

Supplementary Material

Pt/CeMnO_x/diatomite: A highly active catalyst for the oxidative removal of toluene and ethyl acetate

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Content

Item	Page
Catalyst characterization procedures	3–5
Catalytic evaluation procedures	6
Table S1	7
Figure S1	8
Figure S2	9
Figure S3	10
Figure S4	11
Figure S5	12
References	13

Catalyst characterization procedures

The actual contents of noble metals in Pt/CeMnO_x/diatomite, Pt/CeMnO_x, Pt/CeMn₂O_x/diatomite, Pt/CeMn_{0.5}O_x/diatomite and Pd/CeMnO_x/diatomite were determined by the inductively coupled plasma–atomic emission spectroscopic (ICP–AES) technique using a Thermo Electron IRIS Intrepid ER/S spectrometer (Thermo Electron Corporation, Waltham, MA, USA). Each sample was dissolved in a mixture of concentrated HCl and HNO₃ aqueous solutions with a volumetric ratio of 3 : 1 prior to analysis.

The crystal structures of the as-obtained samples were characterized by means of the X-ray diffraction (XRD) technique on a Bruker/AXS D8 Advance diffractometer (AXS, Bruker, Berlin, Germany), with Cu *K*α radiation and nickel filter ($\lambda = 0.15406$ nm).

Laser Raman spectroscopy is an analytical method to study the scattering of compound molecules by light irradiation, the relationship between the scattering light and the incident light energy range and the vibration frequency and rotation frequency of compound. In this experiment, Horiba HR Evolution series of micro laser Raman spectrometer was used to test the samples. The laser wavelength was 532 nm and the scanning range was 100–1500 cm⁻¹.

Scanning electron microscopic (SEM) images of the samples were recorded on a Gemini Zeiss Supra 55 apparatus (operating at 10 kV). Element mapping spectra were acquired on the Gemini Zeiss Supra 55 apparatus (operating at 10 kV).

BET (Brunauer–Emmett–Teller, Micromeritics ASAP 2020 analyzer, Norcross, GA, USA) surface areas and pore-size distributions of the samples were determined via N₂ adsorption at –196 °C on a Micromeritics ASAP 2020 analyzer, with the samples being outgassed at 200 °C under vacuum for 8 h.

The thermogravimetric analysis (TGA) technique was used to measure weight losses of the samples. 10 mg of the Pt/CeMnO_x/diatomite, Pt/CeMnO_x or diatomite sample was heated in a N₂ flow of 100 mL min⁻¹ at a ramp of 10 °C min⁻¹ from 50 to 900 °C using the Setaram Labsys evo instrument (Setaram, Lyon, France).

The X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Fisher

Scientific, Waltham, MA, USA) was used to determine the Pt 4f, Mn 2p, Ce 3d, O 1s, S 2p, and C 1s binding energies (BEs) of the surface species with Mg $K\alpha$ ($h\nu = 1253.6$ eV) as the excitation source. The C 1s signal at BE = 284.6 eV was taken as reference for BE calibration.

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) equipped with a custom-made thermal conductivity detector (TCD). In each measurement, 50 mg of the sample was first pretreated in an O₂ flow of 30 mL min⁻¹ at 250 °C for 1 h and then cooled to RT for the removal of the adsorbed CO₂ and H₂O. The sample was then subjected to a 10 vol% H₂/Ar (balance) flow of 30 mL min⁻¹ and heated at a ramp of 10 °C min⁻¹ from RT to 900 °C. The alteration in H₂ concentration of the effluent was monitored online by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard powered CuO (Aldrich, 99.995 %) sample. The calculation formula of H₂ consumption is as follows:

$$\text{H}_2 \text{ consumption} = \frac{n_{\text{CuO}}}{S_{\text{CuO}}} \times \frac{S_{\text{cat}}}{m_{\text{cat}}} \times 1000$$

where n_{CuO} is the amount of hydrogen consumed by the CuO standard sample (mol), S_{CuO} and S_{cat} are the areas of hydrogen reduction peaks of the CuO standard sample and catalyst sample, respectively, and m_{cat} is the mass of the catalyst sample (g).

