Catalyst Deactivation, Poisoning and Regeneration

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Catalyst life-time represents one of the most crucial economic aspects in most industrial catalytic processes, due to costly shut-downs, catalyst replacements and proper disposal of spent materials. Not surprisingly, there is considerable motivation to understand and treat catalyst deactivation, poisoning and regeneration, which causes this research topic to continue to grow [1]. The complexity of catalyst poisoning obviously increases along with the increasing use of biomass/waste-derived/residual feedstocks [2,3] and with requirements for cleaner and novel sustainable processes, such as those implementing a catalytic assisted chemical looping approach [4,5].

This Special Issue provides insight for several specific scientific and technical aspects of catalyst poisoning and deactivation, proposing more tolerant catalyst formulations and exploring possible regeneration strategies. In particular, 14 research articles focus on heterogeneous catalysts by investigating thermal [6–8], physical [9,10] and chemical [11–19] deactivation phenomena, and also exploring less conventional poisons related to the increasing use of bio-fuels [17]. Some regeneration strategies [11,16], together with solutions to prevent or limit deactivation phenomena [7,9,11,16], are also discussed. Eventually, one review paper [20] analyzes the rich chemistry of rhodium/phosphine complexes, which are applied as homogeneous catalysts to promote a wide range of chemical transformations, showing how the in situ generation of the active species, as well as the reaction of the catalyst itself with other components in the reaction medium, can lead to a number of deactivation phenomena.

More in detail, the effect of the gas flow rate on the formation of hotspots during the Catalytic Partial Oxidation of logistic fuels on Rh-based monoliths for the on-board production of syngas is investigated in [6]. Solutions to prevent the irreversible thermal deactivation of Ni/ZrO_2 catalysts during the Dry Reforming of Methane are proposed in [7] by inhibiting the transition of ZrO_2 into its monoclinic phase via modification with La. For the same reaction, it is well known that coke deposition is often the main cause of the deactivation of Ni-based catalysts—in [10], the authors report on the beneficial addition of barium to NiLa-based catalysts obtained from perovskite precursors to depress coke formation.

Novel La-oxysulfate/oxysulfide oxygen carrier materials promoted with small amounts of Co, Mn or Cu are presented in [8], assessing their reactivity and stability during the cyclic operation of a Chemical Looping Combustion process fueled with either hydrogen or methane.

Experimental data for the ageing and deactivation effects in real-life catalysts are generally scarce in the open literature, so the insight on industrial catalysts operated in full-scale systems in [9,11,15] is an important contribution. In particular, transient operations of the industrial reactor, such as shutdowns with insufficient air purging, are identified to cause an unusual deactivation behavior of a commercial V_2O_5/TiO_2 catalyst used for the production phthalic anhydride, as a consequence of excessive vanadium reduction and coke deposition [9]. A case study [11] on the deactivation of a commercial V_2O_5-WO_3/TiO_2 monolith catalyst operated for 18,000 h in a SCR (DeNOx) unit with tail-end configuration treating the exhaust gases of a MW incinerator highlights the formation and surface deposition of ammonium (bi)sulphates, which occurred due to the low reaction temperature,

even though the inlet feed was rather clean after a desulphurization unit with $CaO/Ca(OH)_2$ and fabric filters. Furthermore, one research article [15] reports a detailed characterization of vehicle-aged oxidation catalysts from heavy-duty diesel and natural gas engines, showing the different effects of thermal ageing and chemical poisons (SO_2, phosphorous, zinc, silicon) on those commercial catalysts containing Pt or Pd dispersed on alumina.

