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Enhanced Product Selectivity in Partial Oxidation of Propane on Multicomponent Oxide Catalysts by Masking of Total Oxidation Sites

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A new method is reported which enables us to effectively poison strong acid sites on multicomponent metal oxide catalysts, responsible for undesired total oxidation reactions, by chemical vapor phase deposition of silane and subsequent oxidation. In the partial oxidation of propane over VSb_2WO_x/Al_2O_3 the selectivity of the primary product propene could be enhanced by 10% using a SiO_x modified catalyst compared to the unmodified sample. The selectivity towards the consecutive product acrolein also increased by a factor of 3; however, it remained low, never exceeding 6%. The effect of poisioning is explained on the basis of the changes in the physico-chemical bulk and surface properties due to the surface silane/N_2O modification and treatment under reaction conditions.

INTRODUCTION

The oxidative functionalization of alkanes to more valuable products, olefins, aldehydes, or acids, is a growing field of interest to researchers all over the world. However, although a lot of work has been performed and documented in literature so far, only one process, the partial oxidation of *n*-butane to maleic anhydride gained the level of commercial application (1). One of the major problems that prevented the technical application of other reactions is the availability of catalysts that transform the saturated hydrocarbon with high yields into the desired product. While high selectivities have often been obtained for a series of reactions at a low conversion level, the selectivity towards the desired product decreased dramatically with increasing conversion (2). The reason for this general trend can be attributed in a simplified manner to the large differences in the C–H or C–C bond dissociation enthalpies of reactants and products (2) which in turn lead to an easy total combustion of the products by consecutive reactions if the weakest bond in the product is lower by more than 30 to 40 kJ/mol (2). Assuming that only one active site on the catalyst exists there certainly will be no chance to overcome this problem since the selectivity to the desired product is then only determined by the kinetics of the reactions of formation and destruction. However, in case of complex multimetal oxides, where the alkane activation and total combustion might occur on different sites there is a chance to enhance the selectivity to the intermediate desired product by selective poisoning of the total oxidation sites. An example for such a complex metal oxide system are the modified vanadium antimony oxides. These are well known to exhibit high activity and selectivity for the oxidative conversion of propane to acrylonitrile in the presence of ammonia (3). Yields to acrylonitrile (ACN) as high as $Y_{ACN} = 39.0\%$ ($VSb_5W_{0.5}Te_{0.5}Sn_{0.5}O_x$ supported on 50% silica-alumina (20% SiO_2, 80% Al_2O_3); $X_{C_3H_8} = 68.8\%$; $S_{ACN} = 56.7\%$) could be achieved. Mechanistic investigations (4) using this catalytic system showed that the insertion of nitrogen occurs via the intermediate formation of propene and acrolein. However, in the absence of NH_3 the sum of the selective products, propene and acrolein, is much less than the sum of selective products in the presence of NH_3, i.e., propene and ACN, as was observed by the present authors (cf. Table 1). Acrolein itself is only observed in traces under these conditions. Since it was found that strong acidic sites on this catalyst exist that have been attributed to be the active sites for total oxidation (5), most probably Broensted acid sites, it was assumed that under ammoxidation conditions these sites are poisoned by the excess ammonia in the reaction gas allowing the intermediates to be selectively converted to the stable product ACN.

Behind this background it was the aim of the present work to find a method to selectively poison the strong acidic sites on the catalyst surface in order to prevent total oxidation of the desired products in the partial oxidation of propane over a VSb_2WO_x/Al_2O_3 catalyst. The modification of surface acidity of oxide catalysts has been successfully

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TABLE 1

Catalytic Performance of a VSb_5WO_x (30 wt%)/Al_2O_3 Catalyst in the Partial Oxidation of Propane in the Presence and Absence of NH_3

Gas mixture	$X_{C_3H_8}$	X_{O_2}	X_{NH_3}	Selectivity/%				
$C_3H_8/O_2/NH_3$/inert	%	%	%	ACN	Acrolein	C_3H_6	CO_x	C_2H_4
1:2:2:2.5	28	58	24	33.1	Traces	30.9	31.0	0.3
1:2:−:4.5	37	56	—	—	1.6	29.9	65.5	2.9

Note. $T_R = 830$ K.

demonstrated in literature applying chemical vapour deposition (cvd) of silicon compounds like silicon alkoxides. The majority of these studies was related to modification of zeolites (6) and only a few studies dealt with oxides like alumina and zirconia (7, 8). However, the tendency of the alkoxides to fully cover the surface forming thin silica monolayers did not allow their application for the present work. Therefore, silane was chosen as the deposition agent, because it exclusively anchors on the acidic sites with no further grow of a monolayer (9). Nitrous oxide was used to stabilize the remaining hydride functions by transforming them into OH-groups. It is important to note that due to this process also a small number of new OH-groups are created. These, however, are less acidic compared to the original OH-groups (10).

