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Europium Oxybromide Catalysts for Efficient Bromine Looping in Natural Gas Valorization

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Abstract: The industrialization of bromine-mediated natural gas upgrading is contingent on the ability to fully recycle hydrogen bromide (HBr), which is the end form of the halogen after the activation and coupling of the alkanes. Europium oxybromide (EuOBr) is introduced as a unique catalytic material to close the bromine loop via HBr oxidation, permitting low-temperature operation and long lifetimes with a stoichiometric feed ($O_2:HBr = 0.25$), conditions at which any catalyst reported to date severely deactivates due to excessive bromination. Besides, EuOBr exhibits unparalleled selectivity to methyl bromide in methane oxybromination, an alternative route for bromine looping. This novel active phase is finely dispersed on appropriate carriers and scaled up to technical extrudates, enhancing the utilization of europium by over an order of magnitude while preserving the performance. This catalytic system paves the way for the sustainable valorization of stranded natural gas via bromine chemistry.

More than 30% of the known world's natural gas reserves are located in remote and scattered wells.^[1] This fact precludes their use as a long-lasting feedstock for the manufacture of chemicals and fuels due to the prohibitive shipping expenses to centralized megaplants.^[2] Consequently, natural gas emitted from these wells is nowadays flared or vented, wasting ca. 3.5% of its global production, which is a fraction worth 13 billion USD.^[3] Among the various routes proposed to overcome the capital intensity of conventional syngas-based processes,^[4] the bromine-mediated functionalization of methane into methyl bromide (CH_3Br), a versatile C1 platform molecule with similar upgrading paths to methanol, emerged as an economically attractive technology for the decentralized manufacture of readily transportable value-added chemicals and fuels in compact plants amenable to decentralization.^[2,5-10] Key steps of the process (Figure 1, Figure S1),^[2,6-9] which could also be applied to ethane and propane,^[2] comprise (1) methane bromination, which provides up to 95% selectivity to CH_3Br , (2) reproporationation of the polybrominated byproducts into

Figure 1. Process flow diagram of bromine-mediated natural gas upgrading.

monobrominated alkanes and olefins by reaction with C1-C5 alkanes, (3) coupling of CH_3Br and reproporationation products into valuable hydrocarbons such as gasolines, olefins, and aromatics, and (4) recycling of hydrogen bromide (HBr), which is generated in stoichiometric amounts in the bromination and coupling steps. The latter step closes the bromine loop and is vital to the feasibility of the entire technology, since the high price and low availability of this halogen necessitate its full recovery. The highly efficient carbon atom utilization enabled by developments in the bromination, reproporationation, and coupling reactions, as well as advances in corrosion resistant construction materials led to a large-scale demonstration of the bromine-based process for the production of petrochemical-grade aromatics from methane, which is nowadays offered for licensing.^[2,10] Nevertheless, little progress has been made towards sustainable bromine looping, which is commonly accomplished via cataloreactant processes or the catalytic HBr oxidation.^[2,8,11] The former approach relies on the absorption of HBr by an oxide or hydroxide, followed by its re-oxidation in a second step to evolve bromine. However, such a cyclic operation necessitates large reactors and is difficult to control due to the limited lifetime of the cataloreactants. Hence, it is highly desirable to develop a catalytic system for the continuous oxidation of HBr into molecular bromine at relatively low temperatures ($T \leq 573$ K) and stoichiometric feed ($O_2:HBr = 0.25$). In addition to enhancing the overall space-time and energy efficiency of the process, this would enable the use of air as an oxygen source, thereby substantially reducing production costs. Nevertheless, such an operating window remains highly challenging due to the extensive bromination of active catalysts like RuO_2 and CeO_2 even under significant oxygen excess, leading to severe deactivation.^[11c,d]

In our quest for a novel catalytically active phase enabling efficient bromine looping, we have investigated the performance of various rare-earth oxides comprising La_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , and Dy_2O_3 in HBr oxidation. Catalysts based on

