

Chromia on Anatase: A Catalyst for Selective Hydrocarbon Combustion in the Presence of CO

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The catalytic activity and selectivity for propane combustion in the presence of CO have been studied with anatase, rutile, eskolaite, chromia-impregnated anatase, and titania-impregnated chromia and its physical mixtures. It was found that the selectivity and activity depend on the TiO_2 modification. Cr-doped anatase converts 80% propane with 100% selectivity, whereas chromia on rutile converts CO preferentially to propane. Cr_{10} @HOM 500/4 (HOM = Hombikat) and the physical mixture Cr_{10} +HOM 500/4 are promising new catalysts for selective pro-

Introduction

The reduction of pollution from combustion engines is based on modern catalysts that have been developed during the last 30 years. The three-way catalytic converter (TWC) is highly active for the oxidation of carbon monoxide (CO) and hydrocarbons (HC) and the reduction of NO_x. This converter shows good stability, but the main drawback is its noble-metal content and its restriction to gasoline four-stroke engines.^[1] Little attention has been paid to another large class of combustion engines, the two-stroke engines found in scooters, small motor bikes, construction equipment, and mobile household machines, such as lawn mowers, chain saws, leaf blowers, hedge trimmers, portable generators, irrigation pumps, and many others. Owing to the oil content of the gasoline-oil mixture as fuel, the exhaust gases of two-stroke engines are dominated by hydrocarbons, their fragments, and CO. Emission standards for two-stroke scooters and motorcycles, stages Euro 2 to Euro 5, show an acceptance of 1000 mg km⁻¹ CO, whereas the HC content ranges from 1200 to 100 mg km⁻¹ depending on the stage.^[2] Apparently, the problem is not so much the CO emission, but the HC fragments that are responsible for odor and toxicity. Noble-metal catalysts are known to preferentially convert CO rather than HCs^[3-6] and are, therefore, not suitable for the cleaning of the two-stroke engine exhaust. Several mixed-metal oxides have been reported as good alternatives to noble-metal catalysts for the oxidation of HCs.^[7-10] Therefore, it is attractive to develop catalysts that preferentially convert HCs in the presence of CO. Based on sol-gel methods, we have used high-throughput technologies in a highly diverse pane oxidation. High-resolution TEM and powder XRD analyses have shown that a solid solution of chromia in anatase is the active phase of these selective oxidation catalysts. Diffuse reflectance UV/Vis spectroscopy demonstrated the effects of Cr-doping of TiO₂, and Rietveld refinement analysis implied a solid solution of Cr³⁺ ions in anatase. Evidence for a Mars-van Krevelen mechanism was obtained. Catalyst deactivation was reduced by increasing the oxygen content in the feed. The catalyst is reactivated by treatment with oxygen.

search for HC-selective mixed-oxide catalysts. Using propane as a HC model led to the discovery of TiCrCeO_x catalysts, which provided a propane conversion of 58% and a CO conversion of only 25% at 350°C in a propane/CO mixture with large CO excess.^[11] Further studies led to a HC-selective TiCrO_x catalyst.^[12] During a detailed mechanistic study Ce-doped TiCrO_x was obtained, this species converted approximately 90% propane at 375°C with 100% selectivity in the presence of a five-fold excess of CO. Mechanistic studies performed by using diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) confirmed that propane forms combustible adsorbates (carboxylates) on the catalyst surface in the presence, as well as absence, of molecular oxygen, whereas CO forms only formates with surface OH groups in the absence of oxygen. These formates are not oxidized, but are reversibly decomposed to CO and OH. The sol-gel-derived catalysts showed good propane activity and excellent selectivity, but their expensive and time-consuming syntheses are a disadvantage.^[13] This disadvantage prompted us to investigate catalysts synthesized by completely different synthetic routes, such as wet impregnation and solid-state reactions. Therefore, the objective of this work was the simplification of the synthesis, the improvement of the sol-gel-derived TiCr(Ce)O_x system discovered previously,^[13] as well as the elucidation of the effect of the defined phases, anatase (TiO₂), rutile (TiO₂), and eskolaite (Cr₂O₃), on catalytic activity and selectivity. For anatase we used the commercially available TiO₂, Hombikat. The catalysts are abbreviated according to preparation procedure; for impregnated materials "@" is used (Cr₁₀@HOM 500/4 stands for 10 at.% chromia impregnated on Hombikat, calcined for 4 h at 500 $^{\circ}$ C), "+" represents a physical mixture ground in a mortar (e.g. Cr₁₀+ HOM 500/4), and "Ti_{62.5}Cr_{37.5}O_x" represents a sol-gel-derived reference material.

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Results

Catalytic-activity measurements have been performed in a gasphase flow reactor as described in a previous publication.^[13] Propane oxidation is highly exothermic, therefore, the catalyst bed was always diluted with catalytically inactive sand (200 mg sand, 20 mg catalyst, sieve fraction 100-200 µm). This ten-fold dilution was necessary to allow reliable temperature control of the catalyst bed. It was surprising to note, that the impregnated Hombikat showed activity and selectivity comparable to the sol-gel reference materials from previous studies. For different Cr loadings (5, 10, 20, and 30 at.%), Cr₁₀@HOM 500/4 was the most active catalyst with a propane conversion to CO₂ and H₂O of 80% at 375 °C. CO conversion was not detected, indicating a propane selectivity of 100% despite the five-fold excess of CO in the feed gas. In fact, a slight CO formation of approximately 2% was observed, indicating incomplete propane combustion. This observation was also supported by the substoichiometric conversion of O_2 related to propane (\approx 5%). The temperature-dependent competitive conversion of propane and CO is shown in Figure 1. When determining the con-



Figure 1. Temperature-dependent conversion of propane and CO with Cr_{10} @HOM 500/4. No CO is converted. The arrows indicate decreasing and increasing the temperature during the measurement.

versions of propane and CO separately (separated feed gases), a CO conversion of 16% at 375 °C was observed, whereas propane showed a conversion of 86%. This result shows that the two gases compete in the oxidation process, but in a mixture, propane combustion is favored. These results are consistent with our mechanistic investigations for selectivity with the solgel catalysts.^[13] DRIFTS spectra were also recorded for Cr_{10} @HOM 500/4, showing the same bands as that of the solgel catalyst (not shown here). This result suggests that the same combustion mechanism is applicable to both systems. Before continuing it was important to rule out any corruption of the study by mass-transport limitation under the reaction conditions with this new catalyst system.

