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Catalytic Oxygen Removal from Coke Oven Gas (COG) over transition metal CoMo/ γ -Al₂O₃

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INTRODUCTION

Carbon2Chem®, a cross industrial network of steel and chemical industries enables the utilization of metallurgical gases for synthesis of value-added chemicals. Coke oven gas (COG) is a valuable source of hydrogen for syngas utilization. The removal of oxygen from COG is an essential step to allow a high H₂ recovery in safe environment of the subsequent pressure swing adsorption (PSA) process. The orientation study uses a factorial experimental design (DoE) to determine the influence of different process parameters on the catalytic removal of oxygen traces (4500 – 9000 ppm O₂). This study focuses on the activity of the transition metal sulphide catalyst. For the removal of oxygen from synthetic COG, the activity of the commercial catalyst CoMo/ γ -Al₂O₃ was compared to the Pt/ γ -Al₂O₃ reference catalyst.

CONCEPT

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- Catalytic oxygen removal from a raw COG in the presence of multiple trace components
- Systematic investigation of trace components, e.g. H₂S, COS, Toluol → catalyst poisoning
- Three catalyst systems from Clariant Produkte GmbH are evaluated for the process; Pt based catalyst versus transition metal based catalysts, Co- and Nickel-molybdenum based systems

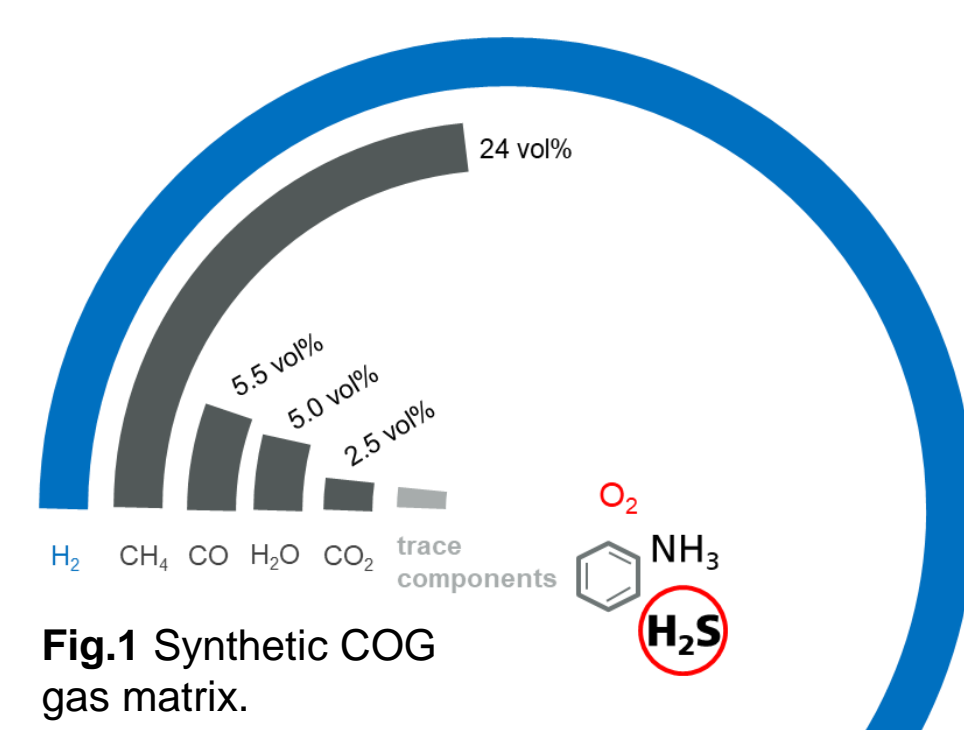


Fig.1 Synthetic COG gas matrix.