Oxygen temperature-programmed desorption (O₂-TPD) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) and a mass spectrometer (OmniStar GSD320). Prior to each test, 60 mg of the sample was preheated in an O₂ flow of 30 mL min⁻¹ at 250 °C for 1 h. After cooling to RT, a helium flow of 30 mL min⁻¹ was switched on to purge the left O₂ in the system for 1 h. After that, the samples were heated in a helium flow of 30 mL min⁻¹ from RT to 900 °C at a rate of 10 °C min⁻¹, and the O₂-TPD profiles were recorded in the meantime.

Temperature-programmed desorption of sulfur dioxide (SO₂-TPD) was carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before

measured, 0.06 g of the sample was pretreated in a 20 vol% O₂/He flow of 30 mL min⁻¹ at 250 °C for 1 h with a ramp of 10 °C min⁻¹. After the sample was cooled to 50 °C at the same atmosphere, the sample was purged in a He flow of 30 mL min⁻¹ for 30 min. Then the sample was treated in a 100 ppm SO₂/N₂ flow of 30 mL min⁻¹ for 3 h, and then the sample was flushed with a He flow of 30 mL min⁻¹ until the baseline was smooth. The system was heated up to 900 °C at a ramp of 10 °C min⁻¹ in the He atmosphere. The products were detected by the mass spectrometer.

(Ethyl acetate + toluene) temperature-programmed desorption (EA + toluene-TPD) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) and a mass spectrometer (OmniStar GSD320). Prior to each test, 60 mg of the sample was preheated in an O₂ flow of 30 mL min⁻¹ at 250 °C for 1 h. After cooling to RT, the He bubble was used to pulse the catalyst for 40 times until the adsorption saturation. After that, the He flow of 30 mL min⁻¹ was used to purge the VOCs mixtures in the system for 30 min. After the purge process was finished and the base line was stabled, we heated the sample in the He flow of 30 mL min⁻¹ from RT to 900 °C, and used a mass spectrometer to monitor the concentration changes of ethyl acetate ($m/z = 88$), toluene ($m/z = 91$), H₂O ($m/z = 18$), and CO₂ ($m/z = 44$).

In situ diffuse reflectance Fourier transform infrared spectroscopic (in situ DRIFTS) experiments of the samples were carried on a Bruker Tensor II spectrometer with a liquid nitrogen-cooling MCT detector (Bruker, Berlin, Germany). Before the in situ DRIFTS experiment, 30 mg of the sample was loaded on a high-temperature IR cell with ZnSe windows, and preheated in an O₂ flow of 30 mL min⁻¹ at 250 °C for 1 h. Subsequently, the sample was cooled to RT and purged with a N₂ flow of 30 mL min⁻¹ for 1 h, and then the background spectrum was recorded at different temperatures. Finally, a N₂ bubble method was used to bring the toluene and ethyl acetate into the reaction tank, and in situ DRIFTS spectra of the samples in the temperature range of 60–300 °C were recorded by accumulating 32 scans at a spectrum resolution of 4 cm⁻¹.

Catalytic evaluation procedures

Toluene and ethyl acetate oxidation performance was determined in a fixed-bed quartz tubular microreactor (i.d. = 6 mm). 50 mg of the catalyst (40–60 mesh) and 0.25 g of quartz sand (40–60 mesh) were well mixed to minimize the effect of hot spots. Before the test, each sample was pretreated in O₂ (20 mL min⁻¹) at 250 °C for 1 h. The measurement conditions were as follows: the gas mixture was 1000 ppm toluene + 1000 ppm ethyl acetate + 40 vol% O₂ + N₂ (balance), the total flow rate was 16.7 mL min⁻¹, and the space velocity (SV) was 20,000 mL g⁻¹ h⁻¹. Before the test, the sample was treated in O₂ (20 mL min⁻¹) at 250 °C for 1 h. When the SO₂ or H₂O was added, 25 ppm SO₂ and 5.0 vol% H₂O were introduced to the reaction system by a mass controller. 25 ppm SO₂ came from a gas cylinder, and the 5.0 vol% H₂O was provided by a water saturator at 34 °C. Reactants and products were online analyzed by gas chromatography (GC-2014C, Shimadzu), equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), using a stabilwax@-DA column (30 m in length) for VOC separation and a 1/8 in Carboxen 1000 column (3 m in length) for permanent gas separation. All of the measurements were carried out under the steady-state reaction conditions.

