



# Impact of feed impurities on catalysts for chlorine recycling



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## ABSTRACT

This study assesses the impact of feed impurities on the design of a robust catalytic process for chlorine recycling *via* HCl oxidation (Deacon reaction). The influence of CO, SO<sub>2</sub>, and COS was investigated over stable catalysts, including RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>/ZrO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>/ZrO<sub>2</sub>, IrO<sub>2</sub>/TiO<sub>2</sub>, and CuCrO<sub>2</sub>. Carbon monoxide is detrimental for RuO<sub>2</sub>- and IrO<sub>2</sub>-based catalysts, since the highly exothermic oxidation to CO<sub>2</sub> under Deacon conditions causes pronounced temperature rises leading to material and reactor instabilities. Advantageously, the other catalysts are practically unaffected by this impurity due to their inactivity for CO oxidation in the chlorinated state. Carbonyl sulfide and particularly sulfur dioxide severely poison all the catalysts investigated due to the strong adsorption of the sulfur compounds and active site blockage. However, the initial activity can be restored by treating the deactivated catalysts in HCl (without oxygen) at the reaction temperature. We discuss process strategies for feed purification and catalyst regeneration depending on the chosen catalytic system, which are of utmost importance for the ultimate sustainability of the process.

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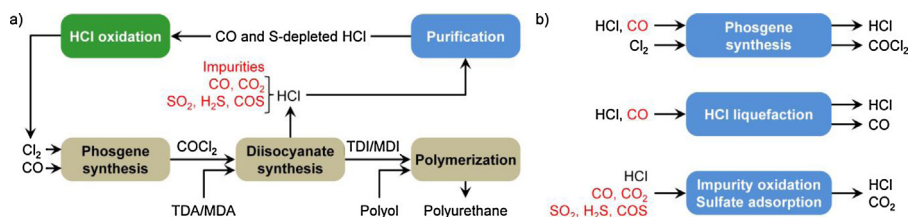
## 1. Introduction

The assessment of catalytic performance in academic studies is generally conducted under ideal conditions, that is, using model mixtures of the pure reactant(s). However, it is well known that feed streams in industry often contain a wide spectrum of impurities, which can detrimentally affect the catalytic performance [1,2]. For example, in the petroleum industry, hydrogenation processes, and catalytic converters, sulfur, nitrogen, halogens, and metals are prominent contaminants, inhibiting and/or poisoning catalysts [2–7]. Usually, these compounds have to be removed prior to the catalytic step by cost-intensive purification processes. Alternatively, the search for catalysts that tolerate impurities is highly attractive. An illustrative example of how critical feed impurities are for catalyst and process design comprises iron-loaded zeolites for N<sub>2</sub>O abatement. Compared to other metals, iron exhibits moderate-to-low activity for N<sub>2</sub>O decomposition in a standard feed containing only nitrous oxide [8]. However, compounds such as NO, CO, and SO<sub>2</sub> present in industrial tail gases boost the N<sub>2</sub>O decomposition activity over Fe-zeolites, a crucial result for its today's wide industrial implementation [9].

In the last decade, the gas-phase oxidation of HCl to Cl<sub>2</sub> (Eq. (1)) has received considerable attention as a sustainable process to recycle the growing excess of byproduct HCl generated in the phosgene-mediated manufacture of polyurethanes and polycarbonates, due to its superior energy efficiency and environmental friendliness over alternative strategies such as HCl electrolysis or neutralization [10]. Intense research efforts led to the development of active catalysts based on RuO<sub>2</sub>, CeO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, IrO<sub>2</sub>, and CuCrO<sub>2</sub>, which satisfy the stability requirements that rendered the original Deacon catalyst based on CuCl<sub>2</sub> and many other analogues impractical [11–15]. However, the performance of these catalytic systems may be affected by various contaminants that are present in industrial HCl-containing streams, such as CO, COS, SO<sub>2</sub>, and H<sub>2</sub>S (Scheme 1a) [16,17]. The patent literature discloses that CO can deactivate RuO<sub>2</sub>-based catalysts for HCl oxidation at high temperatures, due to the formation of volatile metal carbonyls and/or carbonates [16]. Besides, the ability of the catalysts to oxidize CO to CO<sub>2</sub> under HCl oxidation conditions is critical, since the reaction is highly exothermic (Eq. (2)) and thus can lead to uncontrolled local temperature rises in the catalyst bed [16]. The resulting hot spots induce undesired sintering of the active RuO<sub>2</sub> phase and over-oxidation to the volatile RuO<sub>4</sub> [10]. With respect to sulfur compounds, it is known that RuO<sub>2</sub>-based materials are thiophilic, leading to the formation of stable bonds with sulfur and thereby poisoning the active sites for HCl oxidation. Specifically, the presence of COS (11 ppm) and SO<sub>2</sub> (53 ppm) in the Deacon mixture