Mass-transport limitation, already excluded for the sol-gel materials,^[14] was investigated with the most active catalyst, Cr_{10} @HOM 500/4. Although mass-transport limitation was present at flow rates below 30 mLmin⁻¹, the conversion stabilized at flow rates of 50 mLmin⁻¹ and above. Because all other catalysts studied here are less active than Cr_{10} @HOM 500/4, mass-transport limitations can be excluded at our standard flow rate of 50 mLmin⁻¹.

It was also of interest to investigate the catalytic activity and selectivity of the pure oxide phases (see Table 1). For anatase, commercially available Hombikat UV100 was used. Eskolaite

Table 1. Activity, selectivity, and specific surface area of the pure metal oxides and the catalysts.				
	Convers at 375 °C Propane	ion [%] CO	Propane selectivity at 375 °C [%]	Specific surface area [m ² g ⁻¹]
Cr ₂ O ₃ 500/4	15	4	79	11
TiO ₂ (Hombikat UV100)	0	0	-	312
TiO ₂ RUT 800/10	1	1	50	8
Cr10@HOM 500/4	80	0	100	84
Cr ₁₀ +HOM RT	2	2	50	278
Cr ₁₀ +HOM 500/4	35	0	100	78
Cr ₁₀ @RUT 500/4	14	25	36	_ ^[a]
Cr ₁₀ +RUT 500/4	5	2	71	_ ^[a]
(Cr ₈ Ce ₂)@HOM 500/4	78	2	98	110
Ti _{62.} Cr _{37.5} O _x	60	0	100	261
[a] The specific surface area was too low to be determined.				

(Cr₂O₃) was synthesized by calcination of Cr(NO₃)₃·9H₂O at 500 °C for 4 h according to the synthesis of Cr₁₀@HOM 500/4. Therefore, we were interested to discover whether rutile, the thermodynamically stable TiO₂ modification, acts differently to anatase. Rutile was synthesized by annealing the commercial anatase and rutile mixture P25 at 800 °C for 10 h. Diffraction patterns showed no reflections corresponding to anatase, but did show sharp reflections corresponding to rutile (see Figure 9). The rutile powder was impregnated with Cr³⁺ solution and calcined as before. Although anatase was catalytically inactive, eskolaite showed a propane conversion of 15%. Rutile showed very poor conversions of propane and CO and no selectivity was observed (see Table 1). Physical mixtures were prepared by grinding the two powders in pentane with a mortar and pestle, followed by drying. Ball milling was also attempted, but the resulting mixture was catalytically inactive, therefore, the simple mortar approach was used. Although Cr₁₀+HOM RT (RT stands for room temperature) showed only poor conversion and no selectivity, Cr₁₀+HOM 500/4 provided a 35% propane conversion with 100% selectivity (see Table 1). The temperature-dependent catalytic activity of the annealed physical mixture of Cr₁₀+HOM 500/4 is shown in Figure 2. The data for the various catalytic systems studied is summarized in Table 1, which provides conversions as well as surface areas





Figure 2. Temperature-dependent conversion of propane and CO on Cr_{10} + HOM 500/4. No CO is converted. The arrows indicate decreasing and increasing the temperature during the measurement.

and propane selectivities. Propane selectivity is defined as $S_{\text{Prop}} = X_{\text{Prop}}/(X_{\text{Prop}} + X_{\text{CO}})$. Note that we did not define turnover frequencies as usual for catalytic reactions because the number of active centers on such bulk materials could not be determined.

The poor behavior of rutile was confirmed with the impregnation of rutile with chromia. $Cr_{10}@RUT 500/4$ provided a higher CO conversion than propane conversion resulting in a propane selectivity of only 36% (see Table 1). The temperature-dependent catalytic activity of $Cr_{10}@RUT 500/4$ is shown in Figure 3, documenting the reverse selectivity of this catalyst. Apparently, only catalysts based on anatase (Hombikat) and annealed with chromia (Cr_2O_3) display the desired catalytic activity and selectivity.

Impregnation of the chromia with titania ($Ti_{10}@Cr_2O_3 500/4$) resulted in a catalyst less active and less selective than the chromia alone ($X_{Prop} = 8\%$, $X_{CO} = 3\%$), supporting the hypothesis that chromia acts as a catalyst, whereas titania acts as a support.

The lower catalytic activity of Cr_{10} + HOM RT relative to the pure Cr_2O_3 500/4 is attributed to the reduced amount of chromia in the physical mixture because for all experiments 20 mg of catalyst was used.

