-oxide catalysts. It was observed that during the interaction a "π"-complex is

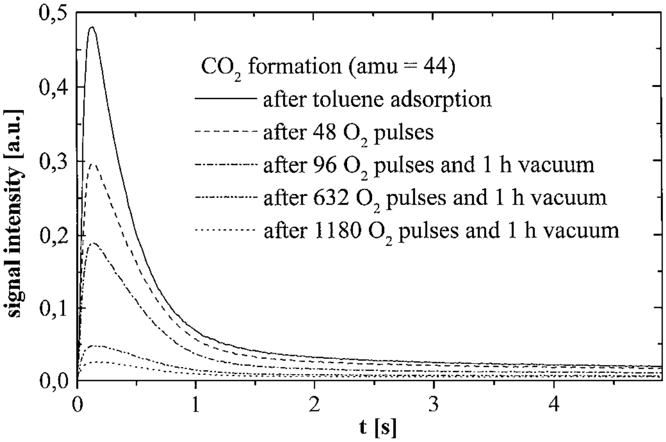

FIG. 10. Response signals of mass 44 (CO_2) on AMM-V_5Si after toluene adsorption (2000 pulses toluene/Ne), 48, 96, 632, and 1180 O_2-pulses.

formed with participation of the V=O groups and that the aromatic ring remains intact even at higher temperatures, where benzyl- and benzaldehyde vibrations were observed in the presence of small amounts of gas-phase oxygen. These results indicate that toluene and its oxidation products are strongly adsorbed on the catalyst. It was also observed that multilayer vanadium on ZrO_2 had a lower activity compared to the monolayer catalyst. It can be assumed that during the interaction of toluene with the AMM-V_5Si catalyst the high concentration of isolated $(\text{-Si-O-})_3V{=}O$ groups is responsible for the strong adsorption of the aromatics, whereas little bonding interaction seems to occur with the V=O groups in bulk V_2O_5.

Continuous flow experiments with toluene/$^{18}O_2$ at reduced pressure. The above-mentioned results could not clarify the role of adsorbed or lattice oxygen in the formation of benzaldehyde over the AMM-catalysts. Therefore, experiments using isotopically labelled oxygen $^{18}O_2$ were performed. Because of the strong toluene adsorption the catalyst mass was reduced for the AMM-catalyst relative to the experiments in the presence and absence of gas-phase oxygen. The gas mixture of toluene, $^{18}O_2$, and Neon (1 : 5 : 54) was passed continuously over the catalyst beds. Figures 11a–11d show the isotopic distribution of the products benzaldehyde and CO_2 independent of the reacted amount of $^{18}O_2$ for the AMM-V_5Si catalyst and V_2O_5.

The preferential formation of ^{16}O-benzaldehyde on AMM-V_5Si and V_2O_5 at the beginning of the reaction (more than 80%) supports the Mars–van Krevelen mechanism for the selective oxidation of toluene (cf. Figs. 11a and 11b). The ^{16}O portion is decreasing with time because the ^{18}O is reoxidising the vanadium centres, leading to an increase in the formation of ^{18}O-benzaldehyde. For the AMM-V_5Si the participation of smaller amounts of adsorbed oxygen has to be assumed since on extrapolation of the isotopic distribution to a 0 converted amount of $^{18}O_2$, a portion of about 20% ^{18}O-benzaldehyde remains, whereas for V_2O_5 only ^{16}O-benzaldehyde is formed under these conditions. The increase of the ^{18}O-benzaldehyde portion is faster for the AMM-V_5Si catalyst compared to the V_2O_5. After an $^{18}O_2$ converted amount of 0.5×10^{19} molecules,