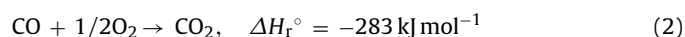
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**Scheme 1.** (a) In the production of TDI (toluene diisocyanate) and MDI (methylene diphenyl diisocyanate), the HCl byproduct can be recycled to Cl<sub>2</sub> via catalyzed oxidation. The gaseous HCl stream, containing carbon monoxide and sulfur compounds, requires purification in order to prolong the catalyst lifetime. The different strategies to remove these impurities are depicted in (b).

(HCl + O<sub>2</sub>) reduced the activity of RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> by 20 and 32% within the first 10 h on stream, respectively [17].



As a consequence, the HCl stream has to be duly purified to ensure catalyst and process stability. Carbon monoxide can be removed by reaction with Cl<sub>2</sub> over activated carbon to form phosgene, which can be subsequently separated from HCl and fed to the diisocyanate synthesis (Scheme 1b, top) [16]. Alternatively, HCl can be liquefied by compression at elevated pressure, followed by the removal of the CO gas from the HCl liquid and the evaporation of the latter in the Deacon reactor (Scheme 1b, middle) [18]. More conveniently, the catalyzed CO oxidation to CO<sub>2</sub> can be conducted over a conventional noble metal-based catalyst prior to the HCl oxidation reactor (Scheme 1b, bottom) [19,20]. The latter approach also removes sulfur compounds by their oxidation and subsequent adsorption of the resulting sulfate on the same catalyst.

With the exception of some patents dealing with RuO<sub>2</sub>-based catalysts, the role of impurities in HCl-containing streams on other relevant Deacon catalysts (possessing very different intrinsic properties and operating temperatures) remains unexplored. We herein assess the individual and combined impact of CO, SO<sub>2</sub>, and COS on the HCl oxidation performance of RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, IrO<sub>2</sub>/TiO<sub>2</sub>, CeO<sub>2</sub>/ZrO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>/ZrO<sub>2</sub>, and CuCrO<sub>2</sub>. The activity and stability patterns of these catalytic materials in relation to these contaminants are quantified by means of temperature-programmed and steady-state tests. This understanding is necessary to evaluate the sensitivity of promising catalysts to technical process conditions, which ultimately determines the extent of the feed purification and the design of suitable regeneration strategies.

## 2. Experimental

### 2.1. Catalysts

The preparation and characterization of the catalysts used in this study have been detailed in recent publications [11–15]. Briefly, RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (2 wt.% Ru,  $S_{\text{BET}} = 29 \text{ m}^2 \text{ g}^{-1}$ ), IrO<sub>2</sub>/TiO<sub>2</sub> (2 wt.% Ir,  $S_{\text{BET}} = 24 \text{ m}^2 \text{ g}^{-1}$ ), CeO<sub>2</sub>/ZrO<sub>2</sub> (7.7 wt.% Ce,  $S_{\text{BET}} = 48 \text{ m}^2 \text{ g}^{-1}$ ), and U<sub>3</sub>O<sub>8</sub>/ZrO<sub>2</sub> (9.8 wt.% U,  $S_{\text{BET}} = 35 \text{ m}^2 \text{ g}^{-1}$ ), were prepared by incipient wetness impregnation of corresponding carriers with aqueous solutions of RuCl<sub>3</sub>·xH<sub>2</sub>O, IrCl<sub>3</sub>·xH<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, respectively, followed by drying and calcination. Bulk CuCrO<sub>2</sub> (1 m<sup>2</sup> g<sup>-1</sup>) was synthesized by static-air calcination of a ball-milled equimolar mixture of Cu<sub>2</sub>O and Cr<sub>2</sub>O<sub>3</sub> at 1373 K for 30 h.