Sulphur, mainly as SO_2, remains one of the main poisons for catalytic systems treating exhaust gases from combustion processes in stationary and mobile applications, since it forms highly stable sulphates. The individual and combined decomposition of aluminum and palladium sulphates, components of DOC, TWC and MOC, is presented in [12]. The same authors also address the role of sulphates formed on the support in restoring the Pd active species under different atmospheres and under simulated exhaust gas [13]. The deactivating effect of SO_2 and the formation of undesired by-products during the NH_3 SCR over a MnFe/TiO_2 catalyst for low-medium temperature is analyzed in [14] by investigating the mechanism of the main and side reactions occurring during the SCR process. On the other hand, in [16] the authors study regeneration strategies (oxidation/reduction) for a Co-Zn zeolite catalyst that was severely poisoned during the SCR of NOx with propane in the presence of SO_2 as a result of coke deposition and the formation of sulphates.

In addition, alkali and alkali earth metals are often responsible for the severe deactivation of SCR catalysts, especially when treating exhaust from the combustion of renewable fuels. Indeed, those elements can potentially come from bio-fuels or urea solutions in diesel engines [17] or even from fossil fuels in thermal power plants burning carbon [18]. Accordingly, in [18] the authors investigate the impact of the deposition of sulphur containing sodium salts onto a V_2O_5-WO_3/TiO_2 SCR catalyst with special regards to the NO removal rate as well as to the oxidation of SO_2 to SO_3. Moreover, as reported in [17], relatively high contents of sodium affect the hydrothermal stability of a Cu/SSZ-13 zeolite catalyst for the NH_3-SCR of a diesel exhaust.

Notably, water is often identified as causing catalyst poisoning, associated with the oxidation of the active metal, acceleration of sintering and even leaching of the active metals. In [19] the authors investigate the role of water addition during the hydrogenation of octanal over two copper-based catalysts and demonstrate that water can indeed promote process selectivity without affecting conversion.

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References

1. Argyle, M.; Bartholomew, C. Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts* **2015**, *5*, 145–269. [CrossRef]
2. Lange, J.P. Renewable Feedstocks: The Problem of Catalyst Deactivation and its Mitigation. *Angew. Chem. Int. Ed.* **2015**, *54*, 13187–13197. [CrossRef] [PubMed]
3. Kim, S.; Tsang, Y.F.; Kwon, E.E.; Lin, K.-Y.A.; Lee, J. Recently developed methods to enhance stability of heterogeneous catalysts for conversion of biomass-derived feedstocks. *Korean J. Chem. Eng.* **2019**, *36*, 1–11. [CrossRef]
4. Hu, J.; Galvita, V.V.; Poelman, H.; Marin, G.B. Advanced chemical looping materials for CO utilization: A review. *Materials* **2018**, *11*, 1187. [CrossRef] [PubMed]
5. Dou, B.; Zhang, H.; Song, Y.; Zhao, L.; Jiang, B.; He, M.; Ruan, C.; Chen, H.; Xu, Y. Hydrogen production from the thermochemical conversion of biomass: Issues and challenges. *Sustain. Energy Fuels* **2019**, *3*, 314–342. [CrossRef]
6. Batista, R.; Carrera, A.; Beretta, A.; Groppi, G. Thermal Deactivation of Rh/α-Al_2O_3 in the Catalytic Partial Oxidation of Iso-Octane: Effect of Flow Rate. *Catalysts* **2019**, *9*, 532. [CrossRef]

7.   Al-Fatesh, A.S.; Arafat, Y.; Ibrahim, A.; Kasim, S.O.; Alharthi, A.; Fakeeha, A.H.; Abasaeed, E.A.; Bonura, G.; Frusteri, F. Catalytic Behaviour of Ce-Doped Ni Systems Supported on Stabilized Zirconia under Dry Reforming Conditions. *Catalysts* **2019**, *9*, 473. [CrossRef]

8.   Cimino, S.; Mancino, G.; Lisi, L. Performance and Stability of Metal (Co, Mn, Cu)-Promoted $La_2O_2SO_4$ Oxygen Carrier for Chemical Looping Combustion of Methane. *Catalysts* **2019**, *9*, 147. [CrossRef]