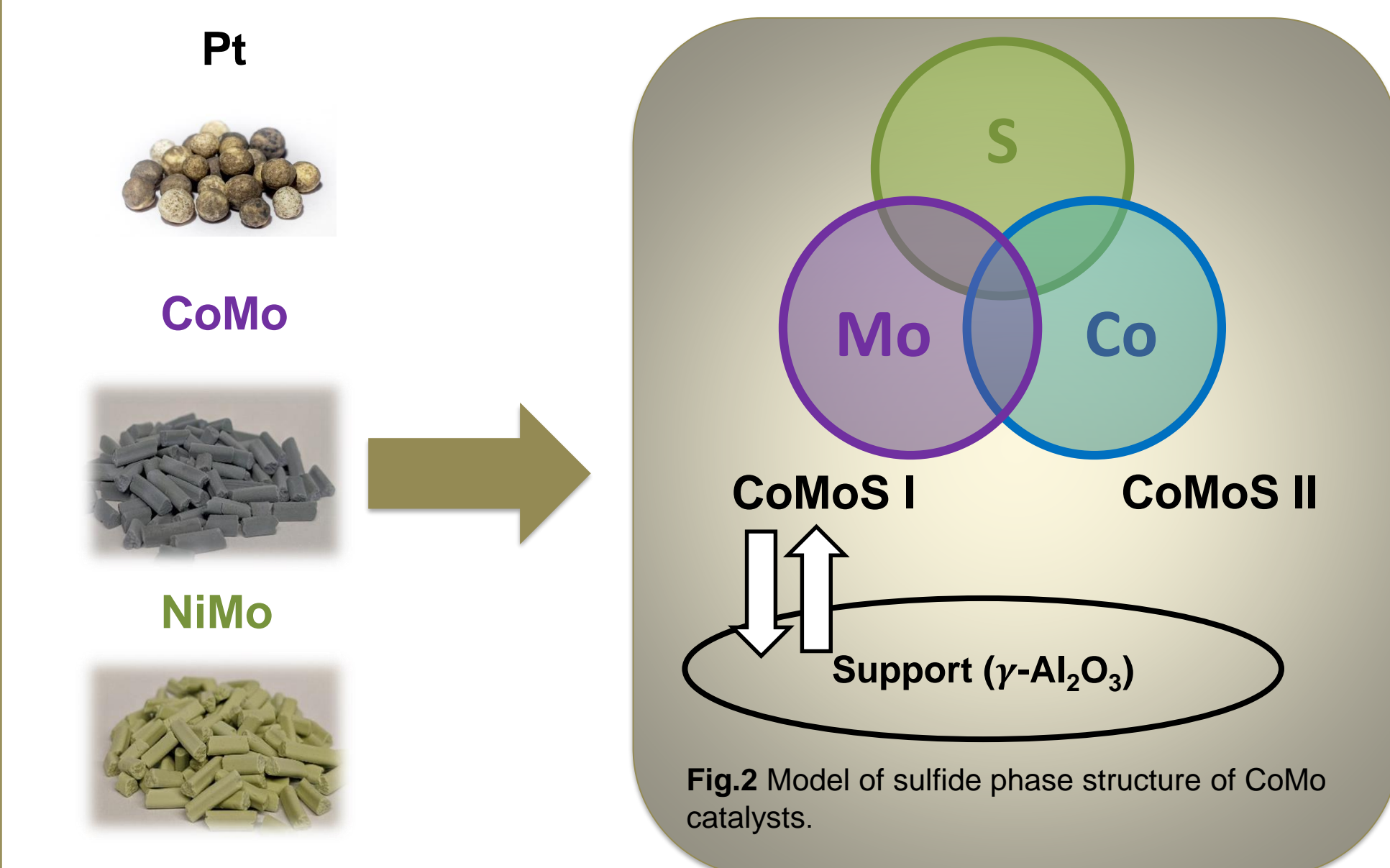


Fig.2 Model of sulfide phase structure of CoMo catalysts.

