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Catalytic Isomerization of Glucose to Fructose using Heterogeneous Solid Base Catalysts in a Continuous-Flow Tubular Reactor: Catalyst Screening Study

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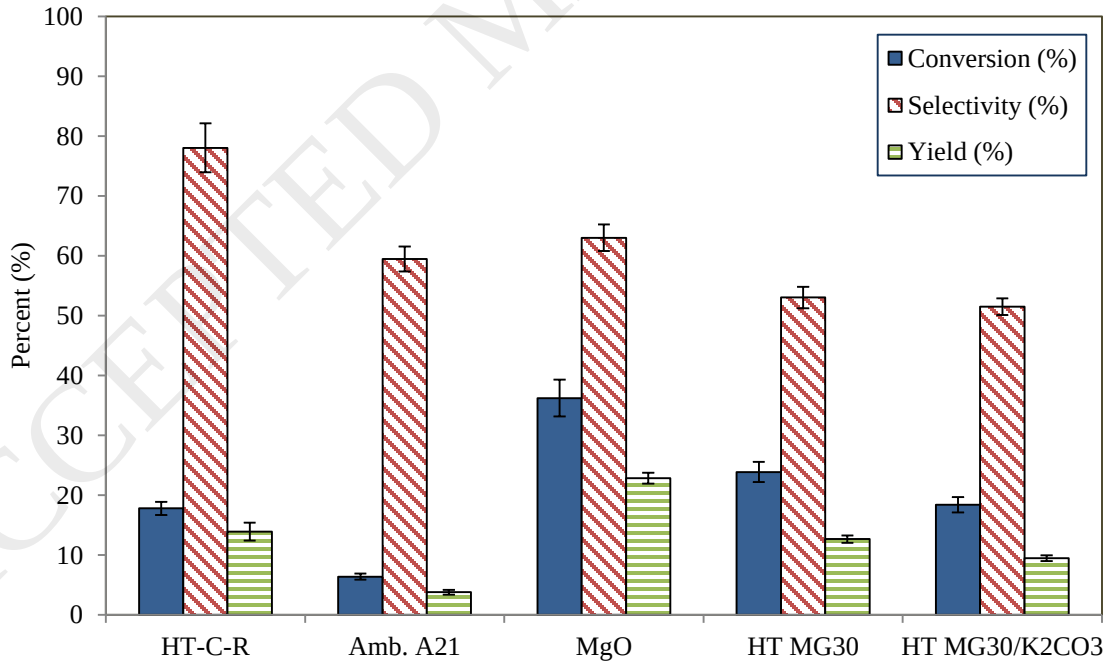
Graphical Abstract:



Activity of the solid base catalysts tested in glucose isomerization reaction at 100 °C

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Highlights:

- Glucose isomerization to fructose was performed in continuous-flow tubular reactor.
- Various heterogeneous solid base catalysts were characterized, tested and compared.
- MgO and HT-C-R catalysts proved to be effective for glucose isomerization reaction.
- Higher reaction temperature led to increased glucose conversion and fructose yield.
- Maximum fructose yield of 25.1% was obtained with MgO catalyst with good stability.

Abstract

Isomerization reactions of glucose into fructose in aqueous media were studied in a continuous-flow tubular reactor using different heterogeneous solid base catalysts, including calcined-rehydrated hydrotalcite, magnesium oxide, Amberlyst A21 ion exchange resin and two commercial hydrotalcite catalysts. The catalysts were characterized and their activities for glucose isomerization were compared. The most active catalyst was found to be magnesium oxide, which showed the highest glucose conversion (36.3%) and highest fructose yield (22.8%) at 100 ^{o}C. Among all catalysts, the calcined-rehydrated hydrotalcite showed the highest selectivity towards fructose, reaching 78% at 100 ^{o}C. It was also found that increasing the reaction temperature had positive effects on glucose conversion and fructose yield for both activated hydrotalcite and MgO catalysts. The fructose yield at 120 ^{o}C attained 19.5% and 25.1% with the activated hydrotalcite and MgO catalysts, respectively. The catalytic activity of

hydrotalcite calcined at 450 ºC for glucose isomerization reaction was found to be greater that calcined at 350 ºC. The hyrdotalcite and magnesium oxide catalysts were observed to be stable in the four hours of continuous tests on stream. TGA analyses of the used catalysts proved the formation of undesired insoluble by-products, mainly humins, on the surface of the used catalysts.