9.   Richter, O.; Mestl, G. Deactivation of Commercial, High-Load o-Xylene Feed VO_x/TiO_2 Phthalic Anhydride Catalyst by Unusual Over-Reduction. *Catalysts* **2019**, *9*, 435. [CrossRef]

10. Gomes, R.; Costa, D.; Junior, R.; Santos, M.; Rodella, C.; Fréty, R.; Beretta, A.; Brandão, S. Dry Reforming of Methane over NiLa-Based Catalysts: Influence of Synthesis Method and Ba Addition on Catalytic Properties and Stability. *Catalysts* **2019**, *9*, 313. [CrossRef]

11. Cimino, S.; Ferone, C.; Cioffi, R.; Perillo, G.; Lisi, L. A Case Study for the Deactivation and Regeneration of a V_2O_5-WO_3/TiO_2 Catalyst in a Tail-End SCR Unit of a Municipal Waste Incineration Plant. *Catalysts* **2019**, *9*, 464. [CrossRef]

12. Kinnunen, N.M.; Nissinen, V.H.; Hirvi, J.T.; Kallinen, K.; Maunula, T.; Keenan, M.; Suvanto, M. Decomposition of Al_2O_3-Supported $PdSO_4$ and $Al_2(SO_4)_3$ in the Regeneration of Methane Combustion Catalyst: A Model Catalyst Study. *Catalysts* **2019**, *9*, 427. [CrossRef]

13. Kinnunen, N.M.; Kallinen, K.; Maunula, T.; Nissinen, V.H.; Keenan, M.; Suvanto, M. Fundamentals of Sulfate Species in Methane Combustion Catalyst Operation and Regeneration—A Simulated Exhaust Gas Study. *Catalysts* **2019**, *9*, 417. [CrossRef]

14. Lee, T.; Bai, H. Byproduct Analysis of SO_2 Poisoning on NH_3-SCR over $MnFe/TiO_2$ Catalysts at Medium to Low Temperatures. *Catalysts* **2019**, *9*, 265. [CrossRef]

15. Kanerva, T.; Honkanen, M.; Kolli, T.; Heikkinen, O.; Kallinen, K.; Saarinen, T.; Lahtinen, J.; Olsson, E.R.L.; Vippola, M. Microstructural Characteristics of Vehicle-Aged Heavy-Duty Diesel Oxidation Catalyst and Natural Gas Three-Way Catalyst. *Catalysts* **2019**, *9*, 137. [CrossRef]

16. Pan, H.; Xu, D.; He, C.; Shen, C. In Situ Regeneration and Deactivation of Co-Zn/H-Beta Catalysts in Catalytic Reduction of NO_x with Propane. *Catalysts* **2019**, *9*, 23. [CrossRef]

17. Wang, C.; Wang, J.; Wang, J.; Wang, Z.; Chen, Z.; Li, X.; Shen, M.; Yan, W.; Kang, X. The Role of Impregnated Sodium Ions in Cu/SSZ-13 NH_3-SCR Catalysts. *Catalysts* **2018**, *8*, 593. [CrossRef]

18. Xiao, H.; Dou, C.; Shi, H.; Ge, J.; Cai, L. Influence of Sulfur-Containing Sodium Salt Poisoned V_2O_5–WO_3/TiO_2 Catalysts on SO_2–SO_3 Conversion and NO Removal. *Catalysts* **2018**, *8*, 541. [CrossRef]

19. Govender, A.; Mahomed, A.S.; Friedrich, H.B. Water: Friend or Foe in Catalytic Hydrogenation? A Case Study Using Copper Catalysts. *Catalysts* **2018**, *8*, 474. [CrossRef]

20. Alberico, E.; Möller, S.; Horstmann, M.; Drexler, H.-J.; Heller, D. Activation, Deactivation and Reversibility Phenomena in Homogeneous Catalysis: A Showcase Based on the Chemistry of Rhodium/Phosphine Catalysts. *Catalysts* **2019**, *9*, 582. [CrossRef]