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Catalytic Bromine Recovery: An Enabling Technology for Emerging Alkane Functionalization Processes

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The functionalization of light alkanes into value-added products represents one of the most relevant and challenging areas in catalysis research.[1] In particular, energy-efficient and cost-effective processes to selectively convert the abundant reserves of natural gas into chemical intermediates and fuels are highly sought. Pioneering work by Olah et al.[2] and more recent studies by McFarland, Stucky, and co-workers[3,4] have shown that the bromination of light alkanes to the corresponding alkyl bromides followed by a catalyzed elimination reaction offers an attractive route to obtain a broad spectrum of desirable products (Figure 1). Bromine-mediated reactions of hydrocarbons are far more selective and occur under much milder conditions (typically 475 K and 100–200 kPa) than classical alkane upgrading processes (steam reforming, steam cracking, and dehydrogenation), which leads to increased product yields, energy savings, and decreased CO_2 emissions.[3] For instance, the conversion of methane into olefins through methyl bromide represents an intensified alternative to the conventional methanol-based process by circumventing the costly intermediate syntheses of syngas and methanol.[4c] Another illustrative example comprises the bromine-based dehydrogenation of propane, which gives a yield of propylene that is three higher than the highest reported yields given by oxidative dehydrogenation.[4e] However, as shown in Figure 1, every mole of alkane converted through this two-step process generates two moles of HBr byproduct. Accordingly, the development of a robust and economic process to recover Br_2 from HBr is essential to enable the sustainable bromine-mediated upgrading of alkanes. A suitable halogen regeneration technology would also aid the valorization of waste HBr streams originating from the manufacture of organobromides employed as flame retardants, polymers, and pharmaceutical intermediates.[5]

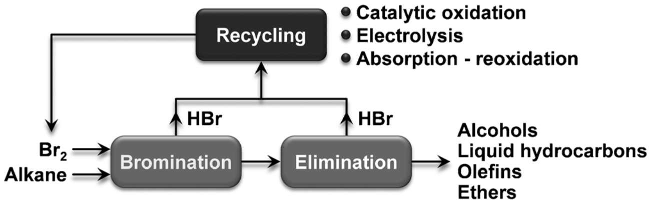

Figure 1. The sustainable Br_2-mediated conversion of light alkanes into valuable chemical intermediates and fuels requires an integrated HBr recycling process to regenerate the halogen.

Bromine recovery can be achieved by HBr electrolysis,[6] HBr oxidation,[5,7] and HBr absorption by a cataloreactant followed by its reoxidation.[4a,b] To our knowledge, none of these processes are established on a technical scale. The catalyzed gas-phase oxidation of HBr with O_2 or air ($2\,HBr + 1/2\,O_2 \leftrightarrow Br_2 + H_2O$, $\Delta H^0 = -138\ kJ\,mol^{-1}$) is particularly attractive owing to its low energy requirement and the relative simplicity of the process. Nonetheless, the identification of highly active and stable catalysts can be anticipated as critical owing to the exothermic and corrosive nature of the reaction. Different materials have been patented,[5] of which supported cerium-based compounds are the most prominent.[7] However, the absence of systematic studies aimed at screening the performance of potential candidates and the limited understanding of the reaction mechanism have hindered the design of suitable HBr oxidation catalysts and their large-scale implementation. Herein, we introduce several efficient heterogeneous catalysts for this reaction that enable bromine recovery at relatively low temperatures. These catalytic materials will improve the present manufacture of organobromides by recycling the HBr byproduct. Moreover, they can be regarded as a key component for the practical realization of bromine-mediated alkane upgrading processes.