### 2.2. Methods

The metal content in the fresh and used catalysts was determined by X-ray fluorescence (XRF) using an Orbis Micro-EDXRF with a Rh source (50 kV) and a silicon drift detector. The amounts

of carbon and sulfur were measured by quantitative infrared spectroscopy performed using a LECO CHN-900 combustion furnace. Powder X-ray diffraction (XRD) patterns were acquired in a PANalytical X'Pert PRO-MPD diffractometer. Data were recorded in the 10–70° 2θ range with an angular step size of 0.017° and a counting time of 0.26 s per step. N<sub>2</sub> sorption at 77 K was measured in a Quantachrome Quadrasorb-SI analyzer. Prior to the measurement, the samples were evacuated at 473 K for 12 h. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed at 473 K under N<sub>2</sub> atmosphere using a Bruker Vertex 70 spectrometer. Prior to the measurement, the samples were dried at 573 K in N<sub>2</sub> (100 cm<sup>3</sup> STP min<sup>-1</sup>) for 1 h. Spectra were recorded in the range of 700–1500 cm<sup>-1</sup> with a nominal resolution of 4 cm<sup>-1</sup> and co-addition of 200 scans.

### 2.3. Catalytic tests

Catalytic tests were performed in a home-made continuous-flow micro-reactor. The catalyst (0.25 g, particle size = 0.4–0.6 mm) was loaded in a quartz tube (8 mm i.d.) between two plugs of quartz wool. Temperature-programmed reactions (TPR) and steady-state experiments were performed at ambient pressure using feed mixtures containing 10 vol.% HCl, 20 vol.% O<sub>2</sub>, with or without addition of 1 vol.% CO, 0.03 vol.% COS, 0.03 vol.% SO<sub>2</sub>, and 2 vol.% Ar, balanced in He, at a total volumetric flow of 166 cm<sup>3</sup> STP min<sup>-1</sup>. TPR experiments in HCl + O<sub>2</sub>, CO + O<sub>2</sub>, and HCl + CO + O<sub>2</sub> were carried out by ramping the furnace temperature in the range of 353–773 K at 5 K min<sup>-1</sup> to derive the light-off temperatures of the catalysts for Cl<sub>2</sub> and CO<sub>2</sub> production. Steady-state tests were performed at temperatures of 603 K (RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>), 703 K (CeO<sub>2</sub>/ZrO<sub>2</sub>), and 723 K (IrO<sub>2</sub>/TiO<sub>2</sub>), to quantitatively determine deactivation behaviors in different feed mixtures as well as to measure the bed temperature rise caused by the presence of carbon monoxide. The apparent activation energies for HCl and CO oxidation were measured between 543 and 660 K under steady-state conditions in a mixture of HCl + CO + O<sub>2</sub>. Kinetic experiments of CO oxidation over RuO<sub>2</sub>/SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were conducted at variable inlet CO concentration (0.5–3 vol.%) and 20 vol.% O<sub>2</sub> at 603 K. The sulfur-poisoned catalysts were regenerated in a feed containing 10 vol.% HCl in He at the reaction temperature of the corresponding system. Selected samples were collected after the catalytic tests for characterization by rapidly cooling down the reactor to room temperature in a He flow.

Online analysis was carried out using an OmniStar mass spectrometer (MS) from Pfeiffer Vacuum equipped with an yttria-coated iridium cathode and connected to the reactor outlet with a quartz capillary (length = 1.5 m, i.d. = 0.75 μm) heated at 413 K. The ion currents of AMU (atomic mass units) 28 (CO), 44 (CO<sub>2</sub>), 64 (SO<sub>2</sub>), and 70 (Cl<sub>2</sub>) were normalized to the internal standard (Ar, AMU 40). The CO signal was calibrated prior to the experiments in order to quantify the CO conversion. The percentage of CO conversion was determined as  $X_{\text{CO}} = [(\text{mol CO}_{\text{inlet}} - \text{mol CO}_{\text{outlet}}) / \text{mol CO}_{\text{inlet}}] \times 100$ . The amount of

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