Toluene Total Catalytic Oxidation by Heterogeneous Catalysts: The Synergic Effect between Cobalt and Mn in a 3DOm System

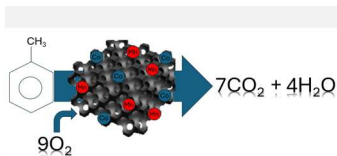*A.E. Ramírez[1], Y.C. Imbachi[1], C.D. Miranda[1], L.C. Urán[2], A. Echavarria[2], C. Ostos[2], M.M. Ballesteros[3], A.R. Ruíz[3]*
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A serie of heterogenous catalysts was prepared, characterized and used in the toluene total abesiment. Metals oxyde of type M_xO_y: Mn_4O_6, Co_3O_4 and Co_3O_4-Mn_4O_6 were deposited on 3D mesoporous ordered carbon (3DOm) and a synergic effect between Co and Mn species was determined. The 3D structure of support leads to adequate dispersion of metals oxyde particles on the surface and permit its interaction as active species.

Introduction

Volatile Organic Compounds (VOCs) are among the major contributors to current worldwide composite air pollution. VOCs and the secondary pollutants they form have a negative impact on human health, and some VOCs are also genotoxic and carcinogenic [1]. Some advanced processes or technologies to reduce the pollution in our atmosphere have been introduced to tackle this issue and some have already been commercialized [2]. Catalytic oxidation is regarded as one of the most promising strategies for VOC removal from industrial waste streams [3].

Generally, noble-metal supported catalysts are more widely applied in low-temperature catalysis than transition metal oxide catalysts. The support materials—such as transition-metal oxides—of noble-metal based catalysts play a vital role, providing high surface areas for the dispersion of noble metals, generating active species, and, particularly, promoting the adsorption capacity for VOCs and O_2 molecules [4]. Compared with single Co-based spinel oxides, catalysts with partial substitution of cobalt by manganese show better catalytic performance [5].

In this work, we present an effective removal of toluene, like as representative carcinogen molecule, via catalytic oxidation using Co_3O_4-Mn_4O_6 system that showcase a synergistic effect between Co and Mn species, when 3D mesoporous ordered carbon (3DOm) was used as support.

Material and Methods

Catalysts Synthesis. The preparation of catalytic systems, it consisted of two stages:

1. Support preparation (3DOm) mesoporous carbon. 3 stages were carried out: i) the synthesis of the respective mesoporous template (SBA-15), ii) filling of the respective mesoporous template with the precursor (sucrose), that is, a carbon source, and iii) elimination of the base template mesoporous silicon oxides with HF until carbon is obtained in three-dimensional form.

2. Metal impregnation. We are following the methodology described in [6] cobalt and manganese salts were added according to the percentages that will be added of each metal, 2.5% and 5% of cobalt from the salt $Co(NO_3)_2 \cdot 6H_2O$. 2.5% and 5% of manganese from the salt $Mn(NO_3)_2 \cdot 4H_2O$. The procedure was carried out by means of wet impregnation for 2 hours and subsequent drying at 100 °C for 12 hours and finally calcination at 350 °C for 3 h, under inert atmosphere (N_2).

Solids Characterization. The solids were characterizated by TEM, XRD, XPS and surface area.

Catalytic Test. A flow of 50 mL/min of dry air was passed through 0.100 g of catalyst at 400 °C for 1 h for the activation of the catalysts. After that, the ignition curves were obtained by cooling at 1.5 °C/min from 450 °C to 100 °C introducing a flow of oxygen saturated with toluene, with a concentration of 1000 ppm

Results and Discussion

Template (SBA-15) characterization.