CATALYST CHARACTERIZATION

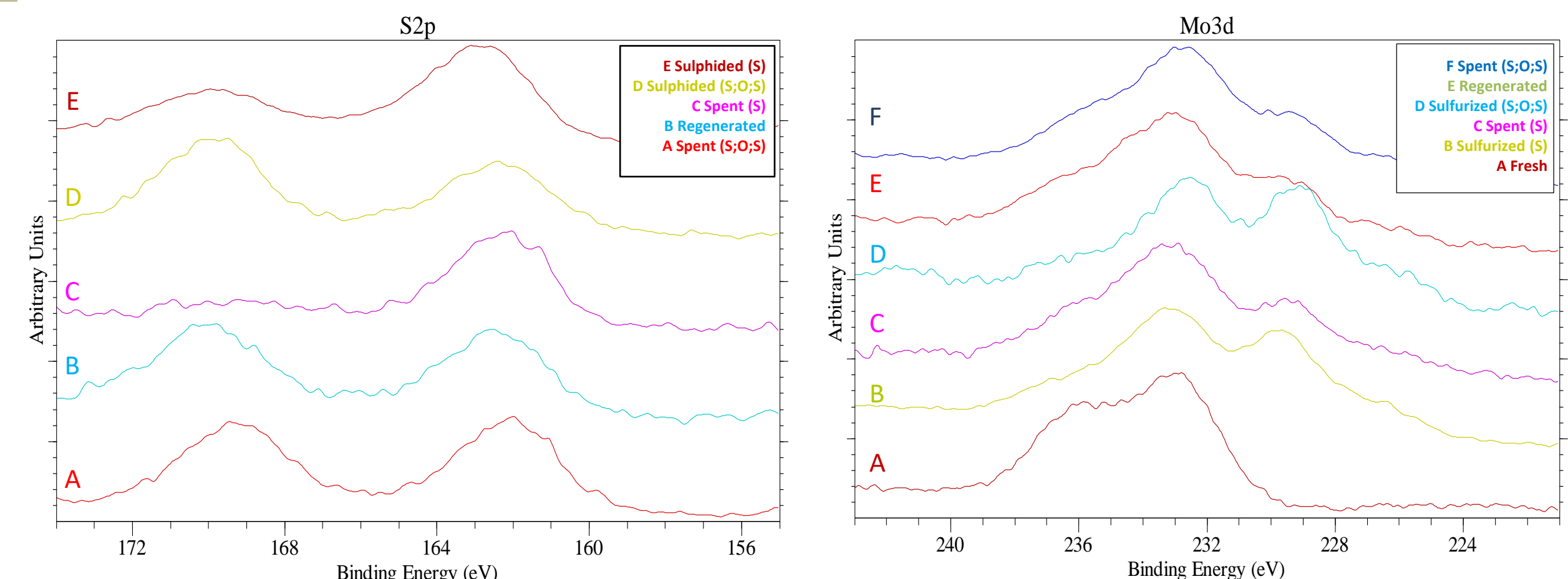


Fig.3 S 2p XPS results of the CoMo catalyst; spent, regenerated, sulphided samples. Fig.4 Mo 3d XPS results of the CoMo catalyst; spent, regenerated, sulphided samples.

- Application of the characterization methods, e.g. XRD, XPS to identify the stable active phase