Keywords: Glucose; Isomerization; Fructose; Continuous-Flow Tubular Reactor; Heterogeneous Solid Base Catalysts

1. Introduction

Glucose is a simple sugar and the monomer unit of cellulose; it is likely to become one of the most important starting chemicals for bulk production of renewable biofuels and biomaterials [1,2]. Hot compressed water (HCW) has been considered as a low cost and environmentally benign reaction medium for glucose conversion. The primary reactions of glucose in hot compressed water can be classified as (1) isomerization of glucose to fructose, (2) dehydration of glucose to 1,6-anhydroglucose (AHG) and dehydration of fructose to 5-hydroxymethyl-2-furaldehyde (HMF), and (3) retro-aldol condensation of fructose to glycolaldehyde and dihydroxyacetone, etc. [3].

Catalytic conversion of glucose into fructose through isomerization as an intermediate step for the production of valuable furan derivatives and platform chemicals has attracted great interests [4,5]. As shown in Fig. 1, the isomerization of glucose to fructose is accompanied by a variety of by-products. As such, highly selective, efficient and inexpensive catalysts are essential to the control of undesirable reactions and to improving the reaction kinetics.

Since this reaction is thermodynamically equilibrium controlled and normally accompanied with variety of by-products, it is important to control the operating conditions such as temperature, reaction time and initial concentration of feedstock in

order to achieve a high degree of glucose conversion and to avoid the undesirable reactions. It has been reported that at a low temperature, the glucose isomerization reaction could be catalyzed by base catalysts [2,3]. Generally, heterogeneous or solid catalysts are more advantageous than homogenous ones due to their lower impact on the systems and global environment and their potential for recycling and reusability. They also facilitate large-scale industrial operations [3,6].

A number of researchers have studied the performances of metal oxides as heterogeneous catalysts for glucose isomerization reaction. Watanabe et al. studied the catalytic activities of ZrO_2 and TiO_2 (rutile and anatase) at 200 ^oC of reaction temperature and 5 min reaction time [1,3]. They also compared the performance of these metal oxides with homogeneous alkali and acid catalysts (NaOH and H_2SO_4 solutions). They reported enhanced glucose conversion rates in the presence of anatase TiO_2. The highest conversion was about 80% with anatase TiO_2. No considerable effect was observed for systems with NaOH and rutile TiO_2 and the fructose formation was inhibited by H_2SO_4 [1]. Cation-exchanged A, X, Y zeolites and hydrotalcites were studied by Moreau et al. at 95 ^oC for the isomerization of glucose to fructose [7]. Among the catalysts tested, Ca- and Ba-exchanged A, X and Y zeolites were found to be less selective, whereas those with a moderate basicity such as NaX and KX showed fructose selectivity of about 90%. However, high fructose selectivity was only obtained at glucose conversions lower than 25%. The hydrotalcite samples were found to be less selective than cation exchanged zeolites due to their relatively stronger basic properties.

The effects of operating conditions on glucose isomerization were also studied by other researchers. Souza et al. conducted experimental studies with NaOH as homogenous catalyst at 40-80 ^oC and 15 min reaction time [4]. They found that there was an optimum temperature for the fructose yield. Increasing temperature from 40 to 80 ^oC enhanced the glucose conversion followed by a continuous drop in fructose yield for temperatures above 50 ^oC. They also reported that glucose conversion increased with increasing reaction time from 0 to 60 min and that fructose yield was higher for short reaction times (10-15 min). They also tested other catalysts including ZrCs, which is a strong solid base, and some synthesized mesoporous ordered molecular sieves from the M41S family, and

found that the hybrid solid base catalysts were much more active than ZrCs for isomerization of glucose to fructose. The best result was obtained with [CTA] Si-MCM-50 at 100 °C and the reaction time of 2 hours, being 22% glucose conversion and 17% fructose yield. Investigation on the effects of reaction conditions was also performed by Yue et al., who studied isomerization of glucose to fructose at 100 °C and reaction times from 0 to 180 min with layered zirconosilicates as heterogeneous catalysts [8]. With the reaction time of 30 min, the glucose conversion was 60% with 26% fructose yield. Increasing the reaction time resulted in a slight increase in glucose conversion and little change in fructose yield.

So far, almost all of the catalytic glucose isomerization reactions have been performed in batch reactors and little attention has been paid to continuous-flow reactors, which are more desirable for large industrial scale and commercial production. To the best of our knowledge, no work has been reported on isomerization of glucose into fructose with those catalysts in a continuous-flow tubular reactor. Actually, a continuous reactor system also allows the researcher to change the reaction time by varying the feeding flow rate and/or catalyst loading. Then, the effects of these factors on the product properties can be investigated.