EXPERIMENTAL

Catalyst Preparation

The catalyst VSb_2WO_x[30 wt%]/Al_2O_3 was prepared by a redox reaction in aqueous medium (5). 1.755 g of NH_4VO_3 (Janssen, purity: >99%), 4.373 g Sb_2O_3 (Heraeus, 99.99%) and 33.325 g $Al(OH)_3$ (Merck, 99.99%) were added to an aqueous 1-*N* ammonia solution at $T = 363$ K. The reaction mixture is continuously stirred under reflux for 24 h. 3.695 g $H_{26}N_6O_{40}W_{12}$ (Fluka, >97%) were added and the stirring under reflux was continued for additional 18 h. The resulting mixture was evaporated to dryness and the resulting solid was kept at $T = 393$ K for 36 h. A calcination procedure followed: 24 h at 623 K, 3 h at 773 K, and 3 h at 900 K. The catalyst was crushed and sieved and particle fraction of $d_P = 250$–$355\ \mu$m was used for the experiments.

Chemical Vapor Deposition of Silane

Silanation was performed *ex situ* in a special experimental setup (11). Mass flow controllers enabled dosing the silane–nitrogen mixture into the reactor, which holds a basket with the catalyst on a metal frit. Differential conversions guaranteed the absence of axial gradients inside the catalyst bed as well as the absence of temperature gradients. Subatmospheric pressures could be adjusted using a back-pressure controller and a vacuum pump. Silanation was monitored by a hydrogen analyzer and by the corresponding increase in weight. A cartridge was used to determine the increase in weight in order to avoid water being adsorbed. About 1.2 g of the sample was placed in the basket and heated to 623 K in a vacuum overnight. After weighing the dried sample silanation was performed using a 10% silane/N_2 mixture (100 $ml_{STP} \cdot min^{-1}$; $P_{tot} = 0.1$ MPa; $T = 473$ K). Silanation was stopped after several times, the sample was purged and evacuated and finally the hydride functions were oxidized at 623 K for 1 h. Three degrees of deposition were achieved: 2.49 wt% (4 min silanation), 5.77 wt% (10 min), and 8.31 wt% (240 min).

Catalyst Characterization

The physico-chemical properties of the catalysts were determined with respect to their bulk and surface properties before and after the catalytic tests applying several methods. Bulk structure properties were determined using XRD and FTIR spectroscopy. XRD spectra were recorded in the range of $2\theta = 10$ to 70° using a Phillips powder diffractometer PW 1050/25 with Cu Kα radiation. TEM/EDX analysis was performed using a Hitachi H-8100 electron microscope. FTIR spectra in the range from 400 to 4000 cm^{-1} were taken from a powdered sample mixed with KBr (1 : 9) using a Perkin–Elmer FTIR-Spectrometer 1720 X equiped with a DRIFT cell. Surface areas were determined using N_2 adsorption at 77 K (1-point method after Haul and Dümbgen (12). Surface acidic properties were determined by recording DRIFT spectra of adsorbed pyridine. The catalyst (10–20 mg, powder) was first heated in the DRIFT cell to 773 K in a flow of N_2 to remove loosely bonded species from the catalyst surface. Then the catalyst was cooled down to room temperature and a saturated gas stream of pyridine/N_2 (10 ml/min) was fed to the catalyst. The reversibly adsorbed pyridine was removed by flushing in N_2 for 0.5 h. Subsequently DRIFT spectra were taken in the range of 400 to 4000 cm^{-1}.

Catalytic Performance

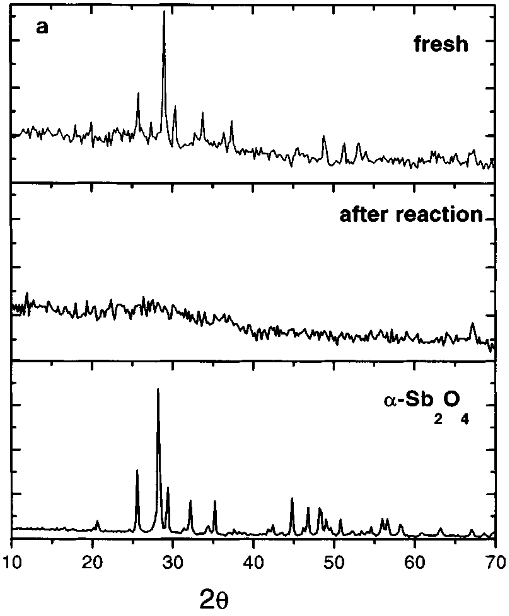
The performance of the prepared catalysts was determined in a microcatalytic fixed-bed reactor (ID = 1.4 cm) made of quartz under steady state operation conditions. A constant inlet gas mixture of $C_3H_8/O_2/N_2 = 2:1:6$ ($P_{tot} = 0.1$ MPa) was applied and the temperature in the reactor was varied between 673 and 823 K. The modified residence time m_{cat}/V was varied from 0.5 to 4 $g \cdot s \cdot ml^{-1}$ ($m_{cat} = 0.5$ to 1.5 g). The catalyst was diluted with quartz at a ratio of 1 : 1 in order to avoid temperature hot spots. The reactor was heated in a fluidized bed of sand to achieve an optimum heat transfer. Temperature gradients in the catalyst bed amounted to 2 K. The precatalytic reactor volume was minimized by filling the voids of the reactor with quartz particles which enabled to suppress the homogeneous gas phase reaction of the inlet gas mixture up to temperatures of 823 K. The feed gas and product gas compositions were analyzed on-line by a SATOChrom gas chromatograph equipped with a molesieve, a fused Silica GS-Q capillary column, an FID, and a micro-volume HCD. The following products were detected: C_3H_8, C_3H_6, C_2H_4, acrolein, CO, and CO_2. Carbon mass balances amounted to $100 \pm 3\%$. Prior to the experiments the catalysts were treated for 5 h at a temperature of $T = 823$ K in the reaction flow mixture of $C_3H_8/O_2/N_2 = 1:2:6$ ($P_{\text{tot}} = 0.1$ MPa) at $m_{\text{cat}}/V = 2\ \text{g} \cdot \text{s} \cdot \text{ml}^{-1}$ to reach a stationary state of catalytic performance.