Cerium can play an important role in this catalytic reaction, as shown in our earlier studies with the sol–gel-based catalysts,^[13] therefore, cerium was added to the chromia-impregnation solution. A cerium-containing catalyst, $(Cr_8Ce_2)@HOM 500/4$, was prepared by impregnation. This catalyst converted 78% propane and approximately 2% CO at 375 °C. On comparison with $Cr_{10}@HOM 500/4$ there was no improvement in catalytic activity, but a slight loss in selectivity (see Table 1). Therefore, the addition of cerium to the catalyst did not improve the catalytic activity of the catalysts prepared by impregnation and was, therefore, abandoned in this study. This result does not

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Figure 3. Temperature-dependent conversion of propane and CO on Cr_{10} @RUT 500/4. Both propane and CO are converted, with a selectivity of 64% for CO.

apply to sol-gel-derived catalysts for which small amounts of cerium led to more active catalysts.^[13]

Another important factor for catalytic applications is longterm stability. As shown by the black squares in Figure 4, Cr_{10} @HOM 500/4 showed a rapid loss of activity during the first 24 h, after which its activity leveled out, after 3 days, to approximately 40% (the same observation was made with solgel-derived $Ce_{2,5}Ti_{50}Cr_{47.5}O_{xr}$ not shown here). Supposedly, the active phase has to be formed at the interphase of the two metal oxides owing to the annealing process. Therefore, the



Figure 4. Long-term stability tests for Cr_{10} @HOM 500/4. The temperature was held at 375 °C. The black squares show the deactivation over 72 h, whereas the red squares show cycles of 24 h with reconditioning in between by pure molecular oxygen for 1 h.



catalyst was annealed at 500 °C for a further 100 h. Counter-diffusion processes of Ti⁴⁺ and Cr³⁺ in the lattice should be promoted under these conditions, which may be the key to the activity and selectivity of the catalyst. Activity tests of these materials (denoted as 500/100) showed that there was no improvement in activity and the selectivity remained the same. Cr₁₀@HOM 500/100 converted 70% propane at 375 °C (not shown here), which is a slight decrease in activity. The physical mixture Cr₁₀+HOM 500/100 also showed no catalytic improvement compared with that Cr₁₀+HOM 500/4. We concluded that annealing at 500 °C for 4 h is sufficient to obtain these active and selective catalysts.

X-ray fluorescence analysis (XRF) before and after the stability test showed no leaching of the metals over three days under the reaction conditions [Ti/Cr = 86:14 fresh and Ti/Cr = 84:16 after 72 h (at.%)], also no phase transformation could be identified in the powder diffraction pattern (not shown). In our previous study, evidence for a Mars-van Krevelen mechanism was obtained.^[13] Therefore, this rapid drop of catalytic activity could result from depletion of lattice oxygen owing to the oxidation process. If this is the case, additional oxygen should result in restoration of catalytic activity, and higher oxygen content in the feed gas should cause a reduction in the activity drop. Cr₁₀@HOM 500/4 was tested again and pure oxygen was introduced at 375 °C for one hour after every 24 h of reaction. This procedure increased the propane conversion after 24 h from 48 to 69%, showing that the catalyst could be reconditioned by molecular oxygen. The catalyst was deactivated again under the reaction conditions, but could be reconditioned with molecular oxygen to increase the propane conversion from 44 to 64% (see Figure 4, red squares). The sol-gelderived $Ti_{50}Cr_{47.5}Ce_{2.5}O_x$ catalyst from our previous work showed the same reconditioning effect (not shown here). If the depletion of lattice oxygen is the main reason for deactivation under the reaction conditions, then an increase in the concentration of oxygen should result in a reduction of the deactivation owing to the higher equilibrium concentration of oxygen.

The effect of doubling the oxygen concentration in the feed gas was investigated. Long-term stability tests with a stoichiometric propane to oxygen ratio (1:5, as used for all measurements) and a propane to oxygen ratio of 1:10, whereby the CO content was not considered are shown in Figure 5. Doubling the oxygen concentration increased the propane conversion at the beginning of the measurement from 78 to 97% (see Figure 5). Surprisingly, it did not cause a higher CO conversion, the selectivity for propane combustion remained at 100%, which may be taken as evidence against hot-spot formation (which should lead to loss of selectivity). The deactivation was slower and leveled out at 56% propane conversion after 72 h. The results strongly support the Mars-van Krevelen mechanism proposed earlier. Although evidence against sintering of the catalysts as the main reason for deactivation has been presented above, we have measured the BET surface of a fresh Cr_{10} + HOM 500/4 catalyst before and after a 72 h oxidation experiment and after a 24 h oxidation followed by 1 h reactivation with oxygen. The experiment was difficult because of the high



Figure 5. Long-term stability tests of Cr_{10} @HOM 500/4 with two different oxygen concentrations at 375 °C. Black squares: stoichiometric propane to O₂ ratio (10.0 vol.% O₂); Red squares: Doubled oxygen concentration (20.0 vol.% O₂).

dilution of the catalyst in the catalyst bed, as described in the Experimental Section, and the small amount of catalyst used in the experiments. The BET measurements provided 84 and $87 \text{ m}^2\text{g}^{-1}$ for the fresh catalyst, $75 \text{ m}^2\text{g}^{-1}$ after 72 h and 81 m^2g^{-1} after 24 h followed by reaction with oxygen for 1 h. Although the observed trend follows the loss of activity reported above qualitatively, its absolute value cannot explain the strong loss observed, especially considering the reproducibility of such BET measurements. Therefore, sintering was excluded as the main reason for deactivation. Another reason for the exclusion of sintering as the main reason for deactivation is that deactivation would not be reversible and would not be affected by oxygen concentration. The main sintering seems to take place during the calcination at 500 °C, as shown in Table 1, for example, the surface area of fresh Cr_{10} + HOM 500/4 decreased from 278 to 78 m²g⁻¹. Nevertheless, the decrease in initial activity over time, shown in Figure 4 and 5, that is not recovered by oxygen treatment, may be attributed to some sintering. However, this decrease could also result from the oxygen treatment being too short or from coking. To investigate a potential contribution to the deactivation from coking, a thermogravimetric analysis (TGA) experiment was carried out under air. The results are shown in Figure 6. Fresh Cr10@HOM 500/4 showed a small weight loss of 2% below 150°C, attributed to the loss of water, and another small weight loss above 550 °C, attributed to carbon-containing surface contamination. The used catalyst (2 days under the reaction conditions) showed the same weight losses and an additional weight increase of <1% above 300 °C, which we can only attribute to the filling of oxygen vacancies in the catalyst lattice. Therefore, TGA supports the Mars-van Krevelen mechanism and provides evidence against the importance of catalyst coking during this reaction. This is also supported by the light-green color of the used catalyst, another indication against serious coking.