In the present work, isomerization of glucose to fructose in a custom-designed continuous-flow tubular reactor was investigated. Catalyst characterizations were first performed followed by catalyst screening study to compare the activities of different heterogeneous solid base catalysts including magnesium oxide (MgO), calcined-rehydrated hydrotalcite (HT-C-R), Amberlyst A21 (Amb. A21), and two commercial hydrotalcite catalysts (HT MG30 and HT MG30/K_2CO_3). Then the effects of reaction temperature on the activity of hyrdotalcite and magnesium oxide catalysts as well as the effects of calcination temperature on the catalytic activity of hydrotalcite were studied.

2. Experimental

2.1. Materials

D-(+)-glucose (>99.5%), synthetic hydrotalcite (i.e., magnesium aluminum hydroxyl carbonate, $Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$, Mg/Al molar ratio of 3:1), magnesium oxide

(beads -30 mesh) and Amberlyst A21 were purchased from Sigma-Aldrich. PURAL MG30 (HT MG30) and PURAL MG30 with K_2CO_3 (HT MG30/K_2CO_3) 5×5 cylindrical tablets (MgO/Al_2O_3 ratio of 30/70) were provided by SASOL Germany GmbH. HPLC grade water for preparing the mobile phase for HPLC analyses was obtained from EMD Millipore Milli-Q water system with a resistivity of 18.2 MΩ.cm.

2.2. Catalyst Preparation

Synthetic hydrotalcite (HT) was first calcined at 450 ^oC in a muffle furnace with the heating rate of 10 ^oC/min for 10 hours (HT-C) and then cooled inside a desiccator followed by rehydration with deionized water to form a soft paste. The paste was dried overnight in an oven at 80 ^oC and then crushed by a mortar and pestle. After sieving, particles between 300-840 μm (Mesh No.50 to Mesh No. 20) were collected as activated solid catalyst (HT-C-R) to be used in the experiments. MgO, HT MG30 and HT MG30/K_2CO_3 were crushed using a Wiley Mill, and particles with the same sizes as HT-C-R were collected as solid catalyst. Amberlyst A21 beads was used as received.

2.3. Continuous-Flow Reactor Setup and Experimental Procedure

The schematic diagram of the lab scale continuous-flow tubular reactor is presented in Fig. 2. It was designed and constructed in-house for testing different heterogeneous solid catalysts as a fixed bed within the tubular reactor for isomerization of glucose to fructose in an aqueous media.

The experimental setup consists of a vertical tubular reactor (SS-316 3/8” tube - 40 cm long) located within an electric cylindrical heater (Omega CRFC Series). The temperature of the flowing media inside the reactor is adjusted and controlled using a PID temperature controller (Omega CSC32) connected to the heater (output) and a thermocouple (input) placed at upstream of the reaction zone (below the catalyst bed) inside the tubular reactor. To achieve a uniform temperature profile inside the reactor, a specialized pre-heating feature was devised and applied using a helical SS-316 1/16” tube along the tubular reactor inside the heater to pre-heat the flowing media before entering the tubular reactor from the bottom.

In a typical test, a certain amount of heterogeneous solid catalyst is preloaded inside the tubular reactor between two quartz wool plugs at the middle of the reactor/heater (reaction zone). An HPLC feeding pump (Scientific Systems Inc. - Mighty Mini Pump) provides adjustable upward flow of aqueous feedstock solution, which is a mixture of pure glucose in deionized water, through the tubular reactor. The temperature of the flowing media after passing the catalyst bed is also monitored using another thermocouple (Omega 1/16" K-Type) located at downstream of the reaction zone (above the catalyst bed) inside the tubular reactor and connected to a digital thermometer. The pressure of the flowing media inside the reactor is adjusted and controlled using a back-pressure regulator valve (Swagelok KBP Series) located on the exit line and the pressure of the system is monitored on a pressure gauge. The aqueous feedstock solution is pumped into the reactor at a specific flow rate. When the reactor is filled up with the feedstock solution, the pressure inside the reactor is increased to the desired pressure (typically 10 bars). This pressure avoids boiling of the water at the reaction temperatures above 100 ^{o}C and the formation of vapor bubbles within the reactor system. The reactor is then heated up to the desired temperature. After it reaches a stable temperature at the set-point and the steady state condition was achieved (depending on the feeding flow rate), liquid samples were taken every hour for analysis.

