

Editorial

# Feature Papers to Celebrate “Environmental Catalysis”—Trends & Outlook

Jean-François Lamonier <sup>1,\*</sup>  and Annemie Bogaerts <sup>2</sup> 

<sup>1</sup> Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181—UCCS—Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

<sup>2</sup> Research Group PLASMANT, Department of Chemistry, University of Antwerp, Campus Drie Eiken—Room B2.09, Universiteitsplein 1, Wilrijk, BE-2610 Antwerp, Belgium; annemie.bogaerts@uantwerpen.be

\* Correspondence: jean-francois.lamonier@univ-lille.fr

This Special Issue collects three reviews, eight articles, and two communications related to the design of catalysts for environmental applications, such as the transformation of several pollutants into harmless or valuable products. Those catalysts are engineered for conventional thermal oxidation catalysis but also sequential adsorption-catalytic, photocatalytic, and plasma-catalytic oxidation processes.

The review by Can et al. [1] gives a general overview of the recent use of WO<sub>3</sub>-based catalysts for DeNO<sub>x</sub> applications, total oxidation of volatile organic compounds in gas phase and gas sensors, and pollutant remediation in liquid phase (photocatalysis). The 431 references cited and discussed in this review allow the authors to highlight the potential of these materials that have acid, redox, and adsorption properties and exhibit a photo-stimulation response under visible light. The authors conclude that the use of these materials as photocatalysts is of growing interest, but their design needs to be improved to enhance their reactivity.

Direct oxidation of methane to methanol (DOMTM) through heterogeneous catalysis and plasma catalysis is reviewed by Li et al. [2]. In heterogeneous catalysis, the use of appropriate oxidants (N<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O) alone or in combination significantly reduces the kinetic energy barrier of the DOMTM reaction, but the over-oxidation of methanol should be avoided. In the field of plasma catalysis an in-depth understanding of the reaction mechanisms by combining computer simulations with experiments is needed because of the lack of information on the interaction between plasma and catalysts. Such fundamental studies will allow experts to refine the design of the catalyst and consequently to improve the CH<sub>4</sub> conversion and target product selectivity.

Finally, the review of Lisi et al. [3] provides a comprehensive and critical analysis of the latest literature on the poisoning of SCR catalysts by the major alkali and alkaline earth metals in combination with various counterions or with the simultaneous presence of other toxic elements or compounds. For the different classes of catalysts discussed such as V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>, zeolites or manganese and cerium oxides, the loss of acidity by alkali poisoning is the main cause of deactivation. The authors also underline the high costs related to the restore, replacement, and disposal of spent SCR catalysts. Finally, the development of a catalyst with more Lewis acid sites little affected by poisoning seems to be an interesting way to improve the lifetime of the catalysts.

Among the eight articles and two communications, six are devoted to VOC abatement, two to CO<sub>2</sub> transformation, one to NH<sub>3</sub> synthesis, and one to NO<sub>x</sub> reduction

With regard to VOC abatement, a novel strategy using a sequential adsorption-catalytic oxidation process was investigated by breakthrough experiments, temperature-programmed reactions, either in He to probe the redox properties or in a He:O<sub>2</sub> (50:50) gaseous mixture to assess the catalytic properties of three different materials [4]. Among the different materials tested, Sonar et al. [4] showed that Hopcalite (CuMnOx) exhibits



