**Catalytic combustion of toluene over cryptomelane-type manganese oxide supported metals**

A. Giroir-Fendler, S. Gil, J. A. Díaz, L. Retailleau, M. Ousmane, M. Pera-Titus and F. De Campo

1 Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l’environnement de Lyon, 2 avenue Albert Einstein, F-69625 Villeurbanne, France
2 Facultad de Ciencias y Tecnologías Químicas, Dpto. Ingeniería Química, Universidad de Castilla-La Mancha, avenida de Camino José Cela 12, 13071 Ciudad Real, Spain
3 Rodia China - EPFL, LLMI 3464, 3066 Jin Da Rd. (former 666 Shen Qiang Rd.), Xin Zhuang Industrial Zone, Shanghai 211408, China.

(*) corresponding author: auro.giroir-fendler@ircelyon.univ-lyon1.fr

**Introduction**

Volatile organic compounds (VOCs), which released from industrial processes, constitute a real concern in the air pollution [1]. Among them, toluene is one of the most important VOC, because it is emitted in high concentrations and its effects over the human health [2]. There are several methods for eliminating VOCs, which can be grouped into two main categories. One category comprises separation-and-recovery techniques such as absorption or adsorption, and the other category comprises the so-called destruction techniques such as incineration or catalytic combustion for VOCs. These latter techniques are more effective when the pollutants are present in trace amounts, but this requires the use of heterogeneous catalysts. Regarding this point, cryptomelane-type manganese oxide materials have been found as effective catalysts for different oxidation reactions [3]. Cryptomelane is an allotropic form of manganese oxide which consists of an octahedral molecular sieve (OMS). It presents special properties related to the lattice oxygen mobility, which moreover could be enhanced by addition of different metals. The aim of this work was to characterize the properties of different OMS supported metals (Ag, Au, Pd, Pt and Ru) and evaluate the catalytic performance of them in the catalytic combustion of toluene.

**Materials and Methods**

To synthesize K-OMS-2, potassium precursors were dissolved in an acidic solution and refluxed at 100°C (24 h). Then the solids were washed and dried at 120°C. K-OMS-2 supported metal catalysts were prepared by the incipient wetness impregnation of aqueous nitrate precursor solutions. After impregnation, the catalysts were dried in a vacuum oven at 110°C overnight. Samples were characterized by chemical analysis, nitrogen adsorption-desorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), transmission electron microscopy (TEM). Catalytic tests were carried out using 0.1 g of catalyst diluted on silicon carbide. Reactant mixture contained 1000 ppmv of toluene in air, with a total flow of 100 NmL·min⁻¹. Catalytic activities were evaluated from 80°C to 350°C in terms of toluene conversion, light-off temperatures and activation energies. Finally, in order to evaluate the catalyst stability, a special test was carried out over the most active catalyst (24 h at 250°C).

**Results and Discussion**

Obtained characterization and catalytic results are described in table 1 and show that K-OMS-2 is an active catalyst for toluene oxidation. The addition of noble metals lowers slightly the light-off temperature. TPD results confirm that the addition of a noble metal affect the reducibility of the supported OMS catalyst and more particularly in the case of platinum supported catalyst. On the other hand, the metal particle sizes evaluated by TEM micrograph show that the larger particles are less active for the oxidation reaction. The smaller the particle size, the higher the catalytic activity was, with the exception of Ru/OMS.

**Table 1. Main characterization and catalytic activity results of the prepared catalysts**

<table>
<thead>
<tr>
<th>Metal content (wt.%)</th>
<th>OMS</th>
<th>Ag/OMS</th>
<th>Au/OMS</th>
<th>Pd/OMS</th>
<th>Pt/OMS</th>
<th>Ru/OMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/OMS</td>
<td>2.54</td>
<td>1.96</td>
<td>2.31</td>
<td>1.73</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>BET surface area (m²·g⁻¹)</td>
<td>85</td>
<td>81</td>
<td>94</td>
<td>83</td>
<td>91</td>
<td>82</td>
</tr>
<tr>
<td>Reduction temp. (°C)</td>
<td>380</td>
<td>312</td>
<td>340</td>
<td>-</td>
<td>165</td>
<td>246</td>
</tr>
<tr>
<td>Metal particle size (nm)</td>
<td>-</td>
<td>13.3±5.9</td>
<td>15.2±4.6</td>
<td>4.9±1.6</td>
<td>3.9±1.7</td>
<td>2.1±0.4</td>
</tr>
<tr>
<td>T(xylene=50%) (°C)</td>
<td>240</td>
<td>237</td>
<td>240</td>
<td>236</td>
<td>232</td>
<td>234</td>
</tr>
<tr>
<td>Act. energy (kJ·mol⁻¹)</td>
<td>28.7</td>
<td>27.6</td>
<td>29.3</td>
<td>25.8</td>
<td>18.7</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Figure 1 shows the light off curve of the OMS and Pt/OMS catalysts and the stability test performed with the Pt/OMS catalyst. Herein, it could be observed that the sample did not show any appreciable deactivation. The catalytic activity reached a steady state after approximately 1000 min of time on stream. This result confirmed that OMS support can be used in an oxidant stream until 500°C.

**Significance**

OMS resulted to be active in the catalytic combustion of toluene. Moreover, the impregnation of platinum metal particles can improve the catalytic properties of this material. Catalyst Pt/OMS was stable for at least 24 h without any appreciable deactivation.

**References**