RESULTS

In the following the bulk and surface physico-chemical properties of the catalysts and their catalytic performance in the partial oxidation of propane are described.

Bulk Characterization of the Catalyst

The V–Sb–W–Al-oxide catalysts prepared in the slurry reaction are known to be very heterogeneous in composition. In a previous study we already mentioned the presence of crystalline α-Sb_2O_4 (JCPDS No. 11-0694) for VSb_5O_x/Al_2O_3 catalysts (13), which is also the only crystalline phase detectable by XRD in the calcined VSb_2WO_x/Al_2O_3 catalysts (cf. Fig. 1a). The XRD spectrum of the silane modified catalyst (cf. Fig. 1b) looks identical but with lower intensity for the α-Sb_2O_4 reflexes. TEM/EDX analyses additionally showed the presence of the nonstoichiometric $\approx SbVO_4$ phase (JCPDS No. 35-1485) (13), a complex alumina rich Al–V–Sb–W-oxide phase and small amounts of V_2O_5. The FTIR spectra of the unpromoted and SiO_x promoted catalysts exhibited mostly the vibrational bands of γ-alumina which is the stable alumina modification at the temperatures applied (14). Additionally, on the fresh prepared SiO_x promoted samples two adsorption bands at 3138 and 3035 cm^{-1} occurred. These might be attributed to adsorbed water or bridged Si–(OH)–Me groups (Me = V, Sb, W), since they do not appear on pure silica modified alumina oxide samples (10). However, interpretation of the spectra is difficult, because the spectra were obtained at 0.1 MPa without evacuation. After treatment of the samples (unpromoted and SiO_x-promoted catalysts) with reaction mixture $C_3H_8/O_2/N_2 = 1:2:6$ for 5 h the solids are totally X-ray amorphous (cf. Figs. 1a and b). TEM/EDX analyses of the unpromoted catalyst after reaction showed preferably particles of the alumina rich Al–V–Sb–W-oxide phase besides small amounts of α-Sb_2O_4, but no pure Al_2O_3 or V_2O_5. The FTIR spectra after reaction indicated that γ-alumina remained the predominant compound in the catalyst. The OH absorption bands at 3138 and 3035 cm^{-1} dissapeared.



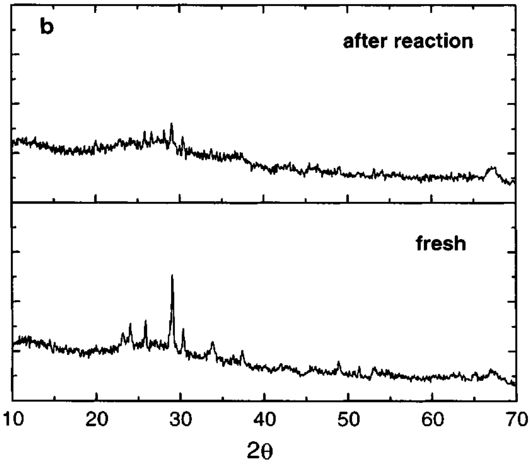


FIG. 1. (a) X-ray diffraction spectra of a VSb_2WO_x/Al_2O_3 catalyst (top) after calcination, (middle) after treatment with a $C_3H_8/O_2/N_2$ mixture (1:2:6) and (bottom) of a reference α-Sb_2O_4 sample, (b) X-ray diffraction spectra of a VSb_2WO_x/Al_2O_3 catalyst modified with silane (bottom) after calcination, (top) after treatment with a $C_3H_8/O_2/N_2$ mixture (1:2:6).