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Figure 2. HBr conversion, $X(\text{HBr})$, over different catalysts versus: a) temperature, T , at a molar $\text{O}_2:\text{HBr}$ ratio of 2, b) molar $\text{O}_2:\text{HBr}$ ratio at $T = 523\text{ K}$, and c) time-on-stream, t_{os} , at $T = 523\text{ K}$ and a stoichiometric $\text{O}_2:\text{HBr}$ ratio of 0.25 ($\text{O}_2:\text{HBr} = 0.25$). Temperature and $\text{O}_2:\text{HBr}$ ratio were decreased from the highest to the lowest value (down), and then increased back to the starting point (up). The colored areas in a) and b) indicate the pronounced deactivation hysteresis of CeO_2 . d) X-ray diffractograms of EuOBr (top) and CeO_2 (bottom) samples recovered after various time-on-stream ($\text{O}_2:\text{HBr} = 0.25$, $T = 523\text{ K}$). Patterns of the reference EuOBr (ICDD-PDF 85-0844) and CeO_2 (ICDD-PDF 81-0792) phases are presented with vertical lines. e) Energy dispersive X-ray spectroscopy elemental maps of CeO_2 catalyst recovered after 1 h of operation ($\text{O}_2:\text{HBr} = 0.25$, $T = 523\text{ K}$) testify its excessive bromination. f) X-ray photoelectron spectroscopy depth profiles of EuOBr and CeO_2 samples recovered after various time-on-stream ($\text{O}_2:\text{HBr} = 0.25$, $T = 523\text{ K}$) demonstrate a constant atomic Br:Eu ratio and a progressive increase in Br:Ce ratio in the surface region of the respective catalysts, as illustrated in c). Conditions: $\text{HBr}:\text{O}_2:\text{He} = 4.5:1.13\text{-}9:94.37\text{-}86.5$, space velocity, $F_T/W_{\text{cat}} = 200\text{ cm}^3\text{ min}^{-1}\text{ g}_{\text{cat}}^{-1}$, $P = 1\text{ bar}$.

lanthanide metals have been widely applied in numerous reactions,^[13] but apart from CeO_2 , no member of this catalyst family has been investigated in HBr oxidation. Initial catalytic tests were conducted using an oxygen-rich feed ($\text{O}_2:\text{HBr} = 2$), which favors the re-oxidation of the catalyst (see the Supporting Information, **Figure S4**).^[11c,d] All of the catalysts were found to transform to the oxybromide phase under these conditions (**Figure S3**). Consequently, the performance of the lanthanide oxybromide phases was considered henceforth. Comparatively, the highest rates of HBr oxidation in the low-temperature window (423–473 K) were observed over EuOBr, substantially exceeding those of the benchmark CeO_2 and TiO_2 catalysts (**Figure 2a**, **Figure S4**). To the best of our knowledge, this is the first report on the application of EuOBr in catalysis. The light-off curve of LaOBr was shifted to ca. 150 K higher temperature compared to EuOBr. Besides, it suffered deactivation (**Figure S4**). Other lanthanide oxybromides were all active at temperatures ($T > 623\text{ K}$), exceeding the preferred operating window.

The performance of EuOBr remained unaltered upon temperature cycling (**Figure 2a**), which simulates the likely spatial and temporal fluctuations in a reactor. In contrast, during the temperature-increasing part of cycle CeO_2 displayed a lower HBr conversion than during the temperature-decreasing part, indicating deactivation caused by a bromine uptake at low temperatures.^[11c,d] On the other hand, TiO_2 , which is the benchmark of the bromination-resistant catalysts,^[11b,d] was much less active compared to EuOBr. The stability of the latter material was also evidenced on cycling the feed concentration of oxygen (**Figure 2b**). Notably, the performance of EuOBr was only slightly affected by the oxygen concentration, showing no

deactivation. Contrarily, the conversion of HBr over CeO_2 drops to almost zero under the preferred stoichiometric feed ($\text{O}_2:\text{HBr} = 0.25$), and is only partially recovered upon returning to higher oxygen concentrations. The outstanding robustness of EuOBr was further demonstrated by its stable activity in a time-on-stream test under stoichiometric feed at 523 K (**Figure 2c**). Under the same conditions, the bromine production over CeO_2 almost completely ceased just after 6 h. The deactivation profiles of this material observed upon temperature and oxygen cycling, as well as with time-on-stream coincide with the behavior of other highly active catalysts in this reaction such as RuO_2 .^[11c,d]