Two parameters ($T_{50\%}$ and $T_{90\%}$) were used to evaluate catalytic activities of the samples, which refer to the temperatures achieving 50 and 90 % conversions of toluene or ethyl acetate, respectively. The balance of carbon in the catalytic system was 99.5 ± 1.5 %. Toluene or ethyl acetate conversion was calculated according to the formula: $(C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}} \times 100$ %, where C_{inlet} and C_{outlet} are the inlet and outlet toluene or ethyl acetate concentrations, respectively.

Table S1. Comparison on catalytic activities for ethyl acetate and toluene oxidation of the Pt/CeMnO_x/diatomite sample prepared in the present work and various catalysts reported in the literature.

Catalyst	Reaction condition		Catalytic activity		Ref.
	VOC concentration (ppm)	Space velocity (mL g ⁻¹ h ⁻¹)	T _{50%} (°C)	T _{90%} (°C)	
	Formaldehyde (100)				
1 wt% Pt/TiO ₂	Acetaldehyde (100)	24,000	–	200	[13]
	Toluene (100)				
Mn _{14,1} /diatomite	Toluene (1000)	30,000	242	267	[52]
MnO _x -CeO ₂	Ethyl acetate (500)	60,000	188	205	[53]
0.3 wt% Pt/diatomite	Benzene (1000)	20,000	185	190	[54]
	Toluene (1500)		225	245	
Pd/ZSM-5	Ethyl acetate (1500)	26,000	203	220	[55]
	Toluene (1000)		230	300	
Fe/OMS-2	Ethyl acetate (1500)	24,000	190	222	[56]
	Toluene (1000)		310	360	
30MnO-50CeO ₂	Propane (1000)	20,000	430	510	[57]
	Toluene (500)		240	260	
Pd/Ce _{0,9} Cu _{0,1} O _{1,9} -Y ₂ O ₃	Ethyl acetate (500)	20,000	242	248	[58]
	Isopropanol (1360)			200-300	
Acidic zeolite (HY)	<i>o</i> -xylene (210)	18,000	–	250-300	[59]
	Ethyl acetate (1000)		182	210	This
0.32Pt/CeMnO _x /diatomite	Toluene (1000)	20,000	218	233	work

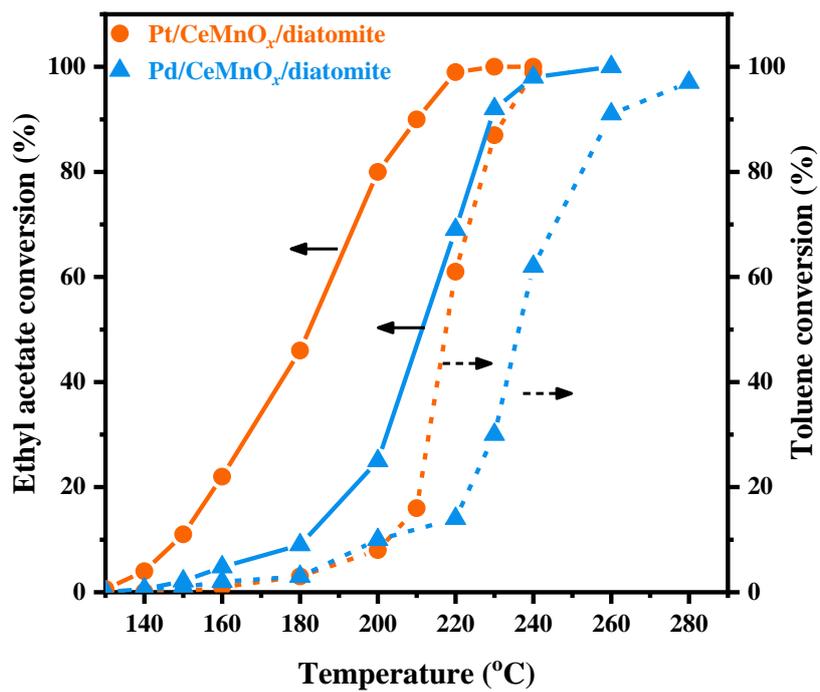


Figure S1. Ethyl acetate or toluene conversion as a function of reaction temperature over the Pd/CeMnO_x/diatomite and Pt/CeMnO_x/diatomite samples at SV = 20,000 mL g⁻¹ h⁻¹.

