Enhanced Photocatalytic Activity of Ternary Al$_2$O$_3$-Nd$_2$O$_3$-ZnO oxides in the Degradation of Phenol

Arturo Barrera*, José Eduardo Casillas, Francisco Tzompantzi, Guadalupe Mendoza-Damián, Sujey Guadalupe Castellanos, Alejandro López-Gaona

*Universidad de Guadalajara, Centro Universitario de la Ciencia, Laboratorio de Nanomateriales Catalíticos, Ocoyucan Jilisco, México

Universidad Autónoma Metropolitana-Iztapalapa, Depto. de Química, México D.F., México

*arturobr2003@yahoo.com.mx

Introduction
Removal of organic pollutants from residual water is a problem of urgent solution [1]. One of them, phenol, shows severe carcinogenic and neurotoxicity effects in human beings [2, 3]. When phenol, as well as its derivatives, is released to environment, it is very stable and refractory to natural decomposition, so it lasts for a long time before degrading itself. That is why phenol must be subject to a more efficient process to degrade it, for example, a photocatalytic one using UV radiation. In this communication we report the catalytic activity of new photocatalytic materials (ternary Al$_2$O$_3$-Nd$_2$O$_3$-ZnO oxides) in the degradation of phenol in aqueous medium.

Materials and Methods
The Al$_3$-Zn-x ternary oxides (x = 0.5, 1.0, 5.0 w/w %) were synthesized by the sol-gel method, with a constant 15% of Nd$_2$O$_3$. The precursors were aluminum sec-butoxide dissolved in 2-methyl-2,4-pentanediol; neodymium acetylacetonate and zinc acetylacetonate dissolved in toluene. The obtained gels were aged for 3h at 90°C, followed by drying at 120°C for 12h and calcination at 550°C for 3h. The solids were characterized by nitrogen physisorption (Quantachrome iQ), DRX (STOE, Theta-Theta, λ=1.546 Å) and Raman Spectroscopy (Thermo Scientific, laser of 532nm). The degradation of phenol was carried out in a batch reactor, filled with 200 mL of a phenol (80ppm) aqueous solution and 200 mg of catalyst with continuous stirring. A PenRay device from UVP was used as radiation source. It provides 254nm UV light with 4400 μW cm$^{-2}$. The degradation of phenol was monitored by UV spectroscopy in the 270nm band.

Results and Discussion
Table 1 shows the BET areas ($S_{BET}$) of the material. It can be seen that the presence of Nd produces an increment in $S_{BET}$. It coincides with which was observed in PdO/γ-Al$_2$O$_3$-Nd$_2$O$_3$ [4]. However, in our materials, that one with the lower content of ZnO reaches the higher $S_{BET}$ value and $S_{BET}$ diminishes as the content of ZnO increases. It can be due to a pore blockage by ZnO which, besides, reduces the pore volume as well.

On the other side, it is worth to note that, while γ-Al$_2$O$_3$ presents unimodal distribution, ternary oxides show bimodal ones which moves towards lower diameter values as ZnO is added. In another work unimodal distribution for Al$_2$O$_3$-Nd$_2$O$_3$ binary oxides is reported [4], which suggests that the porous structure of the ternary oxides is due mainly to the addition of ZnO. There is not a distribution for Nd$_2$O$_3$ because it is a material with a very low porosity.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Surface area (m$^2$/g)</th>
<th>Specific volume (cm$^3$/g$^1$)</th>
<th>Pore diameter of modal peak (nm)</th>
<th>% D, 4h</th>
<th>% D, 5h</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>307.0</td>
<td>1.0</td>
<td>11.0</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td>Al-Nd-Zn-0.5</td>
<td>334.0</td>
<td>0.8</td>
<td>5.7, 8.4</td>
<td>98</td>
<td>100</td>
</tr>
<tr>
<td>Al-Nd-Zn-1.0</td>
<td>328.0</td>
<td>0.7</td>
<td>4.7, 8.7</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Al-Nd-Zn-5.0</td>
<td>325.0</td>
<td>0.5</td>
<td>6.1, 7.7</td>
<td>91</td>
<td>99</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>6.0</td>
<td>0.03</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
</tbody>
</table>

DRX patterns (not shown) informs that ternary oxides have similar structure to that of the amorphous materials, which means that ZnO and Nd$_2$O$_3$ species are highly dispersed and very well mixed with γ-Al$_2$O$_3$ agglomerates. However, by Raman spectroscopy it is found the displacement of bands which correspond to vibrational transitions of Nd$_2$O$_3$. whilst UV-Vis spectra show absorption bands, mainly in visible region.

Results of the degradation of phenol show that γ-Al$_2$O$_3$ transforms 75% of phenol at 4h of photoreaction, surprisingly, a higher activity (almost three times) than that of TiO$_2$-P25 (Degussa) [4]. The photocatalytic activity is increased when 15 %wt of Nd$_2$O$_3$ is present (degradation of 83%) and is even higher, reaching about 100% degradation when ZnO is part of the catalyst at 0.5 and 1.0 % contents. Nevertheless, the activity decreases at 5.0% of ZnO, probably due to the blockage of pores. According with the previous results it can be thought that ZnO works as a promoter of the γ-Al$_2$O$_3$-Nd$_2$O$_3$ binary oxides at concentrations as low as 1.0%.

Significance
This works shows a surprisingly photocatalytic behavior of new oxide materials which promise to be applicable to transform recalcitrant contaminant compounds in aqueous medium.

References