The contrasting performance of EuOBr and CeO_2 was rationalized by in-depth characterization of the catalysts recovered after different time-on-stream in HBr oxidation. The appearance of new reflections in the X-ray diffraction patterns of the used samples evidenced the chemical transformation of CeO_2 (**Figure 2d**), which based on the increasing degree of bromination (vide infra) was tentatively ascribed to the formation of (oxy)bromide phases (**Figure S6**). Besides, pronounced particle sintering was evidenced from a drop in surface area of the catalyst recovered after 6 h of reaction ($13\text{ m}^2\text{ g}^{-1}$) with respect to the fresh material ($27\text{ m}^2\text{ g}^{-1}$) which was also supported by electron microscopy examination (**Figure S7**). Remarkably, the bulk structure of EuOBr showed no significant change after 20 h of use (**Figure 2d**, **Figure S7**), whereby its surface area ($19\text{ m}^2\text{ g}^{-1}$) was slightly lower compared to the fresh catalyst ($22\text{ m}^2\text{ g}^{-1}$). The profound resistance of EuOBr to further bromination and the progressive uptake of bromine by CeO_2 are evidenced by the elemental maps obtained using energy

Figure 3. Selectivity to a) CH_3Br , $S(\text{CH}_3\text{Br})$, and b) carbon oxides, $S(\text{CO}_x)$, versus CH_4 conversion, $X(\text{CH}_4)$, in MOB over bulk EuOBr , CeO_2 , and VPO, and supported EuOBr/ZrO_2 and $\text{EuOBr/Al}_2\text{O}_3$ catalysts at various temperatures. Conditions: $\text{CH}_4:\text{HBr}:\text{O}_2:\text{Ar}:\text{He} = 6:6:3:4.5:80.5$, $F_{\text{T}}/W_{\text{cat}} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$, $P = 1 \text{ bar}$. The legend in a) also applies in b).

dispersive X-ray spectroscopy (Figure 2e, Figure S7), and thermogravimetric analysis (Figure S8). Inspection of the fresh and used CeO_2 by X-ray photoelectron spectroscopy further demonstrated the increase of bromine content in the surface region of this catalyst upon use (Figure 2f), leading to its reduction (Figure S9), ultimately resulting in its deactivation (Figure 2c). On the other hand, EuOBr displayed a constant Br:Eu ratio of ca. 0.7 in the surface region (Figure 2f), confirming the ability of EuOBr to preserve an excess of oxygen under stoichiometric feed. Europium was found to predominantly exist as Eu^{3+} with a minor contribution of Eu^{2+} (Figure S10), suggesting the $\text{Eu}^{3+}/\text{Eu}^{2+}$ redox couple to be responsible for the catalyst activity. Based on these results, the exceptional stability of EuOBr can be ascribed to the structural integrity of this phase, which is preserved in oxygen-rich and HBr-rich feed mixture.

Given the outstanding performance in HBr oxidation, EuOBr was further evaluated in methane oxybromination (MOB), which is an alternative option to accomplish a continuous bromine looping by integrating HBr oxidation and methane functionalization in a single step (Figure 1, Figure S1).^[12] Besides stability and activity constraints, another challenging aspect in the design of a MOB catalyst is to attain a high selectivity to CH_3Br by suppressing the side combustion reactions.^[12] The latter are avoided if methane bromination and HBr oxidation are executed separately, which favors the two-step route over MOB. Notably, the selectivity to CH_3Br over EuOBr (85–65% at 6–33% single-pass methane conversion) substantially exceeded that of the benchmark $(\text{VO})_2\text{P}_2\text{O}_7$ (VPO) and CeO_2 catalysts at comparable reaction rates in the broad range of conditions applied (Figure 3, Figure S11).^[12] EuOBr also provided the highest selectivity to CH_3Br (7–56%) and CH_2Br_2 (2–30%) on the basis of HBr (51–95% single-pass