Figure 6. Thermogravimetric analysis under air of fresh and used Cr_{10} @HOM 500/4 (used for 2 days under reaction conditions).

To learn more about the difference between $Cr_{10}@HOM 500/4$ and $Cr_{10}@RUT 500/4$, high-resolution transmission electron microscopy (HRTEM) studies were performed. $Cr_{10}@HOM 500/4$ showed the expected coagulation of nanoparticles (10–20 nm diameter) displayed in Figure 7a. Figure 7b (amplification of the bottom cluster in Figure 7a) documents the crystalline nature of these anatase particles. Micro-EDX (\approx 10 nm areas, EDX = energy-dispersive X-ray), performed on 15 selected areas of nanoparticles (centers as well as edges) throughout the sample provided a rather constant atomic ratio of Cr/Ti of \approx 0.1 with a variation of 10%. Further details on HRTEM with EDX analysis are shown in Figure S1 in the Supporting Information. This analysis shows that all particles and areas sampled are composed of Cr and Ti in approximately identical concent



Figure 7. a,b) HRTEM micrographs of Cr_{10} @HOM 500/4; b) is an amplification of the lower part of (a) showing the crystalline nature of this anatase catalyst.

tration, indicating that most Cr ions must have diffused into the anatase lattice of all anatase particles. During the HRTEM study only one small Cr₂O₃ particle could be found with a composition of 34 atom % Cr and 58 atom % O. Despite all efforts, no evidence for surface decoration of the anatase particles with chromia could be obtained, confirming that most of the Cr species diffused into the anatase particles and the remaining Cr species are only detectable as Cr₂O₃ particles. The HRTEM of Cr₁₀@RUT 500/4 showed a particle size of approximately 150 nm. All selected-area EDX analysis obtained from the bulk, as well as from the edges, showed different ratios of Cr/Ti, varying from 0 to 50 (see Figure S2 in the Supporting Information). Clearly, Cr is only found on the outer part of particles, whereas the particles themselves consisted of pure TiO₂. This finding indicates that Cr does not diffuse into the rutile, but remains as separate phase. It is also interesting to note, that the particle size of the rutile must result from sintering at 800 °C because P25 is known to have a particle size of approximately 20 nm.

The powder X-ray diffraction pattern (PXRD) of $Cr_{10}@HOM 500/4$ (see Figure 8) showed two phases: Anatase (TiO₂) and eskolaite (Cr_2O_3), confirming the pure anatase nature of Hombikat UV100. The powder diffraction patterns of all three Hombikat-based catalysts are summarized in Figure 8.



Figure 8. Powder X-ray diffraction pattern of selected Cr–HOM catalysts (TiO₂ space group: $I4_1/amd$; inorganic crystal structure database (ICSD): 202242; Cr₂O₃ space group $R\overline{3}c$; ICSD: 26791).

The rather broad and intense reflections correspond to anatase (confirming the nanoparticlular nature seen in HRTEM), whereas the low-intensity reflections with small FWHM (full width at half maximum) correspond to eskolaite, indicative of larger particles. No other phases were observed. Cr_{10} + HOM RT showed the broadest anatase reflections, indicative of the nanocrystalline titania. The specific surface area of these catalysts and the pure oxides were investigated by single-point BET measurements and are summarized in Table 1. Hombikat UV100 showed a specific surface area of $312 \text{ m}^2\text{g}^{-1}$, whereas the physical mixture Cr_{10} + HOM RT revealed $278 \text{ m}^2\text{g}^{-1}$. Annealing Hombikat UV100 and Cr_{10} + HOM RT at $500 \degree C$ for 4 h resulted in a decrease of specific surface area to 92 and $78 \text{ m}^2\text{g}^{-1}$, respectively. After wet impregnation and calcination,



Figure 9. Powder X-ray diffraction pattern of rutile and $Cr_{10}@RUT 500/4$ synthesized by wet impregnation and calcined at 500 °C (TiO₂ space group: $P4_2/mnm$; ICSD: 82085; Cr_2O_3 space group: $R\overline{3}c$; ICSD: 26791).

the Cr₁₀@HOM 500/4 catalyst showed a specific surface area of only 84 m²g⁻¹. In contrast to the sol-gel-derived catalysts of our previous work,^[13] there is no correlation of surface area with catalytic activity and selectivity. The PXRD shown at the bottom of Figure 8 confirms the presence of eskolaite and anatase in the physical mixture Cr_{10} + HOM RT, which showed no catalytic activity (see Table 1). However, after calcination at 500 °C the propane conversion at 375 °C reached 35%, whereas no CO was converted (see Figure 2). Although less active compared to the impregnated Hombikat, this facile solid-state reaction of TiO₂ and Cr₂O₃ with cation counter diffusion is the most simple and low-cost way to obtain an active and selective catalyst for this reaction. Note that no CO conversion was detected despite the high CO excess in the feed gas. Small, but sharp, reflections of eskolaite indicate relatively large residual chromia crystals in $\text{Cr}_{10}\text{@HOM}$ 500/4 and $\text{Cr}_{10}\text{+}\text{HOM}$ 500/4 relative to those in Cr₁₀+HOM RT (Figure 8). This finding indicates that because of the high-temperature treatment most of the original Cr has disappeared (dissolved in the anatase lattice).