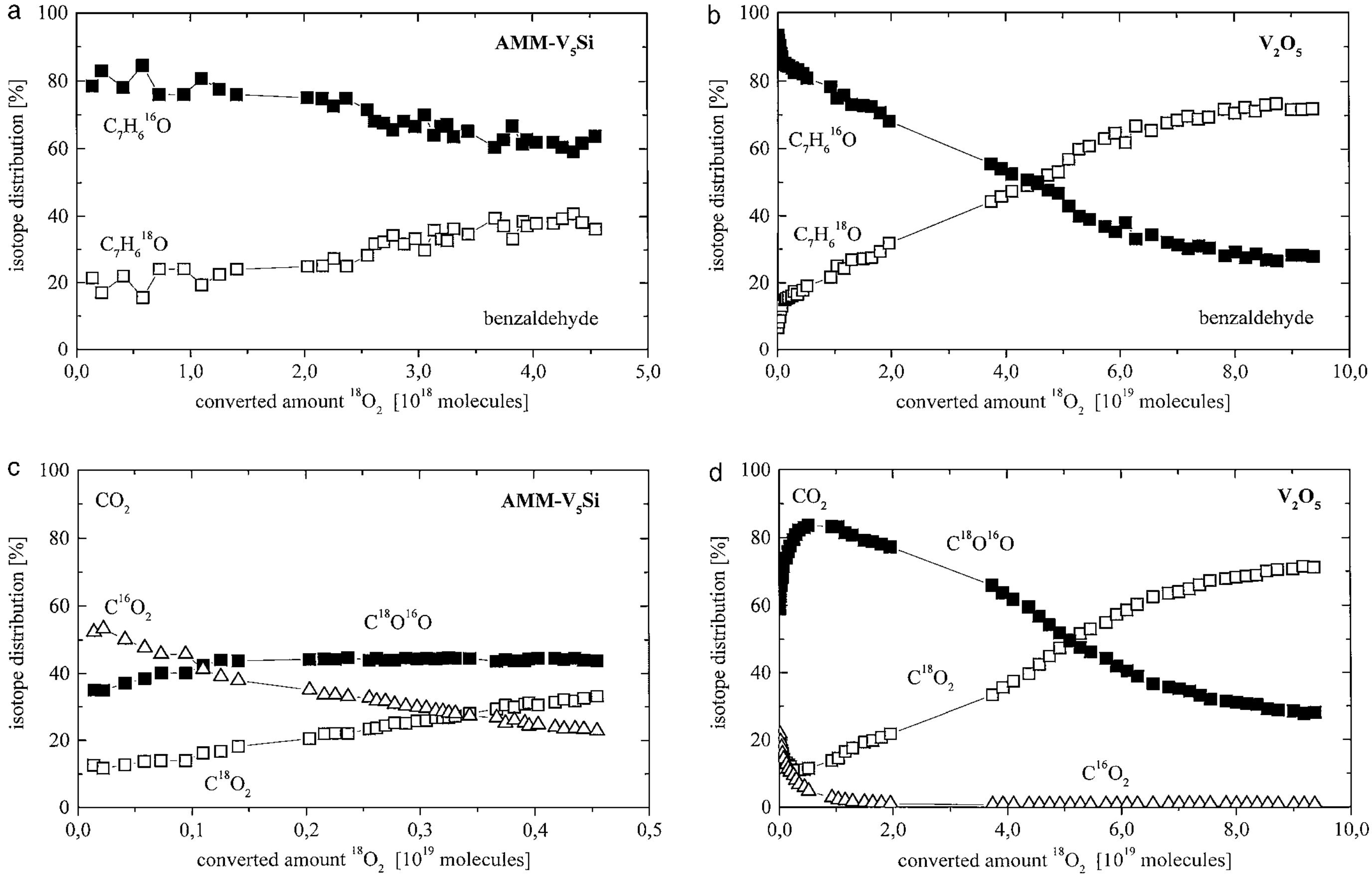

FIG. 11. Distribution of oxygen isotopes in benzaldehyde during continuous flow of toluene/$^{18}O_2$/Ne over AMM-V_5Si. (b) Distribution of oxygen isotopes in benzaldehyde during continuous flow of toluene/$^{18}O_2$/Ne over V_2O_5. (Attention: different scale from that in Fig. 11a.) (c) Distribution of oxygen isotopes in CO_2 during continuous flow of toluene/$^{18}O_2$/Ne over AMM-V_5Si. (d) Distribution of oxygen isotopes in CO_2 during continuous flow of toluene/$^{18}O_2$/Ne over V_2O_5. (Attention: different scale from that in Fig. 11a.)

already 40% of the benzaldehyde formed is labeled with ^{18}O, whereas for V_2O_5 less than 20% is so labeled. This indicates that the gas-phase oxygen used for reoxidation of the AMM catalyst is immediately transferred to the active catalytic sites, while this process is slower in the case of V_2O_5, which may be due to diffusion into the bulk and its exchange against lattice oxygen.