conversion), although the selectivity to bromine (17–90%) was significant (17–90%) (Figure S12). Moreover, it exhibited a low formation of carbon oxides (CO_x), yielding bromine and dibromomethane (CH_2Br_2) as the dominant byproducts, which can be further upgraded via bromination and reproporation, respectively (Figure 1, Figure S1).^[2,9]

To rationalize the activity of EuOBr in MOB, the catalyst was evaluated in methane combustion and methane bromination (Figure S13), which were chosen as the test reactions to probe the catalyst ability to dissociate C–H and form C–Br bonds, respectively. The low activity of EuOBr in methane combustion and absence of its catalytic effect in methane bromination, suggest a low propensity of this material to activate this alkane. Besides, MOB over EuOBr proceeds in the same temperature window ($T > 733 \text{ K}$) as the non-catalytic gas-phase bromination of methane, whereby the two reactions exhibit almost identical apparent activation energy (Figure S13). It is thus proposed that MOB proceeds by the gas-phase reaction of methane with molecular bromine that is (re)generated by the HBr oxidation on EuOBr .^[12b,c] The highly suppressed CO_x formation over this catalyst also agrees with its low propensity to combust methane.

Having identified the outstanding properties of EuOBr in HBr oxidation and MOB, the next step was to develop a ready-to-use technical catalyst based on this material. Besides reducing the price of a catalyst, the dispersion of an active phase over a suitable carrier can improve the intrinsic activity by ensuring both a high surface area and favorable electronic interaction. To study the potential impact of active phase dispersion, EuOBr was supported on three carriers: Al_2O_3 , ZrO_2 , and SiO_2 (9 wt.% europium loading) yielding catalysts denoted as $\text{EuOBr/Al}_2\text{O}_3$, EuOBr/ZrO_2 , and EuOBr/SiO_2 , respectively. These were evaluated in HBr oxidation revealing the following activity trend: $\text{EuOBr/Al}_2\text{O}_3 > \text{EuOBr/ZrO}_2 > \text{EuOBr/SiO}_2$ (Figure 4a). Notably, the conversion of HBr over $\text{EuOBr/Al}_2\text{O}_3$ substantially exceeded that of the bulk system in the low-temperature region, i.e. enabling over one order of magnitude higher rate of HBr oxidation per content of europium, while preserving its resistance against bromination (Figure S13). Characterization of

Figure 4. a) HBr conversion versus temperature in HBr oxidation over bulk EuOBr and supported $\text{EuOBr/Al}_2\text{O}_3$, EuOBr/ZrO_2 , and EuOBr/SiO_2 catalysts ($\text{HBr}:\text{O}_2:\text{He} = 4.5:9:86.5$, $F_{\text{T}}/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$). b) HBr conversion versus time-on-stream in HBr oxidation over $\text{EuOBr/Al}_2\text{O}_3$ -t catalyst ($\text{HBr}:\text{O}_2:\text{He} = 10:2.5:87.5$, $F_{\text{T}}/W_{\text{cat}} = 50 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$, $T = 523 \text{ K}$). c) CH_4 conversion and product selectivity versus time-on-stream in MOB over EuOBr/ZrO_2 -t catalyst ($\text{CH}_4:\text{HBr}:\text{O}_2:\text{Ar}:\text{He} = 6:6:2:4.5:81.5$, $F_{\text{T}}/W_{\text{cat}} = 200 \text{ cm}^3 \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$, $T = 773 \text{ K}$).