Surface Characterization of the Catalyst

The BET surface areas of the catalysts applied are given in Table 2. The surface area of the calcined unpromoted sample is about 20 $\text{m}^2 \cdot \text{g}^{-1}$ larger compared to the SiO_x promoted one. After reaction all surface areas are decreased by 20 $\text{m}^2 \cdot \text{g}^{-1}$. The surface acidity was investigated using pyridine adsorption DRIFT studies. The DRIFT spectra of pyridine adsorbed on the calcined catalysts (undoped

TABLE 2

BET Surface Areas of Unpromoted and SiO_x Promoted VSb_2WO_x/Al_2O_3 Catalysts after (a) Calcination and (b) Catalytic Run

	BET surface/$m^2 \cdot g^{-1}$	
Promotor	Calcined	After catalytic test
—	88.6	67.1
7.4 wt% SiO_x	70.8	50.3

Note. $C_3H_8/O_2/N_2 = 1:2:6$; $T_R = 823$ K; 5 h.

and SiO_x promoted) as well as on reference samples of Al_2O_3 and Sb_2O_4 are presented in Fig. 2. The spectrum of the unpromoted catalyst reveals the presence of Lewis and Broensted acid sites on the catalyst surface. Lewis acid sites are represented by the absorption bands at 1439 cm^{-1} with a shoulder at 1444 cm^{-1} (19b ring vibration), 1488 cm^{-1} (19a ring vibration), 1580 cm^{-1}, and 1593 cm^{-1} (8b/8a ring vibration), and 1607 cm^{-1} (8a ring vibration). Broensted acid sites are reflected by the absorption bands at 1488, 1536, and 1593 cm^{-1}. On the SiO_x-promoted catalyst no significant absorption for Broensted sites (missing band at 1536 cm^{-1}) occurred. The bands for Lewis sites are similar to those for the unpromoted catalyst except that the band at 1607 cm^{-1} is missing. The absorption bands observed are in agreement with those obtained for the pure Al_2O_3 and Sb_2O_4 samples. It is therefore concluded that the acid sites originate mainly from the Al_2O_3 and Sb_2O_4 present in the catalysts.

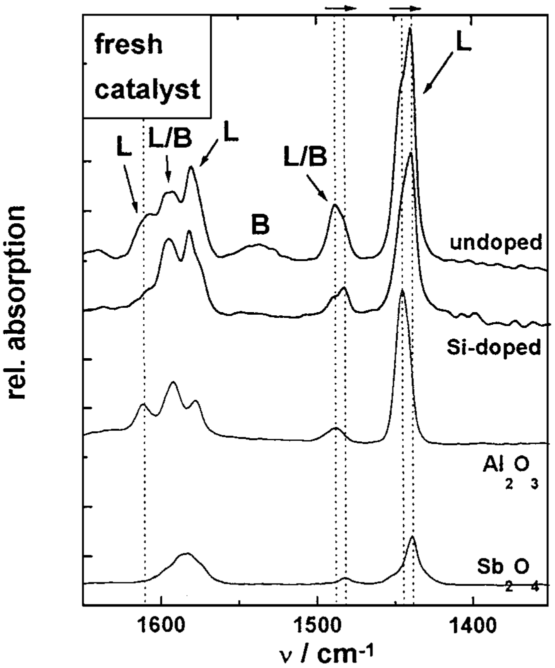


FIG. 2. DRIFT spectra of adsorbed pyridine on the unpromoted and SiO_x (7.4 wt%) promoted VSb_2WO_x/Al_2O_3 catalyst after calcination and on reference samples of γ-Al_2O_3 and α-Sb_2O_4.

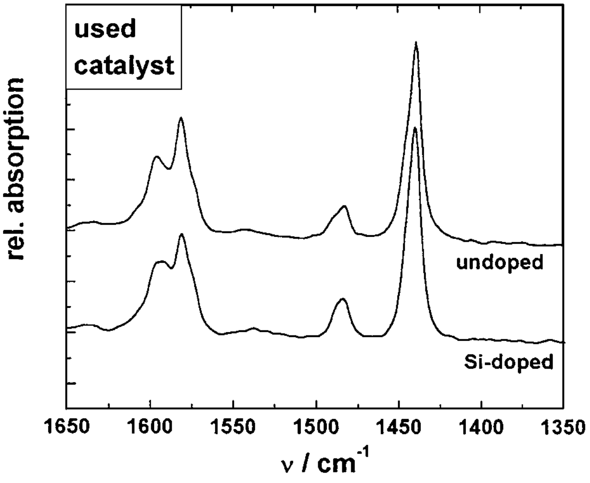


FIG. 3. DRIFT spectra of adsorbed pyridine on the unpromoted and SiO_x (7.4 wt%) promoted VSb_2WO_x/Al_2O_3 catalyst after treatment with a $C_3H_8/O_2/N_2$ mixture (1 : 2 : 6) and on reference samples of γ-Al_2O_3 and α-Sb_2O_4.