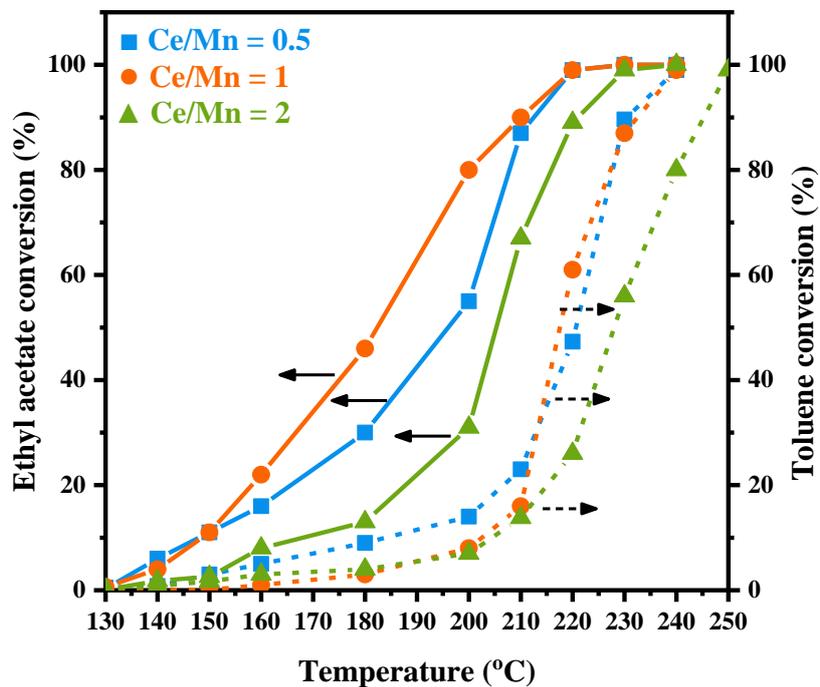


Figure S2. Ethyl acetate or toluene conversion as a function of reaction temperature over the Pt/CeMnO_x/diatomite samples with different Ce/Mn ratios at SV = 20,000 mL g⁻¹ h⁻¹.