The relationship between feedstock concentration, feeding flow rate and catalyst loading in heterogeneous catalytic continues-flow reactions are described by weight hourly space velocity (WHSV), which is an indicator of the reactant retention/residence time within the catalytic bed and defined as follows:

$$WHSV\ (h^{-1}) = \frac{Feed\ Concentration \times Feeding\ Flowrate}{Mass\ of\ Catalyst} \quad (1)$$

2.4. Product Analyses

The product samples collected from the experiments were analyzed using an HPLC (Waters 2690 Separation Module) equipped with an RI detector (Waters 410 Differential Refractometer) with internal detector temperature of 50 ^{o}C to determine the amount of product (fructose) produced and the amount of feedstock (glucose) consumed. Agilent Hi-Plex Pb column (9 μm, 7.7×300 mm) maintained at 60 ^{o}C was used and the mobile

phase was 100% Milli-Q HPLC grade water at a flow rate of 0.6 ml/min. The results for all experiments were analyzed by external calibration curves generated for glucose and fructose separately using standard solutions of glucose and fructose with known concentrations. The results are reported in terms of conversion, selectivity and yield, which are defined and calculated as follows:

$$\text{Glucose Conversion (\%)} = \frac{\text{Moles of glucose converted}}{\text{Initial moles of glucose}} \times 100\%$$

$$= \frac{[(C^F_{Glu} \times Q) - (C^P_{Glu} \times Q)]/M_{Glu}}{(C^F_{Glu} \times Q)/M_{Glu}} \times 100\% = \frac{C^F_{Glu} - C^P_{Glu}}{C^F_{Glu}} \times 100\% \quad (2)$$

$$\text{Fructose Selectivity (\%)} = \frac{\text{Moles of fructose produced}}{\text{Moles of glucose converted}} \times 100\%$$

$$= \frac{(C^P_{Fru} \times Q)/M_{Fru}}{[(C^F_{Glu} \times Q) - (C^P_{Glu} \times Q)]/M_{Glu}} \times 100\% = \frac{C^P_{Fru}}{C^F_{Glu} - C^P_{Glu}} \times 100\% \quad (3)$$

$$\text{Fructose Yield (\%)} = \frac{\text{Moles of fructose produced}}{\text{Initial moles of glucose}} \times 100\%$$

$$= \frac{(C^P_{Fru} \times Q)/M_{Fru}}{(C^F_{Glu} \times Q)/M_{Glu}} \times 100\% = \frac{C^P_{Fru}}{C^F_{Glu}} \times 100\% \quad (4)$$

where,

C^F_{Glu} is mass concentration of glucose in the feedstock solution (mg/ml),

C^P_{Glu} is mass concentration of glucose in the product sample (mg/ml),

C^P_{Fru} is mass concentration of fructose in the product sample (mg/ml),

Q is volumetric flow rate of the feedstock solution (ml/min),

M_{Glu} is molar mass of glucose (=180.16 g/mol),

M_{Fru} is molar mass of fructose (=180.16 g/mol).

2.5. Catalyst Characterization Methods

Catalyst samples were characterized by thermal gravimetric analysis (TGA) for thermal stability of the catalyst structure, X-ray diffraction (XRD) for crystalline phases and structure of the catalyst, N_2 physisorption for Brunauer-Emmett-Teller (BET) surface

area and pore size distribution (PSD) of the catalyst surface, and Fourier transform infrared (FT-IR) spectrometry for functional groups of the catalyst.

XRD measurements of the fresh catalyst samples were conducted on a PANalytical X'Pert Pro diffractometer using Cu-Kα radiation.

BET/PSD measurements of the fresh catalyst samples were performed on a Micrometrics Tristar II 3020 series instrument. The samples were initially degassed under nitrogen flow for 8 hours at 90 ^{o}C.

TGA of the fresh catalyst samples were conducted using a PerkinElmer Pyris 1 TGA in a nitrogen atmosphere. The samples were heated in a nitrogen flow at 20 ml/min from 40 ^{o}C to 100 ^{o}C at 10 ^{o}C/min and then kept at 100 ^{o}C for 10 min to remove the adsorbed moisture and volatile compounds. Then they were heated up to 700-800 ^{o}C at heating rate of 10 ^{o}C/min while the change in the sample weight by temperature was recorded. For the used catalysts, oxygen flow was used to burn the insoluble organic by-products deposited on the surface of the catalysts. Derivative thermal gravimetric (DTG) graphs were obtained from first derivative of TGA results with respect to time or temperature.

