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Supporting Information

Studies on Mg-Ba mixed oxide catalyst for continuous glycerol transesterification to glycerol carbonate

Piyusa Priyadarsan Pattanaik,^{ab} Mallikarjun Geekuri,^{ab} Gunasekar Hariyanandam Gunniya,^{ab} and Lingaiah Nakka,^{*ab}

^aDepartment of Catalysis and Fine Chemicals, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India ^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

1 Experimental section

1.1 Catalyst characterization

The crystalline nature of the catalysts was analyzed by X-ray diffractometer with Nifiltered CuK@ source. The instrument was operated at tube current of 30 mA and tube voltage of 40 kV with step size of 0.0450° and step time of 0.7 s. The diffraction pattern of samples was recorded in the 2-theta range of 10-80°.

The surface area of the catalysts was determined by N_2 physisorption method using BELSORP II (BEL Japan. Inc.) instrument. About 0.2 g of the sample was pre-treated at 200 °C under a vacuum for 2 h to outgas the surface. Then, the adsorption-desorption isotherm was estimated using N_2 gas, and the surface area was calculated using the BET equation.

FT-IR analysis of samples was recorded on a DIGILAB Biorad spectrometer using KBr disc at a resolution of 1 cm⁻¹. Raman spectroscopy was recorded with Horiba Jobin– Yvon Lab Ram HR, using 633 nm He–Ne laser. The spectra were recorded by spreading about 10 mg of solid sample over a glass slide kept under microscope.

The distribution of basic sites and total basicity of the samples were evaluated by temperature-programmed desorption of CO_2 (TPD-CO₂) using BELCAT II Chemisorption (BEL Japan. Inc.) instrument. Approximately 0.1 g of the solid sample was suspended in quartz sample tube and pre-treated at 300°C for 60 min in an inert flow to remove impurities

over the catalyst surface. The sample was cooled to room temperature and then allowed to adsorb CO_2 at room temperature using mixture of 10% CO_2 in He gas. The surface physiosorbed CO_2 was removed by purging He gas. Then, the desorption of CO_2 was carried out by increasing the temperature up to 800 °C with a ramp rate of 10 °C/min and the amount of desorbed CO_2 was estimated.

XPS analysis was performed in AXIS Nova spectrometer. The quantitative parallel imaging of the catalysts was recorded with a 165 mm radius hemispherical analyzer and a spherical mirror analyser coupled with a Delay-line detector. The non-monochromatic Mg K α X-ray equipped with a dual anode of Mg and Al (1486.6 eV) used with a current voltage of 12.5 kV and 16 mA. Prior to analysis, the sample was degassed at 100 °C under vacuum (1 × 10⁻⁷ Torr) for 3 h for cleaning catalyst surface. The instrument was calibrated using Au as a standard and the energy of calibration was made by C(1s) photoelectron with the binding energy of 284.6 eV and the charge neutralization of 2 eV was balanced to charge up the sample.

1.2 Continuous transesterification of glycerol

The transesterification of glycerol with DMC was carried out in a continuous fixed bed down flow reactor at atmospheric pressure. In a typical experiment, 1 g of catalyst volume was diluted with an equal amount of quartz particles and suspended in the reactor at thermostatic zone by plugging quartz wool at both ends. Initially, the catalyst was activated under N₂ gas atmosphere at 450 °C for 1 h. Then, the temperature of the catalyst bed was brought to the desired reaction temperature (200–260 °C). The reactants glycerol and DMC were simultaneously passed into the reactor with the help of two syringe pumps under N₂ flow. The products coming out from the reactor were collected in a cold trap. The products were subjected to analysis using a gas chromatography (Shimadzu 2010 plus, Japan), equipped with a flame ionization detector and a capillary column (Innowax, diameter: 0.25 mm, length: 30 m). The calculation of yield and rate of glycerol conversion was estimated using the following equations.

Yield (%) =
$$\frac{\text{Conversion of Glycerol } \times \text{ Selectivity of Glycerol Carbonate}}{100}$$

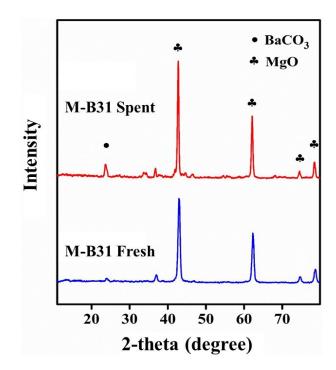


Fig. S1 Comparison of X-ray diffraction pattern of M-B31 spent catalysts after 100h of reaction.

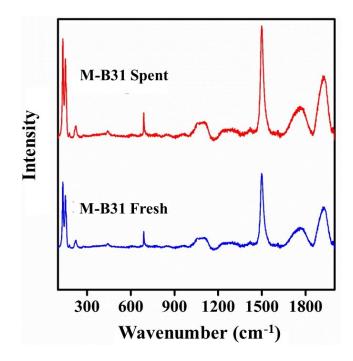


Fig. S2 Comparison of Raman spectra of M-B31 fresh and spent catalyst after 100 h of reaction.

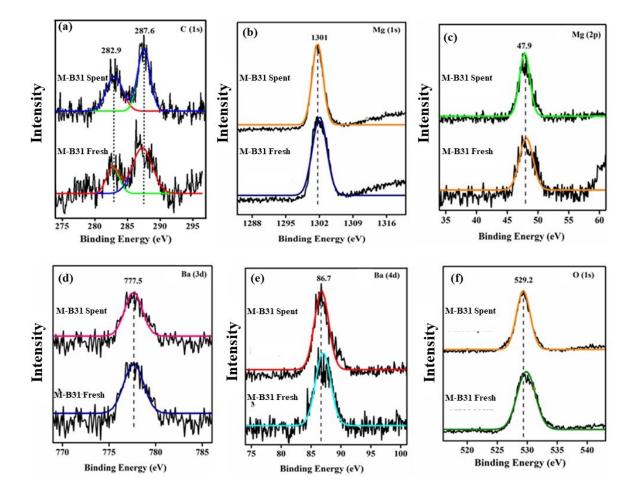


Fig. S3 (a) C(1s), (b) Mg(1s), (c) Mg(2p), (d) Ba(3d), (e) Ba(4d), and (f) O(1s) levels of XPS spectra of M-B31 fresh and spent catalyst after 100h of reaction.