Figure 5. Energy dispersive X-ray spectroscopy elemental maps (left) and high-resolution transmission electron micrographs (right) of the a) EuOBr/Al₂O₃ and b) EuOBr/ZrO₂ catalysts used in the HBr oxidation tests indicate the high and uniform dispersion of the active phase.

the fresh and used samples revealed an atomic level dispersion of europium over all supported catalysts (**Figure 5**, **Figures S15,S16**). The specific surface area of the best performing EuOBr/Al₂O₃ was intermediate between that of EuOBr/ZrO₂ and EuOBr/SiO₂ (**Table S3**), suggesting that the observed activity trend is also affected by the specific interaction with the support. On the other hand, the degree of bromination, ability to evolve bromine, and reducibility of the supported catalysts, which all decrease in the order: EuOBr/Al₂O₃ > EuOBr/ZrO₂ >> EuOBr/SiO₂ (**Figures S16,S17, S18**), strongly correlate with the activity in HBr oxidation. This confirms the impact of the carrier identity on the susceptibility to bromination, whereby the supported systems with a bromine content close to that of the oxybromide display a higher activity in HBr oxidation. The outstanding performance of EuOBr/Al₂O₃ was thus rationalized by the ability of Al₂O₃ to stabilize the brominated form the catalyst and to promote the bromine evolution with respect to the bulk system.

In the case of MOB, the supported systems led to an increased production of CO_x with respect to bulk EuOBr (**Figure 3**, **Figure S19**). This was particularly pronounced over EuOBr/Al₂O₃, which could be attributed to its high oxidizing potential (**Figure S18**) as well as the propensity of Al₂O₃ to combust halocarbons.^[14] On the other hand, an enhanced CO_x formation over EuOBr/SiO₂ is consistent with the low degree of the catalyst bromination, which promotes combustion.^[12c] EuOBr/ZrO₂ shows balanced redox properties and a relatively high degree of bromination, providing the highest selectivity to CH₃Br among the supported systems, which is close to that of the bulk EuOBr and is also preserved at lower Eu loading (**Figure S20**).

Based on the relative performance of the supported systems, Al₂O₃ and ZrO₂ extrudates were chosen to prepare technical

catalysts (i.e. EuOBr/Al₂O₃-t and EuOBr/ZrO₂-t), which were tested in the low-temperature HBr oxidation and MOB under stoichiometric, and substoichiometric feeds, respectively. Their activity matched that of the supported systems in powder form and was stable for over 60 h of operation under these harsh conditions (**Figure 4b,c**), with no detectable loss of europium.

In conclusion, EuOBr was found to be an exceptional catalyst for HBr oxidation, enabling low-temperature operation under a stoichiometric feed, conditions inaccessible to existing systems. This was ascribed to the marked bromine evolution activity and inherent resistance to further bromination of the oxybromide phase. Moreover, this material provided a high selectivity to CH₃Br in MOB, outperforming all previously reported catalysts. The substantially suppressed CO_x production over EuOBr opens the door for the development of catalytic systems that do not produce these side products. Thereby, the conversion of CH₂Br₂ via reproporationation could further enhance the overall selectivity to CH₃Br. To bridge the gap between the activity of EuOBr in bromine recovery processes and its high price, the impact of different carriers on its performance was investigated. Al₂O₃ and ZrO₂ were identified as the best supports for HBr oxidation and MOB, respectively, enabling an order of magnitude improved utilization of europium compared to the bulk catalyst. Technical catalysts prepared using the latter supports displayed robust performance demonstrating their realistic potential for application in bromine-based processes that can enable the decentralized valorization of stranded natural gas.

Experimental Section

Details of the catalyst preparation, characterization, and evaluation are provided as Supporting Information.

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Keywords: bromine looping • C1 chemistry • europium oxybromide • heterogeneous catalysis • natural gas upgrading

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COMMUNICATION

Mind the gap: Europium oxybromide-based materials comprise extraordinary catalysts for both HBr oxidation to Br₂ and CH₄ oxybromination to CH₃Br, enabling a closed bromine loop for the sustainable upgrading of natural gas to fuels and chemicals.

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