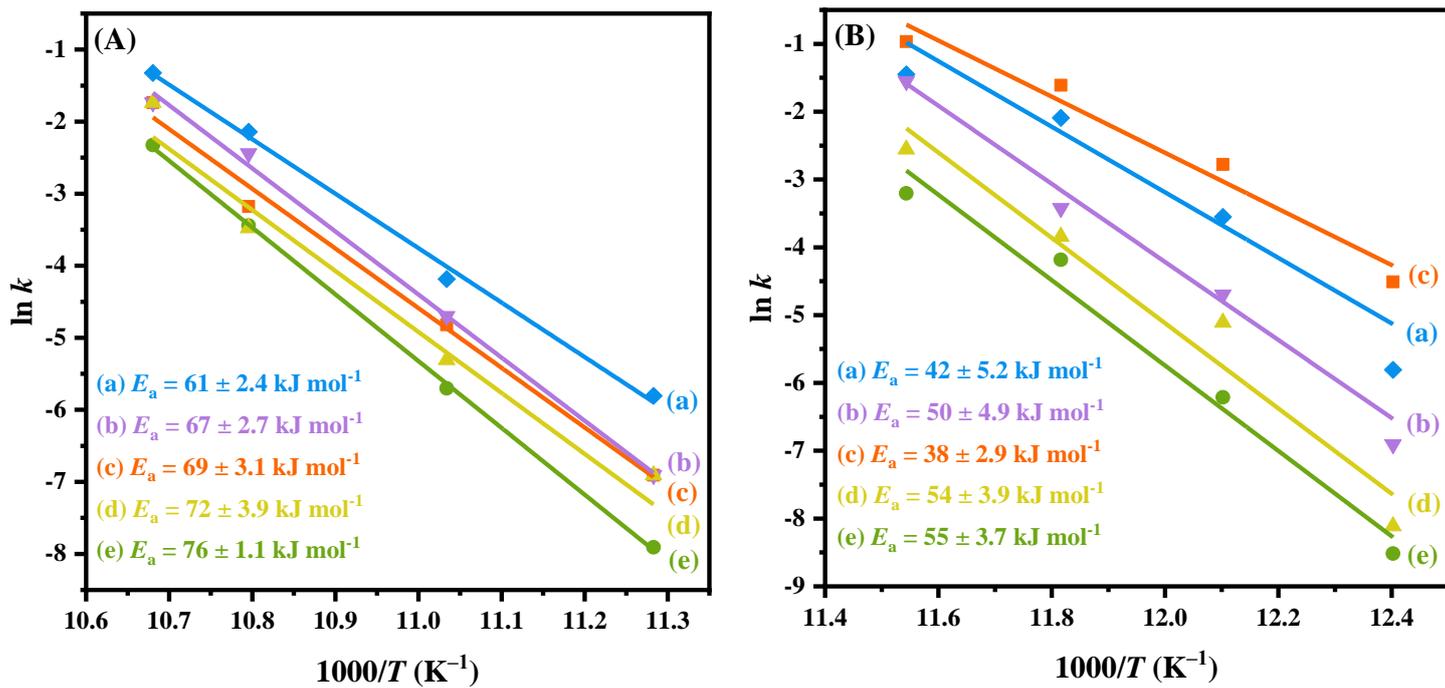


Figure S3. Ln k versus inverse temperature over (a) Pt/CeMnO_x, (b) Pt/CeMn₂O_x/diatomite, (c) Pt/CeMnO_x/diatomite, (d) Pt/CeMn_{0.5}O_x/diatomite and (e) Pd/CeMnO_x/diatomite for the oxidation of (A) toluene and (B) ethyl acetate at SV = 20,000 mL g⁻¹ h⁻¹.

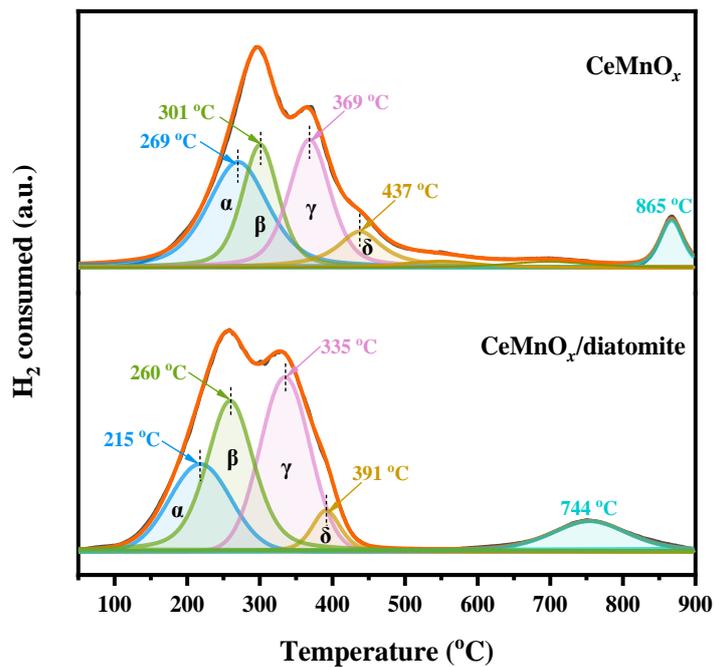


Figure S4. Deconvoluted reduction peaks in H₂-TPR profiles of the CeMnO_x and CeMnO_x/diatomite samples.

