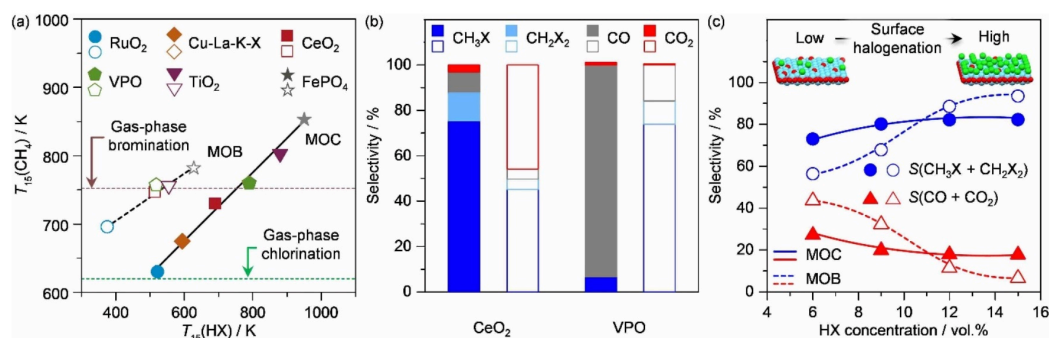


## Catalyst design for selective natural gas functionalization via oxyhalogenation chemistry

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The selective conversion of methane, the major component of natural gas, into value-added chemicals and fuels is one of the greatest challenges in modern catalysis research.<sup>1</sup> Methane oxyhalogenation is attractive for this purpose, as it enables methane functionalization into carbon monoxide or halomethanes, key chemical building blocks, under mild conditions.<sup>1-4</sup> However, its industrial implementation has been so far hindered by (i) the lack of selective and stable catalysts and (ii) the superficial understanding of the interplay between the specific catalyst, the type of halogen, and the operating conditions. To address these aspects, we studied methane oxychlorination (MOC) and oxybromination (MOB) and HX and CH<sub>4</sub> oxidation over RuO<sub>2</sub>, Cu-K-La-X (X = Cl, Br), CeO<sub>2</sub>, VPO, TiO<sub>2</sub>, and FePO<sub>4</sub>. The light-off points for CH<sub>4</sub> oxidation were shifted to higher temperatures compared to the case of methane oxyhalogenation, indicating that the presence of HX promotes methane conversion. The activity in oxyhalogenation depended on the catalyst ability to activate HX (**Figure 1a**), which was measured by the temperature required to attain 15% conversion of CH<sub>4</sub>,  $T_{15}(\text{CH}_4)$ , in MOC and MOB and of HX,  $T_{15}(\text{HX})$ , in the related oxidation. Almost all of the  $T_{15}(\text{CH}_4)$  values in MOC and MOB were greater or equal to the corresponding  $T_{15}(\text{CH}_4)$  in gas-phase methane halogenation, suggesting an important role of the latter reaction in methane activation. The distribution of the  $T_{15}(\text{CH}_4)$  in MOC was also significantly broader than that in MOB. The reaction rate was primarily determined by the evolution of Cl<sub>2</sub> from the catalytic surface in MOC, whereas it was controlled by the gas-phase reaction between evolved Br<sub>2</sub> and CH<sub>4</sub> in MOB. The product distribution strongly depended on the type of halogen (**Figure 1b**). In addition, the halocarbon selectivity was increased by raising the inlet HX concentration, particularly over CeO<sub>2</sub> (**Figure 1c**), due to the (i) faster kinetics of HX oxidation than halocarbon combustion and (ii) enhanced reducing action of HX on the catalytic surface.



**Figure 1.** (a)  $T_{15}(\text{CH}_4)$  versus  $T_{15}(\text{HX})$  over the catalysts studied. (b) Product selectivity in MOC (solid) and MOB (empty) over CeO<sub>2</sub> and VPO at 15% methane conversion. (c) Selectivity to products in MOC (solid line) and MOB (dashed line) versus the feed HX concentration over CeO<sub>2</sub>.

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