The PXRD pattern of impregnated rutile $Cr_{10}@RUT 500/4$ showed sharp reflections of rutile and two broad reflections of eskolaite at 25 and 33° with low intensity (see Figure 9). These reflections correspond to the two most intense reflections of eskolaite; the lower intensity reflections of eskolaite were not observed. In $Cr_{10}@HOM 500/4$, the Cr species is largely incorporated in the anatase phase as shown by HRTEM and Rietveld refinement, but about 1.5% remains as Cr_2O_3 , according to HRTEM large crystals, which may be responsible for the chromia reflections in the PXRD (Figure 8). In $Cr_{10}@RUT 500/4$, the Cr species does not dissolve in the rutile lattice; rather it "decorates" the rutile crystals and as such does not provide chromia reflections.

Rietveld analysis of Cr_{10} @HOM 500/4 showed a change of the anatase lattice parameters (*a* 3.7913; *c* 9.4958) compared to pure HOM (*a* 3.7996; *c* 9.5105), indicative of incorporation of Cr into the anatase lattice (solid solution). Phase composition of the sample was found to be 98.5% anatase and 1.5% chromia, indicating that up to 8.5 at.% of the 10 at.% Cr ions are incorporated in the anatase lattice. In contrast, Rietveld analysis of Cr₁₀@RUT 500/4 showed almost identical lattice parameters (*a* 4.59502; *c* 2.95903) when compared with pure rutile (*a* 4.59426; *c* 295915), indicating that in this case very little, if any, Cr is incorporated into the rutile lattice. This finding was also confirmed by the phase composition, which was 92.3% rutile and 7.7% chromia. This facile migration of Cr³⁺ ions into the anatase lattice is not unreasonable because the ionic radius of Cr³⁺ (75.5 pm) is very similar to that of Ti⁴⁺ (74.5 pm).^[16]

To learn more about the role of the Cr ions in the active phase, the catalyst powder samples were investigated by diffuse reflectance UV/Vis spectroscopy (DR-UV/Vis). It was of interest to clarify whether there is a difference between the inactive physical mixtures and the active catalysts. Indeed, a distinct difference in the reflectance spectra was observed (see Figure 10). Hombikat UV100 started to absorb light at 400 nm



Figure 10. DR-UV/Vis spectra of Hombikat UV100, Cr_{10} + HOM RT, Cr_{10} + HOM 500/4, Cr_{10} @HOM 500/4, and Cr_2O_3 500/4.

and full absorbance was reached at 325 nm, which is typical for anatase. $^{\scriptscriptstyle [15]}$ The physical mixture ${\sf Cr}_{10} + {\sf HOM\,RT}$ showed a similar behavior with a lower reflectance of approximately 45% above 400 nm. The two small reflectance minima at 470 and 600 nm indicate octahedrally coordinated Cr, more precisely Cr₂O₃, coexisting with TiO₂.^[17,18] The band-gap region at approximately 375 nm was unaffected by the presence of Cr. In contrast to this, $\mathrm{Cr}_{10}\!+\!\mathrm{HOM}$ 500/4 showed a drastic change of the reflectance spectrum compared to the physical mixture. We observed additional absorption in the range of 360-600 nm as the most significant difference attributed to the annealing at 500 °C. Consequently, it is not surprising that the impregnated catalyst Cr₁₀@HOM 500/4 showed a similar absorption spectrum with an even broader reflectance ascent in the range 360–620 nm. In the literature for similar (Cr,Ti)O₂ systems the spectral changes are attributed to Cr doping.^[17,18] Cr₂O₃ 500/4 absorbed nearly all of the light over the whole measurement range. Again, two minima at 470 and 600 nm, as already mentioned above, could be observed.

 Cr_{10} @RUT 500/4, which showed the reverse catalytic selectivity, was investigated in the same way by DR-UV/Vis (see Figure 11). The spectral changes of the impregnated catalyst are very similar to those of Cr_{10} @HOM 500/4, the main differ-





Figure 11. DR-UV/Vis spectra of rutile, Cr₁₀@RUT 500/4, and Cr₂O₃ 500/4.

ence is that the additional band is not as broad (400–550 nm) as in the sample mentioned first. This indicates Cr doping into the rutile surface in a similar manner to the case of Cr-impregnated anatase. As with anatase, pure rutile is inactive for propane as well as for CO oxidation. Therefore, Cr doping must also be the key to the activity and selectivity for the rutile-based catalyst. Furthermore, we observed the two minima at 470 and 600 nm, which are also apparent in the spectra of Cr₂O₃ 500/4. This indicates the presence of eskolaite (corundum-type Cr₂O₃), which could hardly be observed in the diffraction patterns of Cr₁₀@RUT 500/4 (see Figure 9), therefore, supporting the surface-decoration argument outlined above.