Upon targeting the discovery of active and stable HBr oxidation catalysts, it is inevitable to assimilate recent developments in the analogous catalyzed oxidation of HCl (Deacon reaction) for chlorine recovery in phosgenation processes.[8] Despite the chemical similarity of these reactions, it is unclear whether straightforward parallels can be drawn for catalyst and process design. To shed light on this basic aspect, the oxidation of HBr was investigated over representative Deacon catalysts. A highly advantageous difference between the two reactions is the absence of thermodynamic limitations in HBr oxidation (Figure S1, Supporting Information), which a priori enables the complete recovery of bromine. In HCl recycling, this can only be attained by the costly combination of catalytic oxidation and electrolysis processes.[8d] As shown in Figure 2, most of the catalysts investigated exhibited significant HBr conversion in the range of 400–600 K, which represents a decrease of 120–330 K in the operating temperature window relative to that required for HCl oxidation for the same conversion level. The case of U_3O_8/ZrO_2, with a shift of approximately 330 K, is exemplary. As a result, the HBr oxidation performance of the least active HCl oxidation catalyst is comparable to that of the most active HBr oxidation catalyst, RuO_2/TiO_2. The performance of

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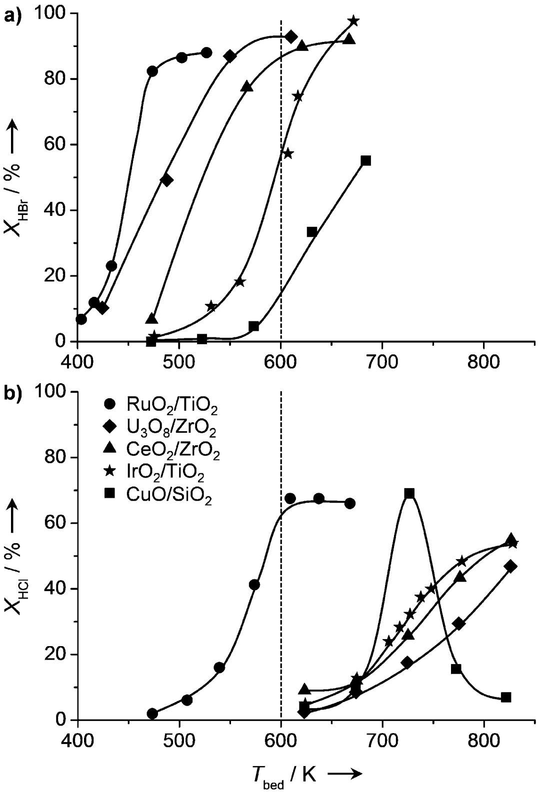

Figure 2. Steady-state conversion of a) HBr and b) HCl over different catalysts versus bed temperature. Other conditions are given in the Experimental Section.

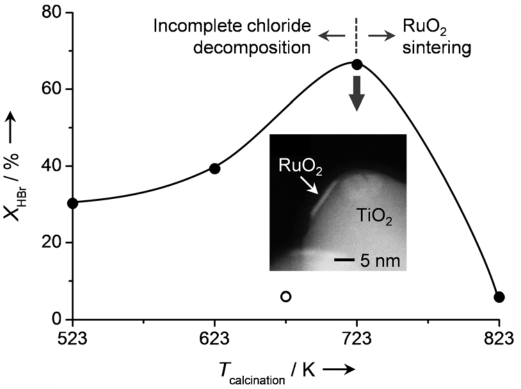

Figure 3. The thermal activation of the impregnated $RuCl_3/TiO_2$ sample (●) should be tuned to maximize the HBr oxidation performance of the resulting RuO_2/TiO_2 catalyst (measured at 433 K). The HAADF-STEM image clearly shows the filmlike nanostructure of RuO_2 on the TiO_2-rutile particles. The corresponding preparation with $RuBr_3/TiO_2$ (○) resulted in a much less active catalyst.

