

Photocatalytic Oxidation of Methyl *tert*-Butyl Ether in Presence of Various Phase Compositions of TiO₂

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Supplementary materials

Characterization techniques

N₂ physisorption was realized in an automated volumetric apparatus 3Flex (Micromeritics Instruments, USA) after sample degassing at 150 °C for 24 h under less than 1 Pa vacuum. The adsorption-desorption isotherms of nitrogen were measured at -196 °C. The specific surface area (S_{BET}), was evaluated according to the classical Brunauer–Emmett–Teller (BET) theory for the p/p₀ range of 0.05–0.25.

Phase composition and microstructural properties were determined using X-ray powder diffraction (XRD) technique. XRD patterns were obtained using Rigaku SmartLab diffractometer (Rigaku, Japan) with detector D/teX Ultra 250. The source of X-ray irradiation was Co tube (CoKα, λ₁ = 0.178892 nm, λ₂ = 0.179278 nm) operated at 40 kV and 40 mA. Incident and diffracted beam optics were equipped with 5° Soller slits; incident slits were set up to irradiate area of the sample 10 x 10 mm (automatic divergence slits) constantly. Slits on the diffracted beam were set up to fixed value 8 and 14 mm. The powder samples were gently grinded using agate mortar before analysis and pressed using microscope glass in rotational sample holder and measured in the reflection mode (Bragg-Brentano geometry). The samples rotated (30 rpm) during the measurement to eliminate preferred orientation effect. The XRD patterns were collected in a 2θ range 5°–90° with a step size of 0.01° and speed 0.5 deg.min⁻¹. Measured XRD patterns were evaluated using PDXL 2 software (version 2.4.2.0) and compared with database PDF-2, release 2015.

UV–Vis diffuse reflectance spectra (DRS) were measured using a Shimadzu UV-2600 (IRS-2600Plus) spectrophotometer in the range of 220 to 1400 nm at laboratory temperature. Reflectance was re-calculated to absorbance using the Schuster-Kubelka-Munk's equation as follows (Eq. (2)):

$$F(R_{\infty}) = \frac{(1-R_{\infty})^{1/2}}{2R_{\infty}}(S1) \quad (1)$$

where R_{∞} is the diffuse reflectance from a semi-infinite layer. The obtained DRS spectra were transformed to the dependencies of $(F(R_{\infty}) \cdot h\nu)^{1/2}$ on $h\nu$ in order to obtain the values of energy of indirect absorption edges.

Total carbon was determined by phase carbon analyzer RC612 (Leco, USA) using temperature ramping method according to DIN19539 (2015) standard. The sample is introduced into oxygen atmosphere furnace and temperature ramp program is executed. Determination of carbon is based on simultaneous CO₂ and H₂O vapor detection in product gas during the gradual rise of temperature. Along the program, organic species produce CO₂ and H₂O simultaneously at low temperatures (up to ca 400 °C), elemental carbon produces CO₂ signal in medium range (up to ca 800 °C) and CO₂ detected high temperature steps (up to 1100 °C) is estimated result of thermal decomposition of inorganic carbonates.

Morphology of particles was observed on a transmission electron microscope (TEM) JEOL 2010 HC (JEOL Ltd., Japan) with LaB₆ electron gun. The accelerating voltage of 200 kV was applied and micrographs were taken by a camera Tengra (EMSIS). The samples were prepared by dispersion in ethanol and then sonicated for 5 min. One drop of this solution was placed on a copper grid with a holey carbon film and dried at room temperature.

Photocatalytic experiment with scavengers

The determination of “driving force” in the photocatalytic oxidation of MTBE was conducted in the same way as described in section “Photocatalytic degradation of MTBE” only with an addition of individual scavenger. All the scavenger tests were conducted in presence of commercial TiO₂ P25. The first test was focused on hydroxyl radicals’ species where 0.19 ml (50 mM) of isopropyl alcohol (IPA) was added to the suspension of MTBE with P25. The second test investigated influence of superoxide anion radical. In this case 0.016 ml (2.4 mM) of chloroform was added to the suspension [1]. Obtained conversions on MTBE without and with each scavenger are shown in Fig. S1.

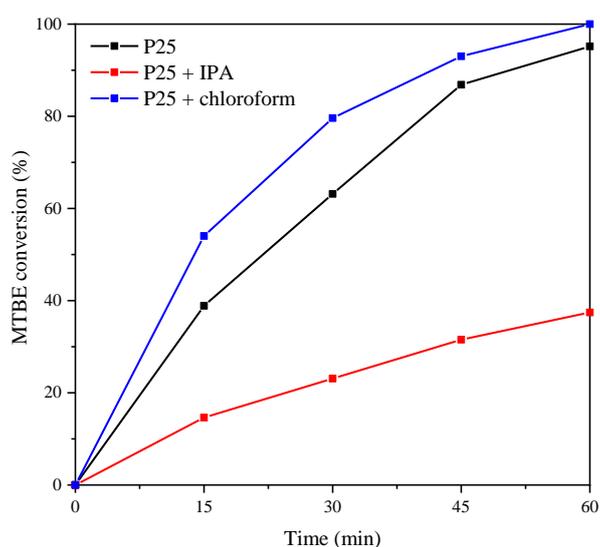


Figure S1. Dependence of MTBE conversion on time in presence of TiO₂ P25 without and with scavengers of OH• and O₂•⁻.

- 1 S. Hwang, S.G. Huling, S. Ko, Fenton-like degradation of MTBE: Effects of iron counter anion and radical scavengers, *Chemosphere*, **2010**, 78, 563–568.