Discussion

Sol-gel-derived TiCr(Ce) oxides have been developed as effective catalysts for selective propane combustion in the presence of CO.^[11-13] Alternative catalysts have been prepared by the more simple impregnation of Hombikat UV100 (anatase) with Cr³⁺ ion-containing solution followed by calcination at 500 °C for 4 h. Chromia (10 mol%) was found to provide the most active impregnated catalysts, this finding is in strong contrast to the sol-gel materials, for which a chromia content of nearly 40 mol % provided the most active material $(Ti_{62.5}Cr_{37.5}O_x)$.^[13] Considering the potential toxicity of chromium oxides, the significantly lower Cr content of the impregnated catalysts may be an advantage for potential applications. Calcination at 500 °C provided the best catalysts, therefore, the defined phases formed at this temperature [anatase (TiO₂) and eskolaite (Cr₂O₃)] may be connected to the unusual catalytic behavior observed. The catalytic performance of the pure phases at 375 °C showed that anatase and rutile are inactive, whereas eskolaite shows a low activity for propane oxidation with a selectivity of 79% relative to simultaneous CO oxidation (see Table 1). This finding points to chromia as the catalytically active phase, whereas anatase acts as a suitable support material, which dissolves the Cr³⁺ ions in its lattice, as shown by the TEM data and the Rietveld analyses. This dissolution of Cr³⁺ into the anatase lattice represents the active and selective phase of Cr₁₀@HOM 500/4. When the two TiO₂ modifications were impregnated with chromia Cr10@HOM 500/4 was more active than and as propane selective as the original sol-gel catalyst Ti_{62.5}Cr_{37.5}O_x, whereas Cr₁₀@RUT 500/4 was CO selective and less active. Therefore, anatase is not only a support for the chromia, but dramatically improves the combustion selectivity, resulting in a highly selective catalyst for hydrocarbon combustion. Rutile, which does not dissolve the Cr³⁺ ions, has the opposite effect as a support for chromia, it improves the CO combustion and reduces the relative hydrocarbon combustion. To the best of our knowledge, this is the first time that the titania modifications have had such a drastic effect on catalytic selectivity. Attempts to reverse the catalyst texture were unsuccessful. Titania (10 mol%) on chromia reduced the catalytic activity and selectivity of the pure eskolaite, confirming the role of titania as support because on the catalyst surface it has a detrimental effect. The results also suggest that anatase has to be doped with chromia to observe the desired catalytic performance. Further support for this hypothesis was obtained by physically mixing chromia with anatase ($Cr_{10} + HOM RT$), which resulted in an unselective material of very low catalytic activity. When the mixture was calcined at 500 °C, the resulting material showed a good activity ($X_{Propane} = 35\%$) and 100% selectivity for propane combustion in the presence of five-fold CO excess. We assume that chromia and anatase form a solid solution comparable to the impregnation of anatase with chromia. The surface areas of the two catalysts are comparable, therefore, the lower activity of Cr_{10} + HOM 500/4 relative to that of Cr₁₀@HOM 500/4 can be attributed to incomplete incorporation of chromia into the anatase lattice by the annealing process relative to impregnation. The lack of catalytic selectivity of Cr₁₀@RUT 500/4 is attributed to the lack of rutile to form a solid solution with chromia because it changes the propane selectivity of pure chromia from 79 to 36%, thus improving the undesired CO oxidation. Ruiz et al. have reported that mixed oxides of chromia-titania with 5-30% Cr upon annealing only show the anatase phase, whereas traces of eskolite formation can only be seen in the 30% Cr material. The dissolved Cr is not visible in the PXRD as was the case in our study. Upon further heating to 900 °C not only a phase change to rutile was observed, but also segregation of additional chromia appeared, indicating that the chromia dissolves in anatase much better than it does in rutile.^[19] This observation is in perfect agreement with our data.

The most active catalyst Cr_{10} @HOM 500/4 for propane combustion in the presence of CO ($X_{Propane} = 80\%$) shows 100% propane selectivity. Calcination for 100 h at 500 °C did not improve the catalytic activity—propane conversion dropped slightly to 70% and selectivity remained stable at 100%, indicating the high structural stability of this new catalyst system. The catalytic performance of Cr_{10} @HOM 500/4 also indicates that TiO₂ and Cr_2O_3 do not have to be mixed from the beginning of the synthesis on an atomic scale, as was originally concluded from the sol–gel materials. HRTEM, as well as Rietveld analysis, indicate that the solid solution of Cr^{3+} ions in anatase is the active site of the catalyst. This analysis also explains the much lower chromia content relative to the sol–gel catalysts, in which a large portion of the chromia is hidden in the bulk material, where it may not contribute to the catalysis. The sol–



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gel procedure used is well known to provide true mixed oxides, which may be best described as solid solutions.^[20] DR-UV/Vis investigations, which mainly sample the surface layers, revealed that Cr is incorporated into the TiO₂ surface. This Crdoped TiO₂ phase on the surface is the key to the observed catalytic activity and selectivity. To determine the oxidation state of Cr in the TiO₂ lattice, X-ray photoelectron spectroscopy (XPS) was considered, but was not used owing to its known problems with differentiation between Cr³⁺ and Cr⁴⁺ ions (overlap of Cr 2p for Cr³⁺ and Cr⁴⁺).^[21] Oxygen XPS was considered to be too complex because Cr oxides and Ti have several O1s signals. The dissolution of Cr in the anatase lattice is strong evidence for the exclusive presence of Cr³⁺ ions owing to ionic radius. Whether Cr^{4+} or Cr^{2+} ions are present or are formed during the catalytic reactions cannot be clarified with our methods and would require additional investigations. More information on the detailed mechanism would require better knowledge about the surface mobility of oxygen during the catalysis. Isotopic exchange studies with oxygen are promising techniques as pioneered by Descorme and Duprez on mixed oxides.^[22] Unfortunately, to date, no studies have been reported on the Cr-Ti mixed-oxide couples.

During the sol-gel-study, addition of $Ce(NO_3)_3$ solution was found to significantly improve the catalytic activity.^[13] It is well known that the Ce^{3+} is converted to Ce^{4+} (CeO_2) during calcination. The role of ceria was further investigated by impregnating Hombikat UV100 with a Ce^{3+} and Cr^{3+} solution. Although there was no improvement in propane combustion activity, the catalyst converted some CO, resulting in a drop in selectivity. The lack of Ce to improve the catalytic performance of the impregnated catalyst is attributed to its exclusive nature to modify the surface. We believe that in the sol-gel synthesis the Ce ions are incorporated into the mixed-oxide lattice (Cr– Ti), where they increase the surface area and may support the lattice oxygen contribution to the combustion.