By TEM and XRD, Figure 1(a) and 1(b), we are confirmed the ordered porous structure of template which is of great importance because it allowed a greater dispersion of carbon source (sucrose) in carbonization step.
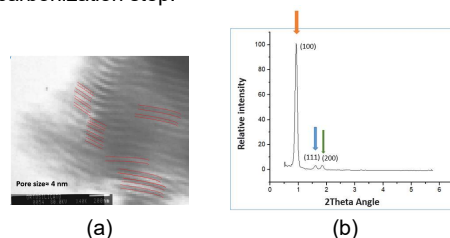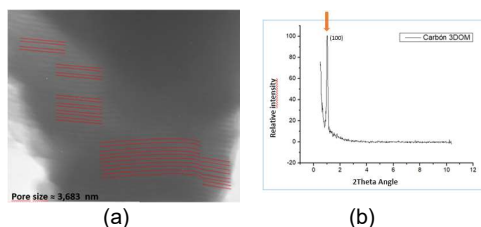

Figure 1. Template (SBA-15) (a) TEM Figure (b) XRD diffractogram

**Support (3DOm) characterization**.

The same as template, by TEM and XRD, Figure 2 (a) and 2 (b); we determine that ordered mesostructure is conserved after carbon deposition on the SBA-15 and this leads to obtaining a 3DOm structure for the support.

(a)   (b)

Figure 2. Support (3DOm) (a) TEM Figure (b) XRD diffractogram

Catalysts characterization.

The diffractograms, Figure 3, confirms the mesorder is retained after metal impregnation on the support, because the reflection (111) is conserved in the systems and leads to $M_xO_y/3DOm$ obtention. The surfaces areas correspond to differents structural arrays and are showed in Table 1.
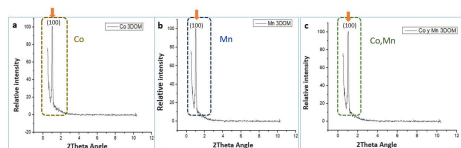
Figure 3. X-ray diffraction for catalyst a) $Co_3O_4/3DOm$, b) $Mn_4O_6/3DOm$ c) Co_3O_4-$Mn_4O_6/3DOm$

Catalytic results

The Figure 4 shows the catalytic behaviour of the different systems and confirms the synergic effect between Co_3O_4 and Mn_4O_6, since the catalytic activity is greater than individual oxydes (Co_3O_4, Mn_4O_6), which is due to the strong interactions between Mn and Co species and the weakened Mn–O chemical bonds [7] as shown in the inset of Figure 4.
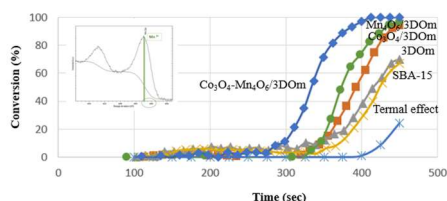
Figure 4. Catalytic results in toluene oxidation (COV probe) by $M_xO_y/3DOm$ systems.

It is also observed that SBA-15 and 3DOm have catalytic activity too, due silicates and carbon functional groups present in its structure. In a every way, the systems overcome the oxydation by termal effect. The main results are showed in Table 1.

Conclusions

Total oxidation of toluene (probe COV molecule) is obtained using $M_xO_y/3DOm$ catalytic systems where the synergic effect between two metallic oxydes, Co_3O_4 and Mn_4O_6, was determined.
Carbon 3DOm turns out to be a great potential support for oxydation reactions being COV total depletion one real option.

References

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Table 1. Textural and structural properties for solid systems and its reaction results

Solid	Surface area [a] (m²/g)	M [b] %	Conversion %	Catalytic activity [c] s⁻¹
SBA-15 (template)	603	-	67	0.69
3DOm (support)	325	-	67	0.69
Co_3O_4 /3DOm	250	5	97	0.84
Mn_4O_6 /3DOm	263	5	100	1.22
Co_3O_4 Mn_4O_6 /3DOm	237	2.5 (Co) 2.5 (Mn)	100	1.35

[a] Obtanied by Brunauer-Emmett-Teller (BET) surface area analysis. [b] Nominal percentage. [c] As Conversion/time