

Catalytic Wet Air Oxidation of Phenol – Deactivation phenomenon and insight into regeneration possibilities

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Introduction

Efficiently removing organic pollutants from industrial effluents has nowadays become an urgent and prior necessity. Amongst the large variety of available pollution abatement processes, oxidation techniques have been widely studied over the past years. In particular, the Catalytic Wet Air Oxidation (CWAO) process revealed to be promisingly efficient.

While less active, heterogeneous catalysts are generally favored to homogeneous ones because of recovery reasons. But those heterogeneous catalysts were shown to be prone to deactivation by sintering, leaching or deposition of carbonaceous species [1,2]. The two first cited catalyst deactivation inducing phenomena can easily be overcome by using adequate and stable supports and active phases. On the contrary, the formation of a carbonaceous deposit seems unavoidable when oxidizing aromatic compounds like phenol [1]. The aim of this work was to study the impact of this deposit on the catalytic activity and to investigate in situ (inside the CWAO reactor) and ex situ (in a tubular calcination reactor) oxidative regeneration protocols.

Materials and Methods

Monometallic 2.5 wt% Pt and 1.25 wt% Ru catalysts supported either on CeO₂ simple oxide or on Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O₂ ternary mixed oxide were prepared and tested in Catalytic Wet Air Oxidation of phenol. Experiments were performed for 3 h in an autoclave heated at 160 °C and stirred at 1000 rpm. Model effluent was a 160 mL solution of phenol at a concentration of 22.3 mmol.L⁻¹. Oxidant was pure oxygen at a pressure of 20 bar and the catalyst concentration was fixed at 4 g.L⁻¹. After reaction, used catalysts were recovered, washed, dried and underwent characterization by Temperature-Programmed Oxidation (TPO), Elemental Analysis, Inductively Coupled Plasma (ICP) or hydrogen chemisorption.

Results and Discussion

“Pre-coked” catalysts were actually less active than fresh ones. In situ regeneration was found to be less efficient than ex situ regeneration (example is given for Pt/CeO₂ catalyst in Fig.1) and to lead to additional deactivation by metal loss and sintering. During the early minutes of catalytic tests, phenol conversion (C) and Total Organic Carbon abatement (ΔTOC) curves were superimposed: the very first step of the reaction is mainly phenol adsorption without degradation into smaller organic molecules. For Pt/CeO₂ catalyst, products selectivities remained nearly unchanged whether the catalyst was fresh or not while “pre-coked” Pt/Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O₂ behaved very differently from the same “uncoked” catalyst (Fig.2). Available catalytic surface is limited and the formation of the carbonaceous deposit is faster

than its degradation. This obviously leads to a more or less rapid saturation of the catalyst surface. The important apparent initial activity is thus due to phenol adsorption. Once the surface is saturated with carbon deposit, the apparent reaction rate corresponds to the real oxidation rate.

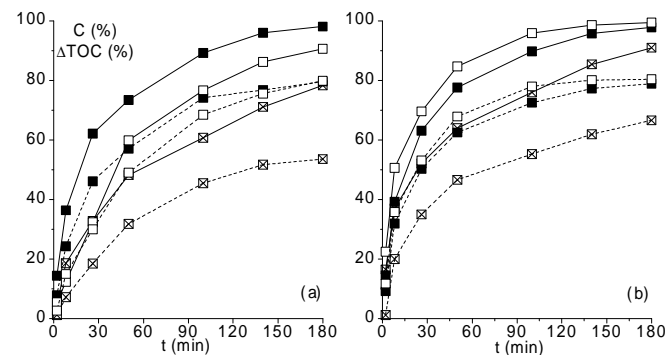


Figure 1. Evolutions of phenol conversion (—) and TOC abatement (---) for fresh (■), “pre-coked” (⊠) and regenerated (□) Pt/CeO₂ catalysts during WAO of phenol for in situ (a) and ex situ (b) regeneration protocols.

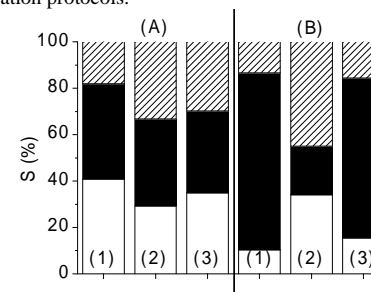


Figure 2. Selectivity of carbon dioxide (□), carbonaceous deposit (■) and aqueous organic intermediaries (⊠) for fresh (1), “pre-coked” (2) and ex situ regenerated (3) Pt/CeO₂ (A) and Pt/Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O₂ (B) catalysts after 3 h of WAO of phenol.

Significance

Deactivation by carbonaceous materials deposition is a significant phenomenon occurring during WAO of aromatic compounds. Learning more about it could help to prevent the formation of this deposit or to develop convenient, efficient and cheap regeneration techniques.

References

1. Pintar, A., Levec, J. J. *Catal.* 135, p. 345 (1992).
2. Besson, M., and Gallezot, P. *Catal. Today* 81, p. 547 (2003).