"Redox Behavior of Manganese Oxide Catalysts in Thermochemical Redox Cycles: Mechanistic Insights from In Situ TEM and DFT Investigations"

Joanna GRYBOŚ[1], Karol GÓRECKI, Monika FEDYNA, Michał PACIA, Zbigniew SOJKA
[1]Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Polska.
* *joanna.grybos@uj.edu.pl*

Significance and Relevance

Due to the complexity of thermochemical redox cycles (*cf.* Figure 1), and an important number of factors influencing their course, despite extensive research, a comprehensive and unambiguous interpretation of the role of redox changes in manganese oxide-based catalysts is still lacking. Scientific literature is lacking detailed mechanistic description of the temperature-induced reduction of manganese oxide catalysts ($K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$) catalysts, the concomitant phase, structure, and morphology changes, sintering processes, mechanisms of surface and bulk oxygen migrations and release, and the mechanism of vacancies formation and migration. This research presents mechanistic insights into temperature-induced structural, morphological, and redox changes in manganese oxide catalysts within the context of thermochemical redox cycles. It provides an understanding of the role of different redox couples (Mn^{4+}/Mn^{3+} or Mn^{3+}/Mn^{2+}), comproportionation and disproportionation of manganese cations ($Mn^{2+}+Mn^{4+}\rightarrow 2Mn^{3+}$). This research can thus guide the implementation of specific manganese oxides in water and carbon dioxide splitting.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Sustainable and clean energy production and transport
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Two-step metal oxide thermochemical redox cycles have often been studied in the context of converting heat to chemical energy, which can be further used for energy storage, renewable fuel production, air separation, and oxygen pump. The development of these applications depends on the selection of appropriate redox materials, which must be optimized for each specific use. A wide range of scientific research indicates that oxides that preserve a complete phase transition during reduction possess significantly higher specific energy storage compared to materials, such as ceria and perovskites, that undergo partial reduction. On the other hand, partial reduction materials generally exhibit faster kinetics and greater activity at lower temperatures. Therefore, the selection of materials for different applications often involves a trade-off between the significance of high specific energy storage and the advantages of fast kinetics and operation at low temperatures. In this context, our objective is to provide comprehensive knowledge regarding the general mechanism and environmental factors governing thermochemical redox cycles on the exemplary materials i.e. manganese oxide-based catalysts. Two types of oxides were selected: those that undergo partial reduction ($K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$). The research aims at explaining the effect of temperature on the redox behavior of the proposed manganese catalysts during the thermochemical redox cycles, including thermal activation of the catalysts, their phase, and structural stability, mechanisms of surface and bulk oxygen migration, and mechanism of vacancies formation and migration, which are all responsible for the catalyst's redox performance and are involved in the sintering processes as well.

Materials and Methods

The research was conducted by employing the complementary use of advanced microscopic (SEM, TEM, STEM, ED, EDX, EELS, including in-situ mode), and theoretical (ab initio DFT and atomistic thermodynamics calculations) methods. In addition, several basic characterization techniques were applied to gain insight into the phase and chemical composition of the materials (XRD, XRF) and to characterize the short-range order of their atomic structures (IR, Raman).

Results and Discussion

The examined manganese catalysts were prepared via hydrothermal and solid-state syntheses, using different precursors (manganese acetate, manganese sulphate, manganese nitrate) and reducing agents (e.g. glucose). Subsequently, only those exhibiting well-defined morphologies were selected for further analysis. Ex-situ microscopic characterization of the catalysts revealed differences in the redox state of manganese ions depending on their position within the catalyst material. For the $K_2Mn_8O_{16}$ catalyst, the ELNES spectra analysis showed a chemical shift of the Mn energy loss to lower values, indicating changes in the Mn valency state from the core (Mn^{4+}) to the tip/surface (Mn^{2+}/Mn^{3+}). In-situ TEM and EELS experiments focused on thermally-induced redox changes demonstrated discrepancies in redox properties and stability between nanorods and layered manganese catalysts. The EELS analysis was complemented by DFT modeling, which provided insights into oxygen vacancies formation and their migration within the atomic structure of the $K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$ catalysts. Through a combination of ex-situ and in-situ experiments with the DFT results, it was possible to identify a temperature window where both catalysts exhibited fully reversible redox behavior, as well as stable structure and morphology. This comprehensive approach contributes to a deeper understanding of the redox processes occurring in the manganese-oxide-based catalysts and their potential applications in thermochemical cycles.

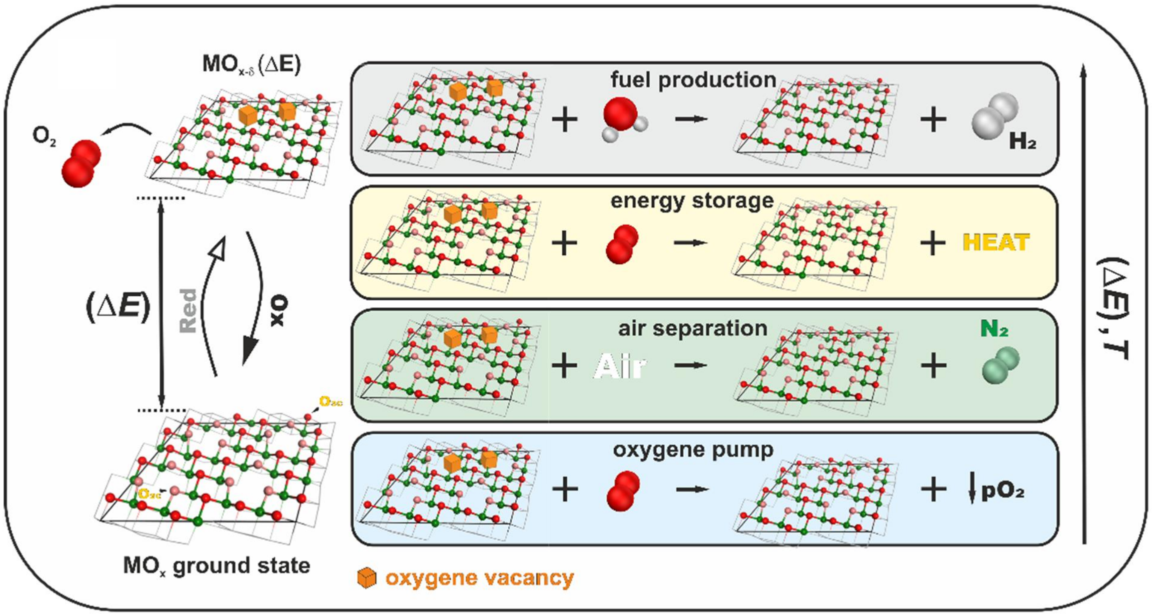

Figure 1 Schematic presentation of two-step thermochemical redox cycles, where the heat-produced chemical energy is applied for renewable fuel production, energy storage, air separation, and oxygen pump.[1]

[1] J.Mater. Chem. A, 2017, 5, 18951

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