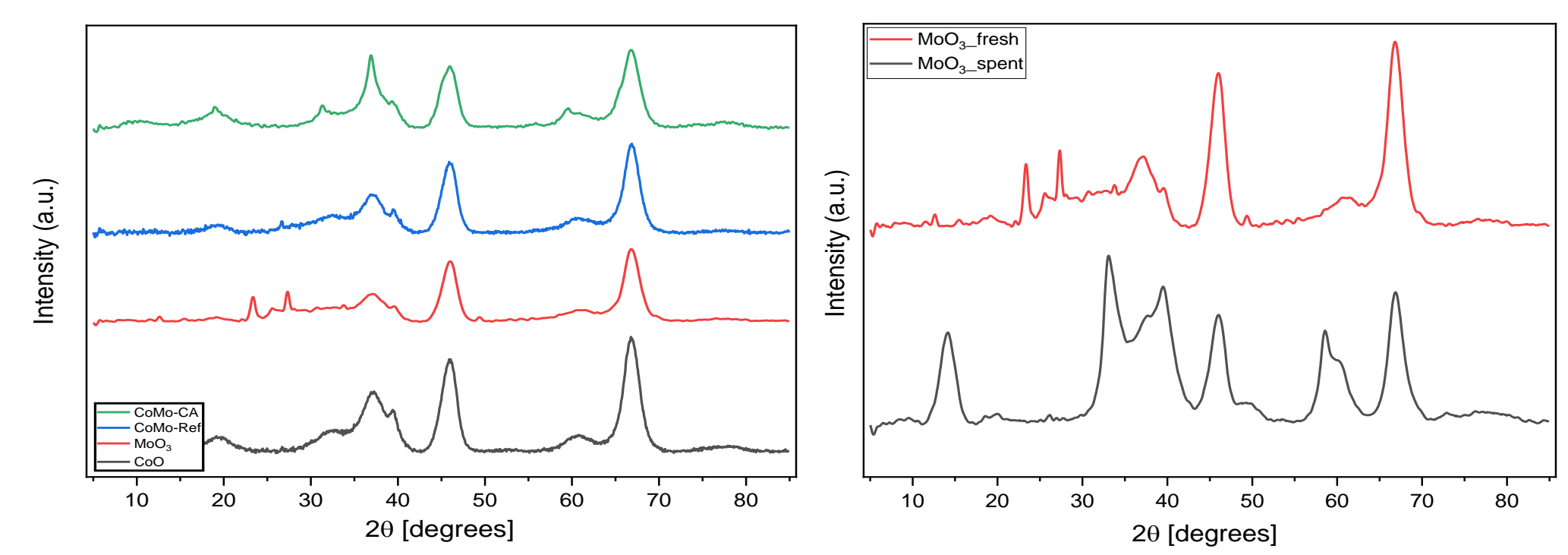


Fig.5 XRD results of the Co and Mo components. Fig.6 XRD results of the Mo components.

CATALYST TESTING

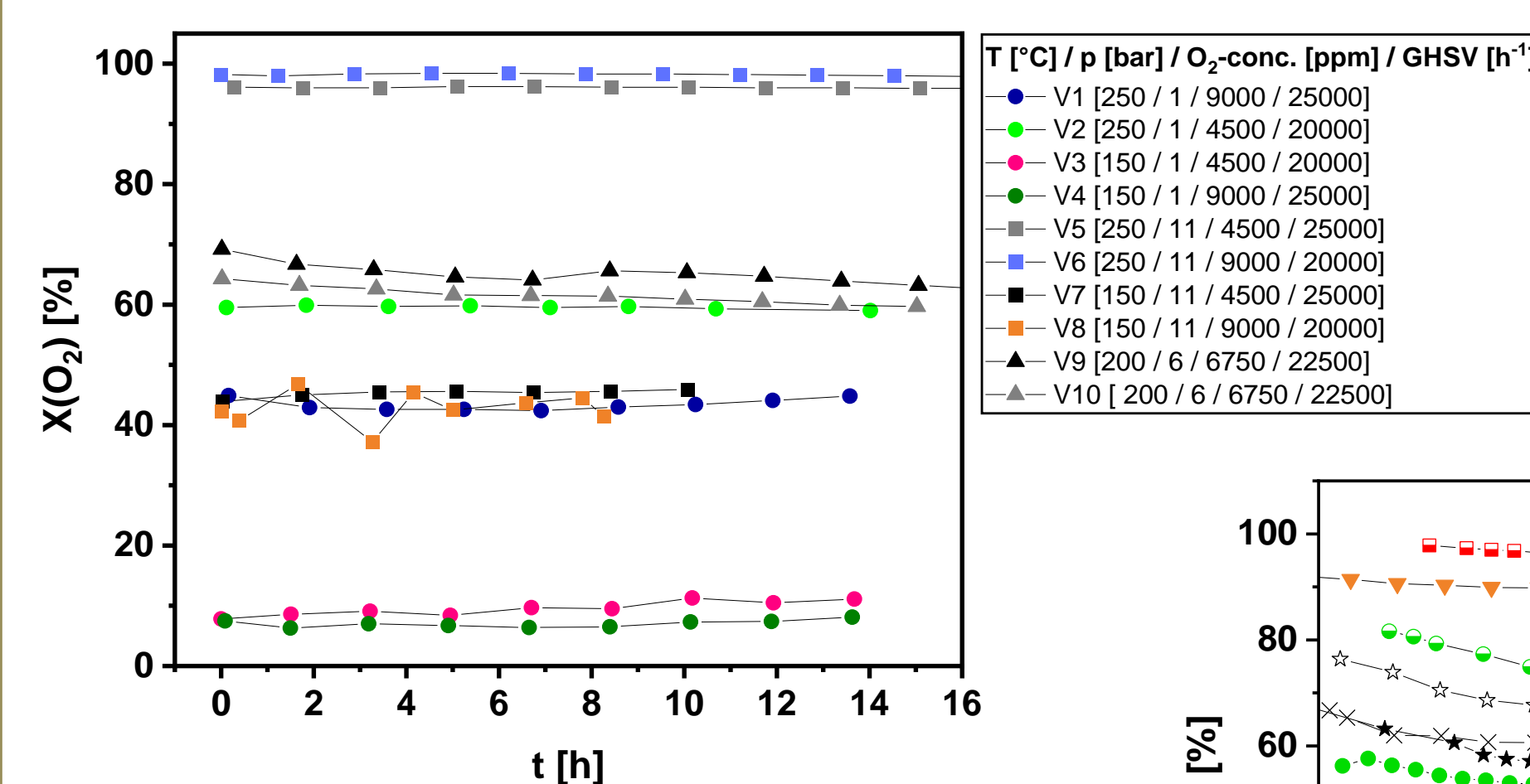


Fig.7 O₂-conversion of the Pt/ γ -Al₂O₃ catalyst in the absence of H₂S; T=150–250 °C, GHSV_(STP)=20000–25000 h⁻¹ at 1–11 bar.