After treatment of the catalysts with the reaction mixture ($C_3H_8/O_2/N_2 = 1:2:6$) at a temperature of 823 K for more than 5 h the DRIFT spectra of both, the unpromoted and SiO_x-promoted catalyst look similar, exhibiting only Lewis absorption bands at 1440, 1483, 1581, and 1593 cm^{-1} (Fig. 3).

Catalytic Performance of the Catalysts

All catalyst samples investigated showed catalytic activity in the partial oxidation of propane. Propene, acrolein, ethylene, CO, and CO_2 were observed as products. With increasing time-on-stream the unpromoted catalyst showed a slight increase in the catalytic performance (cf. Table 3). During the first 5 h an increase in propene selectivity by 0.5% was observed, while that of CO_x decreased by 0.5%. The activity remained fairly constant. After additional 21 h the conversion of propane decreased from 53.1 to 50.9%. No changes in the selectivities were detected in this period

TABLE 3

Influence of Time-on-Stream on Conversions and Product Selectivities of a VSb_2WO_x/Al_2O_3 Catalyst

Reaction time h	$X_{C_3H_8}$ %	X_{O_2} %	S_{CO_x} %	$S_{C_2H_4}$ %	$S_{C_3H_6}$ %	$S_{C_3H_4O}$ %
1.5	54.2	98.2	81.8	1.5	15.7	1.0
3.0	53.8	97.7	81.6	1.5	16.0	1.0
4.6	53.1	97.7	81.3	1.5	16.2	1.0
26.0	49.9	87.0	81.3	1.4	16.3	1.0

Note. $C_3H_8/O_2/Ne = 1:2:6$; $m_{cat}/V = 0.5\ g \cdot s \cdot ml^{-1}$; $T_R = 823$ K.

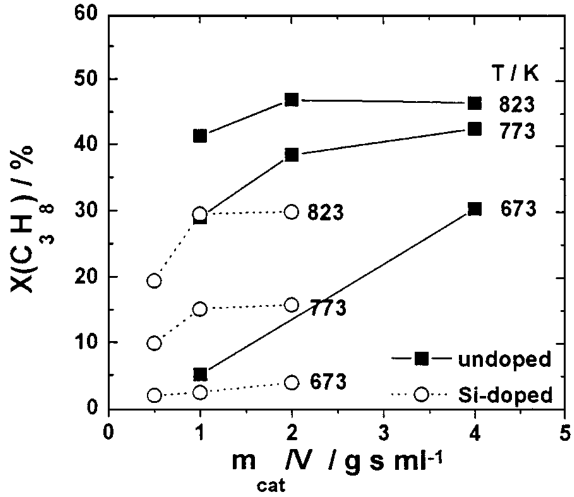


FIG. 4. Propane conversion as a function of modified residence time m_{cat}/V and temperature for a Si promoted ($m_{cat}/V = 0.5$–$2.0\ g \cdot s \cdot ml^{-1}$; $m_{cat} = 1.0$ g; Si content: 7.4 wt%) and unpromoted ($m_{cat}/V = 1.0$–$4.0\ g \cdot s \cdot ml^{-1}$; $m_{cat} = 0.5$ g) VSb_2WO_x/Al_2O_3 catalyst ($C_3H_8/O_2/N_2 = 2:1:6$).

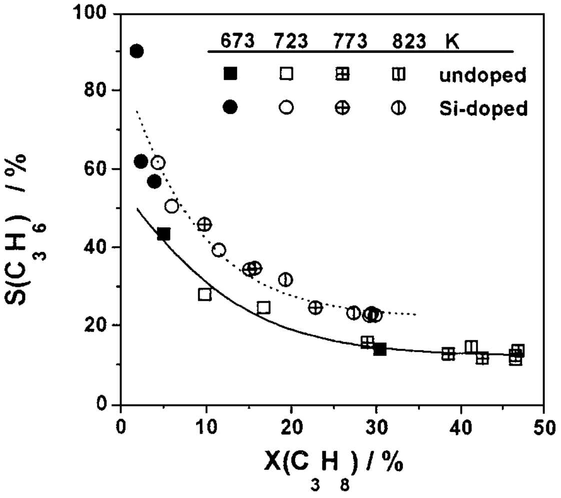


FIG. 5. Propene selectivity as a function of propane conversion and temperature for a Si promoted ($m_{cat}/V = 0.5$–$2.0\ g \cdot s \cdot ml^{-1}$; $m_{cat} = 1.0$ g; Si content: 7.4 wt%) and unpromoted ($m_{cat}/V = 1.0$–$4.0\ g \cdot s \cdot ml^{-1}$; $m_{cat} = 0.5$ g) VSb_2WO_x/Al_2O_3 catalyst ($C_3H_8/O_2/N_2 = 2:1:6$).

of time. All results reported further on were therefore taken after a period of 5 h on-stream.