The isotopic distribution of oxygen in the total oxidation product CO_2 is different for AMM-V_5Si and V_2O_5. On the AMM-V_5Si the CO_2 produced mainly contains ^{16}O (about 71%; $C^{16}O_2 + 0.5\ C^{16}O^{18}O$) at the beginning of the reaction, which underlines the redox type of the reaction. However, the presence of 29% ^{18}O indicates that electrophilic adsorbed oxygen is participating in the total oxidation process. On V_2O_5 the initial portion of ^{18}O in the CO_2 is higher (about 45%), indicating a larger quantity of adsorbed oxygen being involved in the total oxidation pathways. On both catalysts the formation of the mixed isotopic product increased with time, reaching a maximum due to reoxidation of the active vanadium centres with gas-phase $^{18}O_2$. Therefore, with continuous reoxidation of the active sites the formation of $C^{18}O_2$ also increases with time on both catalysts.

The presented results show that formation of atomically isolated active vanadium centres by the acid-catalysed sol–gel process has little effect on the reaction mechanism relative to the bulk metal oxide supporting the mechanistic schemes outlined in Fig. 1. The main active oxygen in the selective pathway to benzaldehyde over the AMM-materials is lattice oxygen, most likely in the V=O group as described by Miyata *et al.* (21). The total oxidation reactions to CO_x, however, occur by participation of lattice and adsorbed oxygen species, as was shown by both vacuum pulse and continuous flow experiments in the TAP reactor. The portion of adsorbed oxygen is more pronounced for the bulk V_2O_5.

CONCLUSIONS

The preparation of vanadium-containing catalysts by the one-step acid-catalysed sol–gel process leads to the formation of amorphous microporous vanadium–silica mixed oxides (AMM-V_xSi). The microporous character was shown by physisorption measurements, which also indicate a narrow pore size distribution (mean pore diameter around 1.0 nm) and high surface areas. Using several characterisation techniques, XRD, FTIR, HRTEM/EDX, and light microscopy, it could be shown that the vanadium is homogeneously distributed in the silica matrix on the atomic scale, being stable even under the reaction conditions of toluene partial oxidation. The AMM-V_xSi were found to be active and selective catalysts for the gas-phase oxidation of toluene to benzaldehyde. To allow a valid comparison of the activity and selectivity of this catalyst with the bulk vanadium oxide, optimal reaction conditions have been worked out for the microporous material. Under kinetically controlled conditions, i.e., where mass transport processes are not rate limiting, a benzaldehyde selectivity of $S = 60\%$ was achieved at a toluene conversion of $X_{\text{toluene}} = 6\%$ ($T_R = 410^\circ C$). In contrast, using the reference material V_2O_5 at identical reaction conditions (T_R, $m_{\text{cat}} \cdot V^{-1}$) resulted mainly in total oxidation products (due to the higher conversion) and a much lower activity relative to the V-content.

The silica matrix is a nonreducible insulator with no oxygen diffusion properties. The vanadium, however, can only be reduced from V^V to V^{III}, which corresponds to the reaction of one oxygen atom per vanadium. The partial oxidation of toluene to benzaldehyde, however, requires the participation of two oxygens according to stoichiometry

$$\text{Ph-CH}_3 + O_2 \Leftrightarrow \text{Ph-CHO} + H_2O.$$

Therefore, a change in reaction mechanism on the isolated vanadium centres in the AMM catalysts relative to the V_2O_5 bulk material has to be postulated, in which the adsorbed or gas-phase oxygen is involved. The transient experiments and the continuous flow experiments using ^{18}O labelled oxygen, however, revealed that the toluene oxidation to benzaldehyde proceeds over the AMM catalyst and over V_2O_5 mainly by insertion of lattice oxygen, i.e., a Mars–van Krevelen type mechanism. Therefore, we postulate a mechanism in which the adsorbed oxygen acts as an acceptant for the hydrogen atoms to be removed and as the reoxidising agent for the reduced vanadium site (cf. Fig. 1a). Pulse experiments in the presence and absence of gas-phase oxygen provided further evidence for a strong adsorption of toluene and its reaction product benzaldehyde on the vanadium centres. The higher activity of the AMM-catalysts relative to the reference V_2O_5 is attributed to the higher number of accessible vanadium centres on a high surface area.

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