- Design of Experiments
An iterative experimental design is determined for the systematic study of the present catalyst system. Therefore, a factorial experimental design applying four factors at two levels is established.

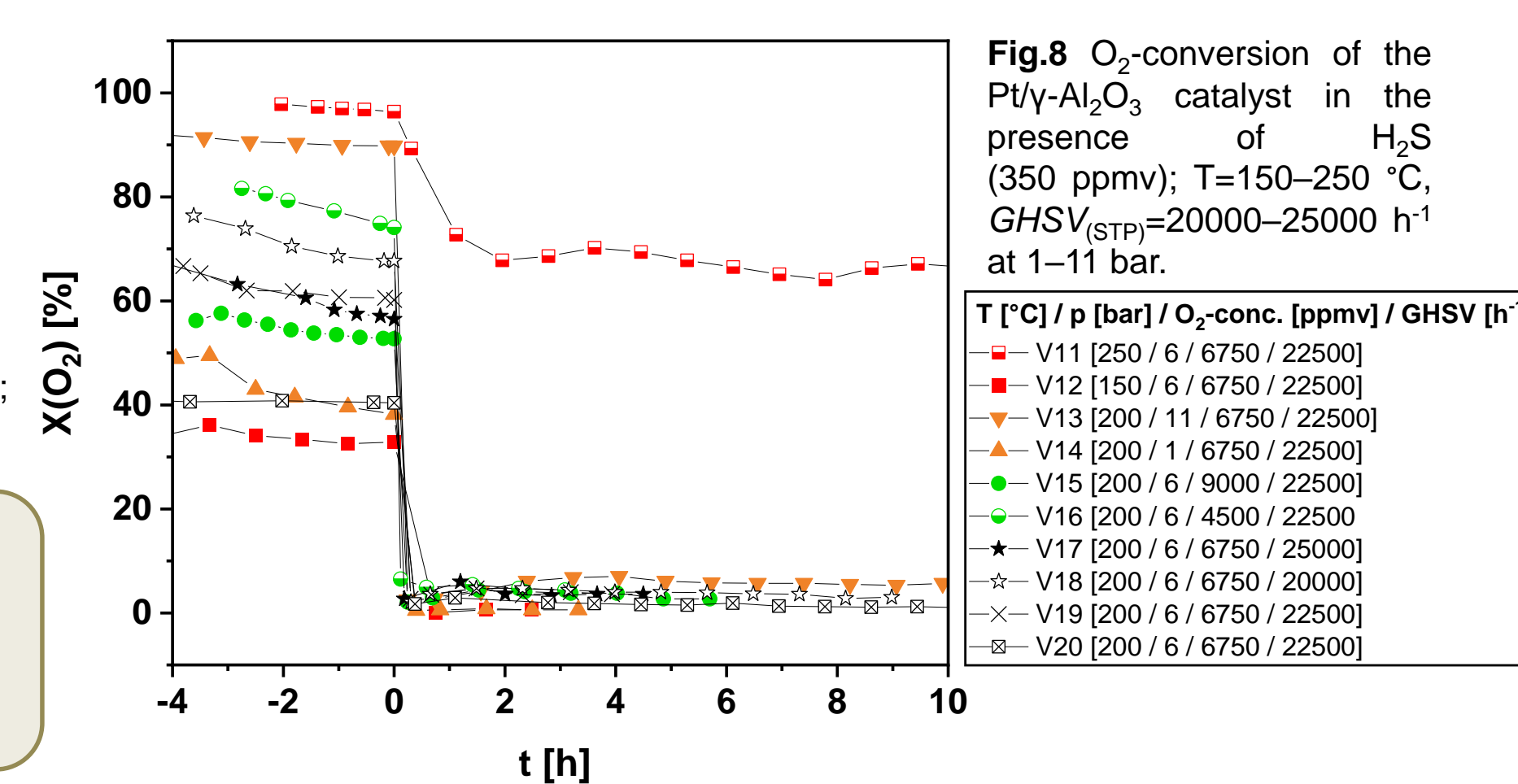


Fig.8 O₂-conversion of the Pt/ γ -Al₂O₃ catalyst in the presence of H₂S (350 ppmv); T=150–250 °C, GHSV_(STP)=20000–25000 h⁻¹ at 1–11 bar.

