

Catalytic activity of commercial oxides for the synthesis of corn biodiesel

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Abstract – This work aims to evaluate the catalytic activity of commercial oxides as CaO, ZnO, SnO₂ and TiO₂ as catalysts for the transesterification of corn oil. The initial result indicates that only the ground CaO is selective for such reaction, due to its relative basic strength. Conversely, the average conversions obtained with the other catalyst were rather reduced. Acknowledgements: The authors acknowledge the financial support of CNPq/MCT and FINEP/MCT

Biodiesel is often produced by transesterification reactions using homogeneous catalysts. However, such processes are strongly influenced by water traces, due to saponification reactions, requiring purification of the yield product [1]. Such limitation can be solved by using heterogeneous-based reactions, for its high selectivity and simple industrial control [2,3].

Therefore, this work aims to evaluate the catalytic activity of commercial oxides (CaO, ZnO, SnO₂ and TiO₂) on transesterification of corn oil to methyl-biodiesel. All samples were milled in an attritor mill with 700 rpm of speed for 2 and 4 h, in commercial ethanol media, using zirconia balls. Subsequently, the solids were dried and thermally activated at 850 °C for 4 h. The oxides were characterized by IR spectroscopy, termogravimetric analysis (TG) and X-ray diffractometry (XRD). Finally, each biodiesel was synthesized with a molar ratio of 1:9 (oil:methanol) and 1.5% (wt/wt) of oxide, at isothermal temperature of 65 °C for 4 h. The biodiesel conversion was evaluated by means of variations in the reagents cinematic viscosities.

According to the TG data, the commercial CaO partially reacted with air, leading to the formation of calcium hydroxide and calcium carbonate. Conversely, only hydration was observed for the other oxides. The CaO IR spectra showed $\nu(\text{C-O})$ bands at 1447, 1103 and 884 cm⁻¹ assigned to carbonate ions and at 3641 and 1627 cm⁻¹ $\nu(\text{O-H})$, due to superficial adsorbed water. For the ZnO, absorptions at 3417 and 439 cm⁻¹ were attributed to $\nu(\text{O-H})$ of adsorbed water and $\nu(\text{Zn-O})$, respectively. For the SnO₂, were detected absorptions at 3641, 3201 and 625 cm⁻¹ assigned to $\nu(\text{Sn-OH})$ and at about 2376 ascribed to $\nu(\text{C-O})$. TiO₂ presented absorption bands at 578 cm⁻¹ for $\nu(\text{Ti-O})$, 1087 cm⁻¹ $\nu(\text{O-H})$ and 1627 cm⁻¹ $\nu(\text{O-H})$ of adsorbed water. The methyl alcoholate formation (catalytic site) was confirmed by the $\nu(\text{C-H})$ absorption at 2920 (CaO), 2923 (ZnO) and 2924 cm⁻¹ (SnO₂), not being observed for TiO₂. The XRD patterns of the CaO (Fig. 1b) evidenced that the secondary phases (portlandite and calcite) were not eliminated by thermal treatment. It was also observed that ZnO (wurtzite) and SnO₂ (cassiterite) were single phase, while TiO₂ was composed of rutile and anatase. The kinematic viscosity of the CaO-based biodiesel indicated an appreciate conversion when CaO was applied as catalyst. The catalytic activity was credited to the Ca(CH₃O)₂ species present on the oxide surface. For ZnO, SnO₂ and TiO₂ oxides, meaningful conversions were not detected.

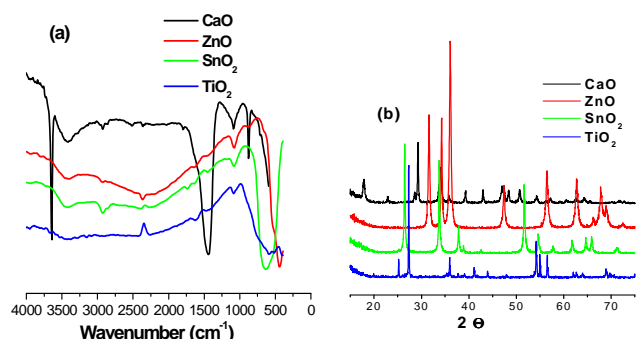


Figure 1: (a) IR spectra and (b) XRD patterns of the treated CaO, ZnO, SnO₂ and TiO₂.

Table 1: Kinematic viscosity for corn oil and its biodiesels.

Catalyst	Reaction time (h)	Kinematic viscosity (mm ² · s ⁻¹)
CaO	2	11.1 ± 0.4
	4	5.73 ± 0.7
ZnO	2	54.8 ± 0.3
	4	53.7 ± 0.9
SnO ₂	2	53.2 ± 0.3
	4	52.4 ± 1.0
TiO ₂	2	53.9 ± 0.4
	4	52.5 ± 0.9
Corn oil	-	58.7 ± 0.9

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