CeO_2/ZrO_2 was inferior to that of RuO_2 and U_3O_8-based catalysts. Cerium compounds have frequently been studied as HBr oxidation catalysts.[5,7] However, the nature of the active phase is unclear. Catalytic evaluation of the bulk phases enabled us to conclude, in contrast to earlier claims,[7b] the inactivity of $CeBr_3$ (Figure S2, Supporting Information). The bromide only became active upon decomposition to CeO_2, that is, above 550 K [the thermogravimetric analysis (TGA) profile is given in Figure S3, Supporting Information]. The absence of $CeBr_3$ was confirmed by XRD phase analysis of the used catalyst (Figure S2, Supporting Information). The same observations were made for $RuBr_3$, which becomes active upon oxidation to RuO_2 over 550 K. However, $IrBr_3$ was inactive up to 700 K owing to its higher oxidation temperature (Figure S3, Supporting Information). These results show that bulk halides are inactive for HBr oxidation. Instead, the oxidic phase is required to catalyze the reaction. This does not exclude the formation of surface oxybromide species under reaction conditions analogous to those under which an oxychloride phase was identified during HCl oxidation over RuO_2.[8a,b,e]

The calcination conditions have a decisive effect on the catalyst activity with respect to the degree of decomposition of the metal halide precursor and to the dispersion of the active phase. This aspect is demonstrated in Figure 3 for the ruthenium-based catalyst derived from the chloride precursor. HBr conversion shows a distinct volcano plot in relation to the calcination temperature and reaches a maximum at 723 K. The incomplete decomposition of the chloride below this temperature and the sintering of RuO_2 above this temperature reduce the activity. The catalyst calcined at the optimum temperature consists of a fully decomposed oxide phase, which is highly dispersed as thin layers formed by epitaxial growth on the surface of the TiO_2-rutile carrier [the high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image is given in Figure 3]. The decomposition temperature of the chloride precursor is significantly higher than the temperature required for HBr oxidation. Considering the TGA results (Figure S3, Supporting Information), it appears advantageous to use $RuBr_3$ as the precursor for the active RuO_2 phase, which enables the catalyst to be calcined at lower temperature, and this leads to improved RuO_2 dispersion. However, this was impractical owing to the low solubility of $RuBr_3$ in water, which led to inefficient impregnation and poor performance of the resulting sample (Figure 3, ○).

The stark performance differences observed over the catalysts is related to the mechanistic and kinetic differences between the two reactions. Toftelund et al.[9] conducted the first theoretical study by using DFT to compare hydrogen halide oxidations over defect-free rutile-type oxides and by selecting the oxygen dissociation energy as the descriptor of catalytic activity. In line with our experimental results, RuO_2 was identified as the most active material in HBr oxidation. However, the computational study also predicted that RuO_2 would exhibit similar activity in the oxidation of both HBr and HCl at high coverage. This is the regime in which our catalytic tests were conducted (ambient pressure and high partial pressures of reactants); we observed an equivalent HX conversion over RuO_2/TiO_2 at a much lower temperature (by 120 K) in HBr oxidation that in HCl oxidation (Figure 2). We confirmed the same differences upon evaluating the activity of bulk RuO_2 (not shown). Accordingly, the use of the oxygen dissociation energy as the only determining parameter for the activity of these catalysts may be a questionable approach. Early studies on the oxidation of HCl demonstrated that the recombination of surface atomic chlorine species is the most energy demanding step.[8a,b] Therefore, the substantially lower operating temperature required for HBr oxidation relative to that required for HCl oxidation over all of the catalysts is expected to be related to the fact that the energy barrier for the recombination of bromine is lower than that of chlorine. This should be associated with the fact that the binding energy of bromides to an active metal surface is weaker than that of chlorides to the same surface. Furthermore, we show that a higher activity, evaluated by the temperature needed to attain 20% conversion (T_{20}), over three of the supported catalysts investigated correlates with a lower oxidative decomposition temperature of their metal halides ($T_{\mathrm{oxidation}}$, Table 1). Thus, as bulk bromides are less stable towards oxidation than chlorides, HBr oxidation operates at a significantly lower temperature than HCl oxidation.

Table 1. Temperature required to achieve 20% conversion of the hydrogen halide over selected catalysts, T_{20}, and oxidation temperature of the bulk metal halides, $T_{\mathrm{oxidation}}$.