ACTIVITY

- Comparison between Pt and CoMo catalyst
Pt/ γ -Al₂O₃ featured the highest activity in the presence of 150 ppmv H₂S [1]
CoMo/ γ -Al₂O₃ deactivates immediately at atm. pressure [1].
The activity of the CoMo/ γ -Al₂O₃ depends on the sulphidation condition [2,3].
The sulphidation pressure significantly influences the sulphidation degree and in consequence the catalytic performance [3].

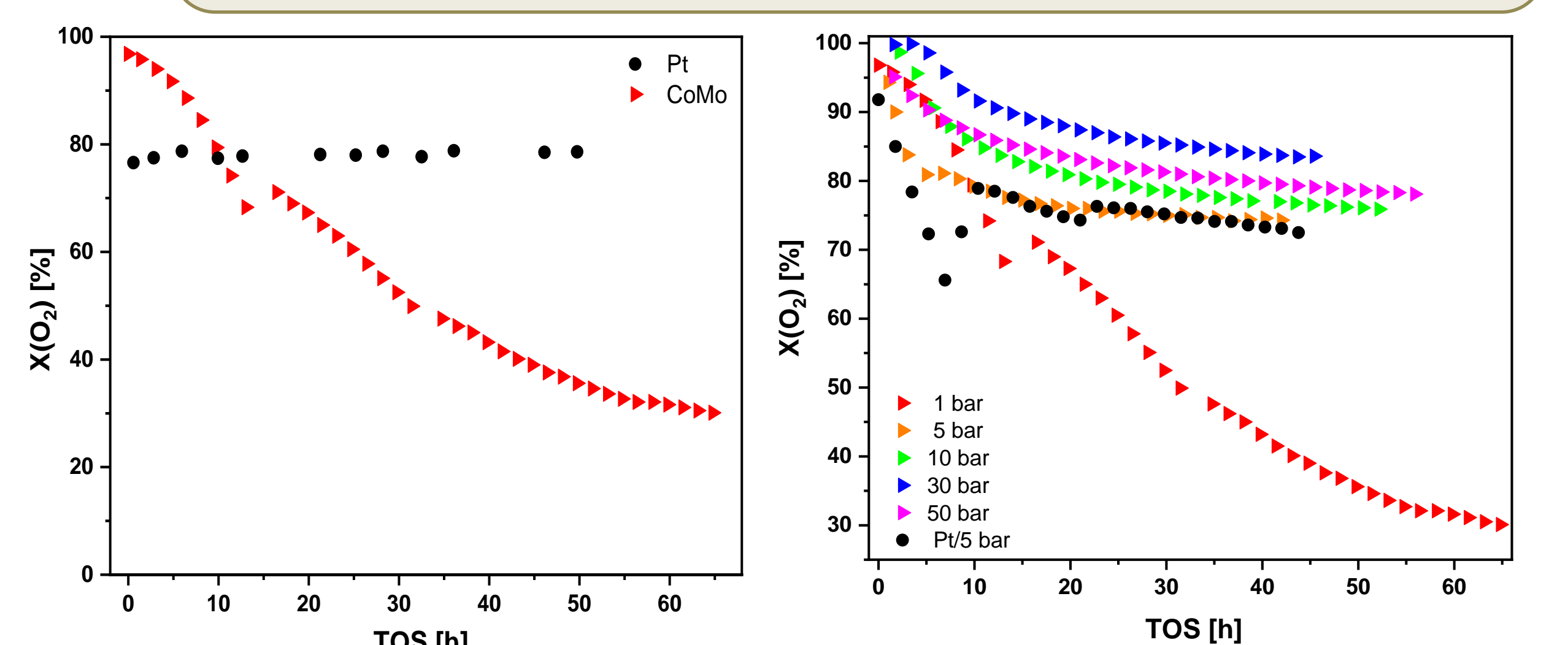


Fig.9 Dependence of O₂-conversion on reaction time over Pt and CoMo at atm. pressure.

Fig.10 Dependence of O₂-conversion on reaction time over Pt and CoMo at various pressure stages.

- References
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