With increasing modified residence time, propane conversion and oxygen conversion increased. For the highest temperature and residence times investigated total oxygen conversion was observed (not shown in a figure). The dependence of propane conversion on modified residence time and temperature for the undoped catalyst and a 7.4 wt% SiO_x modified catalyst is presented in Fig. 4. With increasing residence time and temperature the propane conversion increased up to about 47% for the undoped catalyst. The silica-doped catalyst, however, exhibited much lower activity, which was roughly half as high as for the undoped catalyst. The maximum propane conversion for the SiO_x modified catalyst amounted to 29.9% ($X_{O_2} = 45.7\%$).

With increasing conversion the selectivities to propene and acrolein decreased, while the selectivities to ethylene and carbon oxides increased. The temperature effect on the selectivities in the investigated temperature range from 673 to 823 K was found to be of minor importance. The dependence of propene selectivity on propane conversion and reaction temperature for the undoped and a 7.4 wt% SiO_x modified catalyst is presented in Fig. 5. With increasing conversion from 5.1 to 46.6% the propene selectivity decreased from 43.4 to 12.6% for the undoped catalyst. The propene selectivity was found to be influenced by the SiO_x doping. For all conversion levels the propene selectivity was about 10% higher for the Si-promoted catalyst. With increasing propane conversion from 1.9 to 29.9% the propene selectivity decreased from 90.0 to 22.8%.

The dependence of the selectivity to acrolein on propane conversion and reaction temperature for the undoped and a 7.4 wt% SiO_x modified catalyst are presented in Fig. 6. Similar to the propene selectivity a decrease with increasing conversion was observed for the unpromoted catalyst. The propene selectivity decreased from 1.5% ($X_{C_3H_8} = 10\%$) to 0.5% ($X_{C_3H_8} = 47\%$). It should be mentioned that the detected amounts of acrolein were near the detection limit of the applied gaschromatograph. In the presence of the silane modified catalyst significantly higher selectivities for all conversion levels were detected. For this catalyst the acrolein selectivity decreased from about 5% ($X_{C_3H_8} = 2\%$) to 2.1% ($X_{C_3H_8} = 30\%$). In case of the acrolein a higher selectivity (about 0.5%) could be obtained when increasing

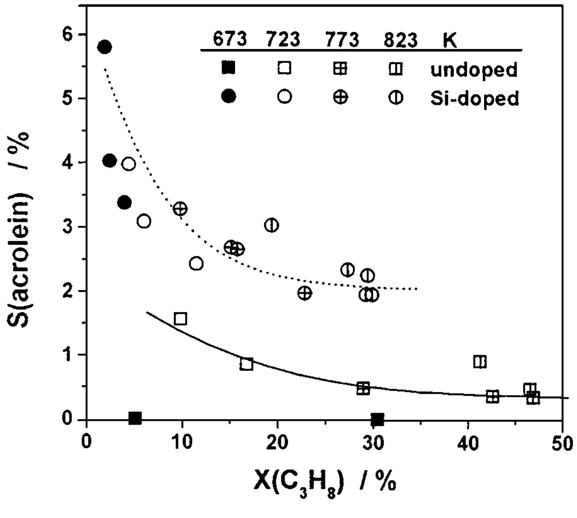


FIG. 6. Acrolein selectivity as a function of propane conversion and temperature for a Si promoted ($m_{cat}/V = 0.5$–$2.0\ g \cdot s \cdot ml^{-1}$; $m_{cat} = 1.0$ g; Si content: 7.4 wt%) and unpromoted ($m_{cat}/V = 1.0$–$4.0\ g \cdot s \cdot ml^{-1}$; $m_{cat} = 0.5$ g) VSb_2WO_x/Al_2O_3 catalyst ($C_3H_8/O_2/N_2 = 2:1:6$).

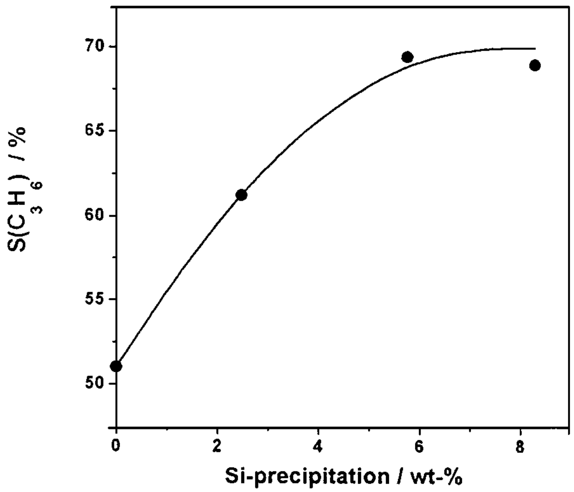


FIG. 7. Propene selectivity as a function of amount of precipitated Si ($X(C_3H_8) = 7\%$; $C_3H_8/O_2/N_2 = 2:1:6$; $T_R = 773$ K).

the temperature by 50 K. The yields to acrolein, however, remained low not exceeding $Y_{\text{acrolein}} = 1\%$.