Catalyst	T_{20}[a] [K]		$T_{\mathrm{oxidation}}$[b] [K]	
	HBr oxidation	HCl oxidation	Metal bromide	Metal chloride
RuO_2/TiO_2	430	544	612	686
CeO_2/ZrO_2	495	705	585	840
IrO_2/TiO_2	566	700	900	930

[a] Determined from Figure 2. [b] Determined from the derivative of the weight loss profiles in Figure S3 c (Supporting Information).

An important aspect for the practical realization of these catalysts comprises their long-term durability under operating conditions. We observed the stable performance of the materials (with the exception of CuO/SiO_2 and Cr_2O_3/SiO_2) on the basis of the identical conversion profiles obtained by following multiple cycles in the temperature ramping tests shown in Figure 2. These conclusions were verified by the stable HBr conversion attained in isothermal tests up to 60 h over the most active catalytic materials identified in this study, RuO_2/TiO_2 (at 523 K) and U_3O_8/ZrO_2 (at 563 K). The notable stability of these catalysts, which did not experience any metal loss, can be related to the fact that the samples retained their oxidic active phase and crystalline structure upon use (Figure S4, Supporting Information). The lower temperatures required for HBr oxidation with respect to HCl oxidation favor a higher stability in the former reaction. Bulk bromination of the catalysts would induce fast deactivation by volatilization of the halide phases. This is what happened in the case of CuO/SiO_2 and Cr_2O_3/SiO_2 catalysts, which are also highly unstable in HCl oxidation.[8f,g] Consequently, these two materials are the least active catalysts in HBr oxidation (see Figure 2 a and the Table of Contents graphic).

In conclusion, we have demonstrated various supported catalysts, based on RuO_2, U_3O_8, and CeO_2, which are suitable for the oxidation of HBr to Br_2 in a continuous flow reactor. Considerably superior performances were obtained relative to those obtained in the analogous oxidation of HCl to Cl_2 owing to the absence of thermodynamic limitations and the ease of bromine evolution from the catalyst surface. The latter is related to the fact that the surface bromide species are less stable than the surface chloride species. This enables the attainment of approximately 100% Br_2 recovery at mild temperatures (500–600 K). None of the above catalysts experience bulk bromination under the reaction conditions, which secures the stable performance. These catalysts can be applied to regenerate bromine from HBr waste streams produced in the manufacture of organobromides and will definitively aid the future realization of sustainable bromine-mediated alkane functionalization processes.

Experimental Section

Table S1 (Supporting Information) summarizes all the supported catalysts evaluated in this work. In their preparation, the chloride, bromide, and nitrate precursors of the active phases were dissolved in water according to the desired metal loading and subsequently applied to the carrier (rutile TiO_2, monoclinic ZrO_2, and SiO_2) by dry impregnation, followed by drying and calcination. The gas-phase oxidation of HBr was studied at ambient pressure in a continuous-flow fixed-bed reactor setup similar to that used for HCl oxidation.[8g] The line downstream of the reactor was heated at 423 K to prevent the condensation of Br_2. The catalyst (0.25 g, particle size = 0.4–0.6 mm) was loaded in an 8 mm i.d. quartz microreactor and pretreated under an atmosphere of N_2 at 473 K for 30 min. Thereafter, a total flow of 166 cm^3 STP min^{-1} with 10 vol.% HBr (or HCl) and 20 vol.% O_2 balanced in N_2 was fed to the reactor at temperatures in the range of 400–823 K. Steady-state catalytic data were collected after at least 1 h stabilization at each condition. The absence of diffusion limitations was secured by the fulfillment of the Carberry and Weisz–Prater criteria. The amount of Br_2 (or Cl_2) at the reactor outlet was quantified by iodometric titration by using a Mettler Toledo G20 compact titrator. The percentage of HX (X = Br, Cl) conversion was determined according to Equation (1). After the test, the reactor was rapidly cooled to room temperature, and the catalyst was recovered for characterization.

$$X_{\mathrm{HX}} = \frac{2\,\text{mole X}_2\text{ at reactor outlet}}{\text{mole HX at reactor inlet}} \times 100 \quad (1)$$

Keywords: alkane activation · bromine recovery · hydrogen bromide · heterogeneous catalysis · oxidation

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