Catalysts for selective propane oxidation in the presence of carbon monoxide: Mechanistic aspects

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Simon Swislocki, Klaus Stöwe, Wilhelm F. Maier *

Technische Chemie, Saarland University Campus C4 2, D-66123 Saarbruecken, Germany

A B S T R A C T

The competitive combustion of propane and carbon monoxide was investigated with regard to its selectivity for propane oxidation. Based on variations in the sol–gel synthesis and the composition, the $TiCrO_x$ catalysts were optimized. Specifically, the addition of small amounts of cerium led to a catalyst, which converted 89% propane at 375 °C but no carbon monoxide. The origin of this excellent and unusual selectivity has been investigated. The method of choice was diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS), which allowed recording adsorbed species on the catalysts surface. Hopcalite was taken as reference catalyst due to its selectivity (although opposite to $TiCrO_x$) for the combustion of carbon monoxide in the presence of hydrocarbons. The spectroscopic investigations showed that carbon monoxide is linearly adsorbed on Cu^+ at lower temperatures and formed carbonates at higher temperatures, whereas propane formed no detectable adsorbed species on hopcalite. The $TiCrO_x$ catalyst formed formate species with carbon monoxide above 250 °C and carboxylates with propane above 150 °C. The mixture of propane and carbon monoxide led to the formation of both species. By the addition of oxygen to the gas feed, only propane formed adsorbates on the catalysts surface, whereas CO seemed not to interact with the surface. Pre-adsorbed oxygen probably inhibits the adsorption of carbon monoxide but is not necessary for propane activation. The formation of carboxylates from propane also takes place in the absence of molecular oxygen, pointing to a Mars-van-Krevelen-like mechanism, in which lattice oxygen is involved in the oxidation process. A physical mixture of TiO_2 and Cr_2O_3 showed no catalytic activity, and spectroscopic investigations showed no adsorbates on the sole oxides. Since only anatase and eskolaite could be identified in the powder diffraction patterns of the catalysts, a third phase has to be responsible for the propane oxidation, most likely surface decorations or solid solutions of the metal ions.

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1. Introduction

Reduction of pollution and energy waste belong to the challenging problems of today's energy research. Lowering fuel consumption and pollution of combustion engines in vehicles or for power generation will continue to play a major role, in part required by new emission standards. Light-off temperature, selectivity and costs are parameters of catalytic converters still subject of optimization. In the automotive sector, the three-way-catalyst (TWC) is well established and could always be adapted to the given emission standards. Small vehicles such as motor scooters and household engines with two-stroke engines, such as chain saws, lawn-mowers, leaf-blowers, hedge trimmers a.o. are not yet affected by these emission standards, although they contribute to

pollution. Because of the oil content of its gasoline–oil-mixture, the exhaust gases of two-stroke engines are dominated by hydrocarbon fragments and CO. Due to its rapid dilution, CO is here less a problem, while the hydrocarbon fragments are responsible for odor and smoke and should be removed. Pt, Pd, and Rh work well in the TWC, but are rare and expensive [1–3]. All of these noble metals oxidize carbon monoxide (CO) easily at $T > 200$ °C; only Pt, which does not form oxides at these conditions, provides adsorption sites for the chemisorption of hydrocarbons (HC). However, even on Pt, the adsorption of CO and the chemisorption of O_2 are both favored over the adsorption of alkanes. Therefore, the oxidation rate for saturated HC is an inverse function of the oxygen partial pressure [4,5]. This behavior is different for other HCs such as olefins and aromatics. So, the selectivity for CO is high and this noble metal system offers low scope for tuning this selectivity. The two competitive oxidation processes in the TWC are shown in the following equations.

* Corresponding author. Fax: +49 681 302 2343.
  E-mail address: w.f.maier@mx.uni-saarland.de (W.F. Maier).

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (1)$$

$$CO + 1/2O_2 \rightarrow CO_2 \qquad (2)$$

If new emission regulations are passed for two-stroke engines, new catalytic converters will have to be developed, since the TWC based on Pt is not suitable. It is too expensive for such small combustion engines, and the oil-rich exhaust gases will be problematic for the catalytic system [6].

Therefore, new low cost catalysts that convert selectively HC are of interest. Mixed metal oxides, synthesized via sol–gel processes, provide potential catalysts of high diversity with a wide variety of composition and synthesis parameters. We have synthesized and tested over 2000 mixed oxides using high-throughput technologies. The powder samples were prepared with pipetting robots and for prescreening emissivity corrected infrared thermography (ecIRT) has been applied [7–10]. During the search, the ternary compound $Ti_{33.3}Cr_{33.3}Ce_{33.3}O_x$ was discovered, which showed a propane conversion of 58% and CO conversion of 25% at 350 °C in conventional tests. The composition of the catalyst was further optimized to $Ti_{50}Cr_{30}Ce_{20}O_x$. Investigations on the effects of the Ti, Cr, and Ce ions led to the binary $Ti_{62.5}Cr_{37.5}O_x$ catalyst, which converts 42% propane but no CO, providing a selectivity of about 100% [9]. This observed selectivity is unusual considering the facile oxidation of CO and the energy-demanding C—H activation in propane. Common catalysts preferentially oxidize CO, such as TWC or hopcalite. Therefore, there must be a specific mechanism, which provides the HC-oxidation selectivity observed with the Ti–Cr oxide. We have chosen diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for investigation. With DRIFTS, Daniel et al. showed that the Pt surface of a Pt/Al_2O_3 catalyst is almost completely covered by adsorbed CO up to 190 °C. With increasing temperature, the band of linearly adsorbed CO at 2065 cm^{-1} disappears in the absorbance spectrum and gaseous CO_2 is formed. This marks the light-off temperature at which adsorption sites for oxygen become available and the catalytic conversion of CO starts [11]. Further studies on mechanistic aspects such as methanation of CO over Ru/TiO_2 or the water–gas-shift reaction over Pt—Sn on activated carbon were done by other groups using DRIFTS techniques [12,13]. X-ray photoelectron spectroscopy (XPS) has been considered; however, its known problems with differentiation between Cr(III) and Cr(IV) (overlap of Cr-2p for Cr^{3+} and Cr^{4+}) led us to not use it [14].