Testing the long-term stability of Cr₁₀@HOM 500/4 provided further insights into the oxidation mechanism. The doped catalysts showed almost the same activity loss as the sol-gel-derived catalysts. Activity decreased from 80 to 40% within 72 h. Neither XRF nor PXRD showed any changes in the solid after this period, which could indicate leaching of the metal ions or phase changes. In our mechanistic study we observed, by DRIFTS analysis, that propane formed carboxylates with the lattice oxygen of the catalysts,^[13] supporting a Mars-van Krevelen mechanism. When propane is oxidized by the solid, the solid itself is reduced and is afterwards oxidized by the molecular oxygen of the gas feed. Apparently, the oxidation of propane and consequently the reduction of the solid are faster than its reoxidation by O₂. At the point where propane activity remains constant (X = 40%, see Figure 4), the reduction and the oxidation of the solid are equilibrated. Clearly, with a gas-feed composition of 2.0 vol.% propane, 10.9 vol.% CO, and 10.0 vol.% O₂ the reaction was operated under reductive conditions (stoichiometric combustion of CO and propane would require 15.5 vol.%), which may restrain oxidation processes. After 24 h of reaction pure molecular oxygen was introduced, at 375 °C for 1 h, and most of the initial catalytic activity was restored, which implies that the lattice oxygen in the solid is replenished, supporting the above hypothesis. When the reaction was continued, the catalyst deactivated again and reconditioning with molecular oxygen again increased the catalytic activity (see Figure 4). An increase of the oxygen content in the feed should result in a higher equilibrium conversion with the risk that CO oxidation may be promoted owing to excess oxygen. Doubling the oxygen concentration in the gas feed resulted in a higher propane conversion and a smaller loss in activity after 72 h with an equilibrium conversion of 56% (see Figure 5) and, surprisingly, no additional CO was oxidized, so the propane combustion selectivity was maintained. Owing to experimental limitations and the explosion risk, higher oxygen concentrations could not be studied, although they may be promising. In this case microreactors should be used. We have shown that most of the activity loss during the experiments can be attributed to loss of lattice oxygen, which is not filled fast enough by the oxygen concentrations used in the feed. The fact that the original catalytic activity was not recovered fully could be due to irreversible sintering, it could also be due to incomplete reoxidation or to some coking. Evidence against coking was provided by the TGA experiment, which also supported the Mars-van Krevelen mechanism. Because the particle size of P25 changed from 20 to approximately 250 nm upon sintering at 800 °C, sintering remains the most likely option to explain the unrecovered activity loss.

More evidence for the origin of the selective propane combustion activity was obtained with DR-UV/Vis spectroscopy. The physical mixture of Hombikat UV100 and Cr₂O₃ showed that both phases coexisted alongside each other. The annealed mixture ($Cr_{10} + HOM 500/4$) and the impregnated material (Cr₁₀@HOM 500/4) showed an additional band ranging from 360 to 600 nm and 360 to 620 nm in the DR-UV/Vis spectra, respectively. This is taken as evidence that Cr is incorporated into the TiO₂ lattice.^[17,18] The wide range of this band could be an indication for gradual doping. Because this band was accompanied by increased propane combustion activity, this is further evidence for the Cr-doped TiO₂ phase as the key to the selective propane oxidation. The impregnated rutile showed a similar DR-UV/Vis spectrum, indicating that the additional band may be associated with the catalytic activity, but does not explain the catalytic selectivity. Our hypothesis on the role of anatase as a support is strengthened by the poor activity of the Ti-impregnated Cr₂O₃. The DR-UV/Vis spectra and the powder diffraction pattern showed that there are two separate phases of TiO₂ and Cr₂O₃ and in addition Cr-doped TiO₂ is also present. These measurements give further insights into the origin of the active phase, but the roles of the two phases and the doped phase in the selective oxidation of propane need to be investigated in more detail by other techniques.

Conclusion

Doping of anatase with chromia (Cr_{10} @HOM 500/4) provided a propane-selective combustion catalyst in the presence of a five-fold excess of CO (100% selectivity). The same catalyst, when prepared with the TiO₂ modification rutile, was CO selec-



tive and much less active for propane combustion. HRTEM studies have shown that the chromia does not decorate the anatase nanoparticles, but dissolves completely, whereas chromia on rutile does decorate the crystal surface and shows a lower tendency to dissolve in this lattice. These findings were supported by Rietveld refinements. Surface-sensitive DR-UV/Vis spectroscopy provided evidence that Cr is incorporated into the surface of the anatase and to a lesser extent also into the surface of the rutile phase. Rapid initial deactivation could be assigned to loss of lattice oxygen, supporting a Mars-van Krevelen mechanism. Catalyst activity could be restored by purging with pure oxygen. Deactivation of the catalysts was attributed to depletion of lattice oxygen by the reductive gas feed, underlining the proposed Mars-van Krevelen mechanism. TGA with the deactivated catalyst showed a slight weight increase at 300 °C, which is related to filling of oxygen vacancies, thus further supporting the Mars-van Krevelen mechanism. Increasing the oxygen concentration in the feed resulted in improvements of initial and long-time conversion without causing undesired CO oxidation. The most active and selective catalyst, Cr₁₀@HOM 500/4, was obtained by impregnation of Hombikat with Cr³⁺ solution, which is a significant improvement of the synthesis compared with our earlier sol-gel synthesis. Further simplification of the synthesis was achieved by physically mixing the two oxide phases, which after calcination were also catalytically active and propane selective ($Cr_{10} + HOM 500/4$). Catalyst deactivation that could not be restored could be attributed to further sintering. Coking was excluded by TGA experiments.