Additional catalytic experiments were performed aiming in determination of the optimum amount of SiO_x loading by applying catalysts with variable SiO_x amount. The observed dependence of the propene selectivity on SiO_x-loading at a constant conversion level of 7% is shown in Fig. 7. The data presented were interpolated from the data originally obtained from the experiments. With increasing SiO_x precipitated to the VSb_2WO_x/Al_2O_3 catalyst the propene selectivity increased from 51% (unpromoted) to 68% (5.8 wt% SiO_x). With higher loadings no further increase in the selectivity could be observed.

DISCUSSION

Catalytic Performance

The catalytic results presented above clearly show that the selectivity to propene and acrolein in partial oxidation of propane can be enhanced by modifying the catalyst surface with SiO_x. Using the SiO_x-(8.4 wt%) promoted catalyst yields to propene as high as 8.9% ($X_{C_3H_8} = 19\%$) could be achieved. This result is in the range of typical propane dehydrogenation catalysts reported in literature, e.g., $Y_{C_3H_6} =$ 9–12% for Co- and Mg–Mo-oxides (15) and V–Mg-oxides (16). However, the achievable yield to propene over the applied catalyst is significantly lower compared to the B_2O_3 (30 wt%)/Al_2O_3 catalyst ($Y_{C_3H_6} = 18\%$ (17)), but an increase in propene selectivity and yield for the SiO_x promoted catalysts might be expected on optimization of the reaction conditions.

Active Sites for Total Oxidation

In the following the differences in the catalytic performance of the SiO_x promoted and unpromoted catalyst are explained on the basis of the observed physicochemical properties before and after treatment with reaction gas mixture.

The characterization results clearly indicate that the surface acidic properties of the VSb_2WO_x/Al_2O_3 catalyst can be modified by modifying the catalyst with SiO_x. The original catalyst mainly consists of Lewis and Broensted acid sites located on the Sb_2O_4 and Al_2O_3 crystallites as indicated by a comparison of the pyridine absorption bands for the V-Sb-oxide and the pure substances Sb_2O_4 and Al_2O_3 in the 1490 and 1440 cm^{-1} range. The absorption bands in the range of 1570 to 1610 cm^{-1} reveal the presence of different Lewis acidic sites on the surface. The band at 1607 cm^{-1}, which was found to be irreversible upon flushing the pyridine with nitrogen at ambient temperature in our experiments, has been ascribed to tetrahedal coordinatively unsaturated (cus) Al^{IV}_{cus} surface (defective) centers (18). The bands at 1580 and 1593 cm^{-1}, which were found to be reversible upon flushing the pyridine with nitrogen, partly belong to (i) pyridine weakly coordinated to regular octahedral cus Al^{VI} centers, (ii) to pyridine adsorbed by H-bonding onto some surface OH groups (18), and (iii) to pyridine coordinatively adsorbed to Lewis sites on Sb_2O_4 (cf. Fig. 2) and/or $\approx SbVO_4$ (13). For the SiO_x modified V–Sb–W–Al–O catalyst the missing pyridine absorption band at 1536 cm^{-1} reveals that the number of Broensted centers is strongly reduced as expected. However, also the number of the defective Al^{IV}_{cus} sites resulting in an absorption at 1607 cm^{-1} is strongly reduced. Also the intensity of the band at 1444 cm^{-1} is strongly reduced while that at 1439 cm^{-1} remained. From these results it can be concluded that the SiO_x clusters formed upon the SiH_4/N_2O treatment of the catalyst reduce the number of Broensted acid sites and additionally block the defective Al^{IV}_{cus} sites.

During reaction the pyridine absorption spectra does not change for the SiO_x modified catalyst. However, the pyridine absorption spectrum for the unpromoted catalyst is modified under reaction conditions and looks similar to that for the SiO_x promoted catalyst. In consequence, also in this case it must be concluded that the number of Broensted sites is reduced and the defective Al^{IV}_{cus} sites are blocked. This thoroughly healing of the defective sites cannot be explained by the alumina itself, because such surface changes are only observed at higher temperatures of about 1473 K, where α-Al_2O_3 is formed (18). Phase transition of γ-Al_2O_3 to δ,θ-Al_2O_3 which occurs at temperatures near the ones applied in the catalytic reaction of the present work does not result in a disappearing of the Al^{IV}_{cus} band of adsorbed pyridine.