There are two objectives of this work. First is the increase in the catalytic performance. Sol–gel processes provide plenty of parameters, such as composition and synthesis parameters, which can be altered easily and influence the most important properties such as activity and selectivity. With the best binary catalysts developed, the catalytic mechanism leading to the observed selectivity is studied. This is performed by infrared spectroscopy, more precisely DRIFTS, by investigating adsorbed species of propane and CO and their competition on the catalyst surfaces and control materials.

2. Experimental

2.1. Synthesis

The $Ti_{50}Cr_{47.5}Ce_{2.5}O_x$ catalyst was prepared via sol–gel synthesis. 1 M solutions of $Ti(OiPr)_4$ (Alfa Aesar), $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich) and $Ce(NO_3)_3 \cdot 6H_2O$ (ChemPUR) in ethanol (Sigma Aldrich, p.a.) were prepared in separate beakers. 0.25 ml of Ce-solution, 4.75 ml of Cr-solution and 5.00 ml of Ti-solution were combined with 3.74 ml 4-hydroxy-4-methyl-2-pentanon (Alfa Aesar) as complexing agent and hydrolyzed at room temperature for 11 d and at 50 °C for 7 d. The resulting gel was calcined at 400 °C for 5 h with a starting ramp of 20 °C/h.

2.2. Activity measurement

The activity measurement setup consisted of a glass tube reactor (i.d. 6 mm) and encased by a heating unit. Twenty milligram of catalyst (100–200 μm) diluted in 100 mg SiO_2 (200–300 μm) was filled into 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 vol.%) and the synthetic air (O_2/N_2 = 20/80 vol.%) had a total gas flow of 50 ml/min. The feed gas composition was rechecked through a bypass before the first (375 °C) and after the last run (275 °C) by gas chromatography (GC) (Agilent GC 6890). The product gas composition was also analyzed by GC, passing first a cold trap to condense water formed during the combustion of propane. Between each sample run, there is a hold time of 25 min. Stability tests were done in the same way, holding the temperature at 375 °C for 72 h.

2.3. Characterization

To specify the surface area of the catalysts, nitrogen physisorption measurements were carried out on a Carlo Erba Sorptomatic 1990. The adsorption isotherms were recorded in static volumetric technique at −196 °C with the sieve fraction of 100–200 μm for all catalysts. The samples were outgassed at 200 °C for 2 h.

Powder X-ray diffraction patterns were obtained using a PANalytical XPert PRO system with Ni-filtered Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation (1.54060 and 1.54443 Å). The instrument has a Bragg–Bretano-geometry and a PIXcel detector. The shown diffraction patterns are background corrected with X'Pert Highscore Plus software.

2.4. DRIFTS measurements

The samples for DRIFTS measurements were ground, dried and outgassed at 80 °C in vacuum. The powders were pretreated at 400 °C for 90 min in the sample cup of the DRIFTS gas cell under continuous N_2 flow with a flow rate of 25 ml/min. After pretreatment, the sample was cooled down to room temperature and the reaction gas was introduced into the cell. The spectrometer used was a BRUKER Vertex 70 with a modified Harrick Praying–Mantis cell and a liquid nitrogen cooled MCT detector (see Fig. 1). All FT-IR spectra were recorded in reflectance and with open beam as background. Two hundred scans were recorded for the background spectra and 50 scans for the sample spectra with a spectral resolution of 4.0 cm^{-1}. The actual spectrum was obtained by dividing the sample spectrum by the background spectrum. Usually, −log R plots are displayed in DRIFTS measurements, in which R stands for reflectance. To attain these graphs, the following measurement sequence was performed. It started by taking the background spectrum of KBr in N_2 atmosphere. Then spectra of KBr in CO (CO/N_2 = 10.9/89.1 vol.%), propane (C_3H_8/N_2 = 2.0/98.0 vol.%), and propane + CO ($C_3H_8/CO/N_2$ = 2.0/10.9/87.1 vol.%) were recorded. Each of these three spectra was divided by the N_2 spectrum for background correction. The same procedure was then applied to hopcalite and $Ti_{62.5}Cr_{37.5}O_x$ (here abbreviated to $TiCrO_x$). The corrected hopcalite and $TiCrO_x$ spectra were divided by the corrected KBr spectra, obtaining the −log R spectra. Spectra at 35, 100, 150, 200, 250, 300, 350, and 375 °C were taken with a hold time of 10 min between the measurements. The Cr_2O_3 spectra were recorded using a mixture of Cr_2O_3 and KBr (1:10). The reduction of the Cr_2O_3 powder took place in the DRIFTS sample holder, purging the cell with CO at 400 °C for 24 h. In this case, Cr_2O_3 was not diluted in KBr. Spectra in oxidizing atmosphere were taken with the same CO or propane mixtures as ascribed above, replacing N_2 with 10.0 vol.% O_2. In this case, the pretreatment was carried out in synthetic air (O_2/N_2 = 20.0/80.0 vol.%).