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the best performances due to both its toluene adsorption capacity and its good catalytic performances in the toluene total oxidation. The study of Wang et al. [5] combines the investigation of the gas phase and the adsorbed phase of acetone to provide a new insight on plasma–material coupling. The authors first demonstrated the different behavior of two materials ( $\text{TiO}_2$  and  $\text{CeO}_2$ ) with respect to the adsorption of acetone but also with respect to the adsorption of ozone. It is interesting to note that the formation of organic species resulting from the reactive adsorption of acetone significantly impacts the adsorption of ozone, which is no longer dependent on the composition of the adsorbent material. Finally, the study on the ozonation of the two materials reveals the key role of the reactive adsorption of acetone for an efficient oxidation and mineralization under the post-plasma exposure. Chlala et al. [6] investigated Mn-doped hydroxyapatite catalysts for HCHO total oxidation. The authors showed that the nature of Mn species changed significantly with Mn loading.  $\beta$ - $\text{MnOOH}$  species predominated for low Mn content (5 wt.% and 10 wt.%), while  $\epsilon$ - $\text{MnO}_2$  phase is present for higher Mn loading (20 wt.% and 30 wt.%). The catalytic behavior of Hap-supported MnOx is closely related to the nature and local environment of the manganese species. The best catalytic activity obtained for the lowest Mn loading (5 wt.%) was associated with well-dispersed manganese oxides on the support hydroxyapatite with a medium Mn average oxidation state. Interestingly, the authors showed that the presence of water in the feed enabled the maintenance of the catalytic activity due to the regeneration of the consumed surface OH by water. In order to minimize the cost of the catalyst for the VOC total oxidation, Pande et al. [7] have studied the possibility of using red mud waste from the aluminum industry as catalyst. The authors showed that red mud modified by leaching followed by precipitation boosted the catalytic activity in the toluene total oxidation compared to the use of non-activated red mud. The authors attributed this improved performance to the enhanced textural and redox properties of the modified red mud due to the better dispersion and higher enrichment of Fe oxides at their surface. Mytareva et al. [8] investigated the ozone catalytic oxidation of alkanes by using an alumina-supported manganese oxide catalyst. They demonstrated that the presence of a small amount of ozone in air allowed to significantly decrease the temperature range of n-alkane oxidation, since 80–100% conversion is achievable in the temperature range 70–200 °C over Mn (10 wt.%)/ $\text{Al}_2\text{O}_3$  catalyst. The authors concluded that  $\text{O}_3$  decomposition over MnOx species enabled the production of very active oxygen species, allowing the low-temperature abatement of the short-chain hydrocarbons. Finally, the catalytic oxidation of an odorous and harmful air pollutant dimethyl disulfide (DMDS), over bimetallic Cu–Au and Pt–Au catalysts, has been studied by Nevanperä et al. [9]. The big challenge is the design of a catalyst able to resist to sulfur poisoning. The strategy was to incorporate Au to Pt and Cu catalysts via surface redox reactions aimed at the deposition of Au onto Pt or Cu. The authors showed that the addition of Au improved the activity of the  $\text{Al}_2\text{O}_3$ -supported Cu and Pt catalysts and had a positive effect on  $\text{SO}_2$  production by widening its production window, especially for the platinum-based catalyst. Although promising for its excellent selectivity (less by-products), the Pt-Au/Ce-Al catalyst proved to be not very stable over time and further developments are still needed.

With regard to  $\text{CO}_2$  transformation, the design of a novel gold catalyst supported by  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  for the selective hydrogenation of  $\text{CO}_2$  to methanol has been studied by Lu et al. [10] while the coke-resistant catalyst supports have been particularly investigated by Nambo et al. [11] in the reaction of dry methane reforming. Lu et al. [10] showed in particular that the addition of Zr remarkably improves the activity of the Au/ $\text{In}_2\text{O}_3$ .  $\text{H}_2$  species can be activated on Au NPs strongly interacting with the support. The increase in the amount of oxygen vacancies as well as the improvement in  $\text{CO}_2$  adsorption are assumed to be the reasons for the significant improvement in catalytic activity. In comparison with nickel supported on commercial titania powder, Nambo et al. [11] showed that the use of nickel supported on titania nanowires enables the maintenance of a stable activity of >90%  $\text{CO}_2$  conversion with the dry methane reforming reaction, in agreement with higher coke resistance of titania nanowires. Furthermore, Nambo et al. [11] proposed that nanowire-

supported Ni particles with cubic-octahedral morphologies with high density of non-(111) surface sites are responsible for enhanced activity and reduced graphitic coke deposition.

The synthesis under mild conditions of ammonia was investigated by Nishi et al. [12] so that the ammonia then produced could be used as a fuel to produce energy. A series of new Ba-promoted Ru catalysts supported on mesoporous carbon with Ba/Ru ratios of 0.1–1.6 and a Ru loading of 10 wt.% were synthesized. Nishi et al. showed that a synergistic effect of Ba and Ru species, which were stabilized in the mesoporous carbon framework, could effectively catalyze the mild synthesis of ammonia (280–450 °C and 0.99 MPa) even under intermittently variable conditions, especially in the presence of catalysts with Ba/Ru ratios >0.5.

For the NO<sub>x</sub> reduction by CO, Cheng et al. [13] demonstrated the influence of the interaction strength of Rh with two alumina supports. In particular, they showed that the theta phase of alumina in comparison to the gamma phase not only reduced the amount of occluded Rh but also stabilized Rh better during the hydrothermal aging treatment. The aged Rh/theta-Al<sub>2</sub>O<sub>3</sub> catalyst showed higher NO reduction activity at low temperatures due to the weaker interaction of the phase with Rh. Through the hydrothermal aging treatment, the authors showed that the turnover frequency of NO at 350 °C can be significantly improved, probably due to the different surroundings of non-interacting Rh and the formation of the Rh clusters.

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