Chromia-doped anatase is a new heterogeneous catalyst with unusual catalytic selectivities for hydrocarbon oxidation. It may also have yet unrecognized properties as a selective oxidation catalyst for a variety of reactions not studied yet.

Experimental Section

Catalysts are identified by their relative molar composition given as subscript after the element symbol. "@" is used for wet impregnation, "+" for a physical mixture, "HOM" for Hombikat UV100 (a commercial nanocrystalline and pure anatase TiO₂ from Sachtleben Chemie), "P25" for TiO₂ P25 from Degussa, and "RUT" for rutile. Calcination is characterized by final temperature (°C) and duration (h).

Synthesis

The Cr₁₀@HOM 500/4 catalyst was prepared by wet impregnation and final calcination at 500 °C for 4 h. To obtain 20 mmol catalyst, Cr(NO₃)₃·9H₂O (800 mg, Sigma Aldrich) was dissolved in deionized H₂O (5 mL). Hombikat UV100 (1.438 mg) was added under stirring, followed by treatment in an ultrasonic bath for 2 h. The suspension was stirred again for 15 min, dried at 110 °C for 12 h and calcined at 500 °C for 4 h. The heating ramp was 10 °Ch⁻¹.

Cr₁₀+RUT 500/4 was prepared by solid-state reaction. First, P25 (TiO₂ from Degussa) was annealed at 800 °C for 10 h to obtain pure rutile, Cr(NO₃)₃·9H₂O (Sigma Aldrich) was annealed at 500 °C for 4 h to obtain Cr₂O₃. TiO₂ (72.6 mg) was ground with Cr₂O₃ (7.27 mg) in n-pentane by using a mortar and pestle. The powder was dried at 110 °C for 12 h and calcined at 500 °C for 4 h.

All the other catalysts were prepared in a similar way. For Ce impregnation of Hombikat a $Ce(NO_3)_3$ - $6H_2O$ solution was used.

Activity measurement

The activity-measurement setup consisted of a glass-tube reactor with an internal diameter of 6.1 mm. 20 mg of catalyst (100-200 μ m) diluted with 200 mg SiO₂ (100–200 μ m) was added to the glass tube and pretreated in synthetic air at 375 °C for 90 min. The feed gas $(C_3H_8/CO/CO_2/O_2/N_2 = 2.0/10.9/15.8/10.0/61.3 \text{ vol. \%})$ and the synthetic air ($O_2/N_2 = 20/80$ vol.%) had a total gas flow of 50 mLmin⁻¹. Both, the reactor containing the catalyst and the reactor that acts as bypass (filled with SiO₂) were encased in the same brass heating unit. The feed gas composition was analyzed flowing through the bypass by a micro gas chromatograph (GC) (Varian CP-4900) before the first (375 $^\circ\text{C})$ and after the last run (275 $^\circ\text{C}).$ Measurements were taken at 275, 300, 325, 350, and 375 °C, product gas composition was monitored by GC. Between each sample run, there was a hold time of 15 min. Investigations without propane or CO in the gas feed were carried out by replacing one of the gases by N_2 .

Mass-transport limitation was investigated at 375 °C with the same setup as that described above. The gas flow rate as well as the catalyst mass and SiO_2 mass were changed by the same factor to obtain a constant residence time. For each measuring point, fresh catalyst was filled into the reactor and pretreated at 375 °C for 90 min in synthetic air.

Long-term stability tests were also carried out in the same arrangement, holding the temperature at 375 °C for the chosen period. For the reconditioning, pure molecular oxygen was introduced at 375 °C for 1 h at a gas flow rate of 50 mLmin⁻¹.

Characterization

To specify the surface area of the catalysts, nitrogen physisorption measurements were carried out on a single-point BET Fisons Instruments Sorpty 1750. The adsorption isotherms were recorded at -196 °C with ground materials. The samples were outgassed at 200 °C for 2 h.

Powder X-ray diffraction patterns were obtained using a PANalytical X'Pert PRO system with

Ni-filtered Cu-K α_1 and Cu-K α_2 radiation ($\lambda = 1.54060$ Å and $\lambda = 1.54443$ Å, respectively). The instrument has a Bragg–Bretano geometry and a PIXcel detector. The shown diffraction patterns are background corrected with X'Pert Highscore Plus software.

Diffuse-reflectance UV/Vis (DR-UV/Vis) measurements were obtained with a PerkinElmer UV/Vis-NIR spectrometer Lambda 19 equipped with a Labsphere RSA-PE-19 Ulbricht sphere. All samples were ground and measured in a sample holder covered by quartz glass.

X-ray fluorescence (XRF) analyses were performed on an EDAX Eagle II μ -Probe instrument with a rhodium anode as a radiation source and evaluated with the program Vision 32 (Version 3.35). The excitation voltage was 40 kV. Each powder sample was measured at three different spots for 60 s and the results were averaged.

For high-resolution transmission electron microscopy (HRTEM) a Hitachi HF-2000 instrument was used. Energy-dispersive X-ray analysis (EDX) was performed by using a Noran EDX system with a liquid nitrogen cooled Si(Li) detector. For sample preparation the



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catalyst powders were deposited on Holey carbon grids (Cu, 400 mesh, 3 mm diameter).

Thermographic analysis was performed on a Mettler Toledo TGA/ DSC 1 Star^e system (Software Star^e version 12.00a, 70 μ L corundum crucible, 30–900 °C with 2 °C min⁻¹, synthetic air 30 mL min⁻¹).

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Keywords: chromium • exhaust gas treatment • hydrocarbons • heterogeneous catalysis • propane combustion • carbon monoxide • titania

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