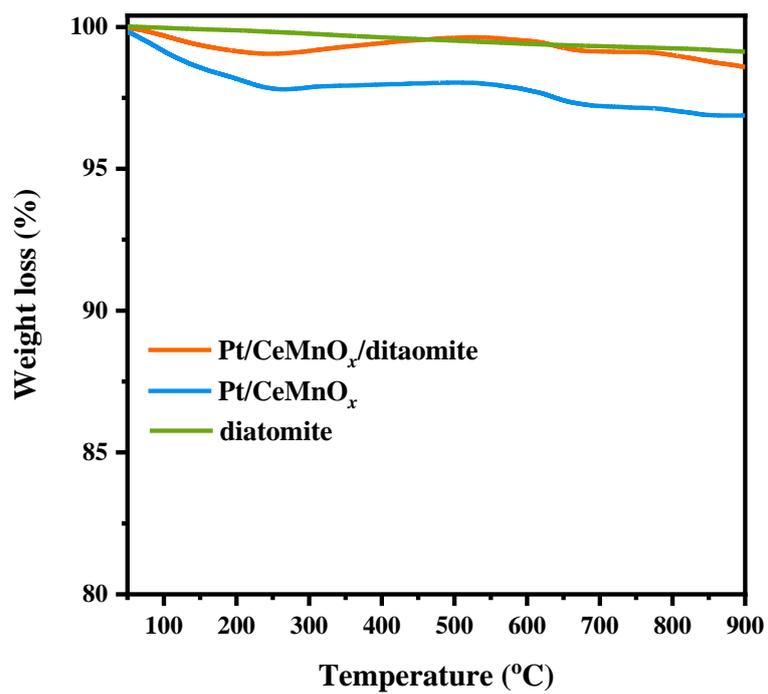


Figure S5. TGA profiles of the diatomite, Pt/CeMnO_x, and Pt/CeMnO_x/diatomite samples.

References

13. Lee, Y.J.; Vikrant, K.; Szulejko, J.E.; Kim, K.H.; Dong, F. Thermocatalytic oxidation of a three-component mixture of volatile organic compounds by a titanium dioxide-supported platinum catalyst. *J. Clean. Prod.* **2021**, *325*, 129279.
52. Liu, P.; He, P.; Wei, G.L.; Liu, D.; Liang, X.L.; Chen, T.H.; Zhu, J.X.; Zhu, R.L. An efficient catalyst of manganese supported on diatomite for toluene oxidation: Manganese species, catalytic performance, and structure activity relationship. *Microporous Mesoporous Mater.* **2017**, *239*, 101–110.
53. Jiang, Y.; Gao, J.; Zhang, Q.; Liu, Z.; Fu, M. Wu, J.; Hu, Y.; Ye, D. Enhanced oxygen vacancies to improve ethyl acetate oxidation over MnO_x-CeO₂ catalyst derived from MOF template. *Chem. Eng. J.* **2019**, *371*, 78–87.
54. Li, Q.; Zhai, Z.; Xu, Y.; Jia, L.S.; Huang, J.L.; Sun, D.H.; Li, Q.B. Diatomite supported Pt nanoparticles as efficient catalyst for benzene removal. *Ind. Eng. Chem. Res.* **2019**, *58*, 14008–14015.
55. He, C.; Li, P.; Cheng, J.; Hao, Z.P.; Xu, Z.P. A Comprehensive study of deep catalytic oxidation of benzene, toluene, ethyl acetate, and their mixtures over Pd/ZSM-5 catalyst: Mutual effects and kinetics. *Water Air Soil Pollut.* **2010**, *209*, 365–376.
56. Dong, N.; Chen, M.Y.; Ye, Q.; Zhang, D.; Dai, H.X. An investigation on catalytic performance and reaction mechanisms of Fe/OMS-2 for the oxidation of carbon monoxide, ethyl acetate, and toluene. *J. Environ. Sci.* **2022**, *112*, 258–268.
57. Saper, S.M.; Kondarides, D.I.; Verykios, X.E. Catalytic oxidation of toluene over binary mixtures of copper, manganese and cerium oxides supported on γ -Al₂O₃. *Appl. Catal. B* **2011**, *103*, 275–286.
58. Su, X.W.; Jin, L.Y.; Lu, Q.; Luo, M.F. Pd/Ce_{0.9}Cu_{0.1}O_{1.9}-Y₂O₃ catalysts for catalytic combustion of toluene and ethyl acetate. *J. Ind. Eng. Chem.* **2009**, *15*, 683–686.
59. Beauchet, R.; Magnoux, P.; Mijoin, J. Catalytic oxidation of volatile organic compounds (VOCs) mixture (isopropanol/*o*-xylene) on zeolite catalysts. *Catal.*

Today **2007**, 124, 118–123.