In the bulk structure XRD analysis it was observed that the intensity of the reflexes of the only detectable phase, α-Sb_2O_4, in the calcined samples becomes mostly microcrystalline and/or reacts under reaction conditions. This effect was also observed under reaction conditions with a propane/oxygen mixture in the presence of ammonia for a variety of $\mathrm{VSb_5O}_x/\mathrm{Al_2O_3}$ catalysts (5). Andersson and coworkers (19) observed the formation of complex $\mathrm{(Al,Sb,V)_2O_4}$ phases when heating mixtures of solid $\mathrm{Sb_2O_3}$, $\mathrm{Al(OH)_3}$, and $\mathrm{V_2O_5}$ in air at only slightly higher temperatures of 953 K compared to the present study (900 K) but for longer times of 4 days compared to 3 h in the present work (plus the time under reaction conditions at 823 K for the used samples) indicating that antimony is able to migrate onto the surface and into the bulk of aluminum oxide. The small changes only in the FTIR spectra before and after reaction indicate that these processes occur on the surface and/or in surface near regions only. From these observations it might be concluded that under the conditions applied in the present work antimony migrates over the alumina particles becoming smaller in particle size and/or forming a mixed oxide with the alumina, i.e. $\mathrm{AlSbO_4}$, which might preferably occur at the $\mathrm{Al}^{\mathrm{IV}}_{\mathrm{cus}}$ defect sites or by condensation of Sb–OH and Al–OH groups. The vanadium oxide found in the fresh catalysts using EDX analysis also reacts with the antimony and/or the alumina forming a $\mathrm{(Al,Sb,V)_2O_4}$ phase (19). On the catalysts pretreated with $\mathrm{SiH_4/N_2O}$ the Al–V–Sb-oxide formation might not appear at the favoured formation sites, defective $\mathrm{Al}^{\mathrm{IV}}_{\mathrm{cus}}$ and Al–OH, which are already occupied by SiO_x groups. It should be mentioned that due to the migration of antimony not only the properties of the alumina are changed but also those of the $\approx\mathrm{SbVO_4}$ phase, which builds up an antimony-enriched surface layer (20).

The conclusions drawn on the basis of the characterization results are in agreement with the observed catalytic behaviour of the unpromoted and SiO_x promoted catalyst in partial oxidation of propane. The observed changes in activity during the first hours on-stream for the unpromoted catalyst can be explained by the migration of the Sb onto the alumina forming Al–Sb-oxide at the alumina defect sites (cf. Fig. 8). Al–Sb-oxide, however, known to act unselectively in propane conversion similar to $\mathrm{Al_2O_3}$ even under the protecting presence of $\mathrm{NH_3}$ (19). The enhanced surface area of the α-$\mathrm{Sb_2O_4}$, however, is assumed not to influence the catalytic properties, since α-$\mathrm{Sb_2O_4}$ exhibits only a very low activity at all. In the presence of SiO_x the formation of Al–Sb-oxide at the defective $\mathrm{Al}^{\mathrm{IV}}_{\mathrm{cus}}$ sites is prevented by blocking (cf. Fig. 8), the α-$\mathrm{Sb_2O_4}$ remaining on the surface with diminished particle size covering the alumina surface together with the inactive SiO_x. This, however, results in a strong decrease in activity, but total oxidation is (partly) prevented; in consequence, an increase in selectivity towards the desired products propene and acrolein is observed. Besides the above argumentation the effect of silane modification might also be attributed to the formation of a new selective phase in the presence of the SiO_x. However, no indication for such processes were found in the characterization results. Additionally, the application of $\mathrm{SiO_2}$ as a carrier material, which might also lead to the formation of such a selective phase, has already been proven in the presence of ammonia in the reaction gas to result in a poorer catalystic performance (21).

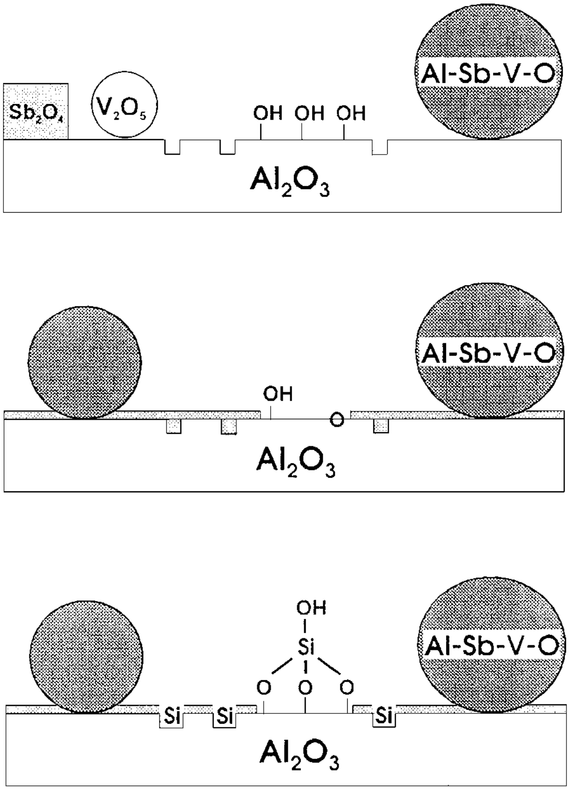


FIG. 8. Simplified model for the surface properties of a $\mathrm{VSb_2WO}_x/\mathrm{Al_2O_3}$ and a SiO_x modified catalyst: (i) calcined sample (unmodified); (ii) sample after partial oxidation of propane; (iii) SiO_x modified sample after partial oxidation of propane.

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