FT-IR spectrometry analyses of the fresh catalyst samples were performed on a PerkinElmer FT-IR spectrometer and the spectra were recorded in the region of 4000-550 cm^{-1}.

3. Results and Discussion

3.1. Characterization of Fresh Catalysts

The XRD patterns of the catalysts are presented in Fig. 3. Hydrotalcites are double layered hydroxides composed of MgO and $MgAl_2O_4$ and the patterns for HT-C-R, HT MG30 and HT MG30/K_2CO_3 clearly confirms the layered structure, which is consistent with the previous hydrotalcite characterization studies [9–11]. The peaks observed at 2θ = 11.6^{o}, 23.3^{o}, 34.7^{o} correspond to the basal (003), (006) and (009) planes, respectively. The difference between the intensities of the reflections from one sample to another indicates different degrees of crystallinity and structure when the cationic composition or

Mg/Al ratio varies [12]. The Mg/Al molar ratio of HT-C-R (3:1) is much greater than that of HT MG30 and HT MG30/K_2CO_3 (1:2), which results in higher intensities for the peaks and different basicity. The basal peaks for HT-C-R are narrower in width and higher in intensity compared to the commercial HT MG30 and HT MG30/K_2CO_3. Since the crystal size is inversely proportional to the half band width according to Scherrer's equation [13], it indicates that the HT-C-R has more uniform crystals and larger crystal size. The peaks observed at $2\theta = 39.1^o$, 46.4^o, 60.6^o and 62.1^o correspond to the non-basal (015), (018), (110) and (113) planes, respectively. Magnesium oxide showed peaks at $2\theta = 37.1^o$, 42.9^o, 62.4^o, 74.7^o and 78.7^o, which correspond to (111), (200), (220), (311) and (222) planes, respectively. The patterns are compatible with those reported in literature [14,15]. No major peaks were observed for Amberlyst A21 catalyst, indicating that this catalyst is amorphous and does not have a crystalline structure.

The textural properties of the catalysts obtained from BET/PSD analyses are summarized in Table 1. The two commercial HT MG30 and HT MG30/K_2CO_3 exhibited the largest surface areas and total pore volumes compared to the other catalysts tested. The surface area of HT-C-R (19 m^2/g) was much lower compared to the two commercial hydrotalcites; however, it had larger average pores diameter. MgO was found to have the smallest BET surface area of 0.22 m^2/g and total pore volume of 0.0004 cm^3/g, suggesting a nonporous structure.

TGA results for the fresh catalysts are presented in Fig. 4. According to TGA graphs the total weight losses for HT-C-R, HT MG30 and HT MG30/K_2CO_3 are 38.5%, 19.7% and 28.4%, respectively. All three hydrotalcite catalysts showed two stages of weight loss with sharper and more distinct curves for HT-C-R than others. The percentage of the first and second weight losses for each catalyst is reported in Table 2. The first weight loss for hydrotalcite catalysts occurred between 100 and 250 ^oC corresponding to the loss of interlayer water molecules and the second took place after 250 ^oC, which is attributed to the simultaneous removal of condensed water molecules and loss of carbonate anions via the formation of carbon dioxide from the brucite layer [10,16,17]. This is also confirmed by DTG graphs of the hydrotalcite catalysts (Fig. 5a-c). The maximum weight loss rates for HT-C-R were greater and they occurred at higher temperatures (213 and 390 ^oC)

compared to other commercial hydrotalcite catalysts. The Amberlyst catalyst exhibited a great weight loss (88%) after 300 ^{o}C. This indicates that this catalyst is mostly composed of organic compounds, which are decomposed with increasing temperature. The maximum weight loss rate for this catalyst was at 407 ^{o}C (Fig. 5d).

The structure of the studied catalysts was also characterized by FT-IR analysis and is presented in Fig. 6. Hydrotalcite catalysts showed a broad absorption at around 3460 cm^{-1}, which is attributed to the O-H stretching vibration of the interlayer water molecules and hydroxyl groups in hydroxide layer of the catalyst. The intensity of this peak is stronger for HT-C-R than HT MG30 and HT MG30/K_2CO_3 indicating the presence of more water and hydroxyl groups in the hydroxide layer of this catalyst. The weak absorption at 1550-1630 cm^{-1} is attributed to the bending vibration of water molecules in the interlayer. The sharp peak at 1370 cm^{-1} indicates the stretching vibration of carbonate anions. The FT-IR spectra for Amberlyst A21 showed different peaks indicating the presence of a large number of functional groups in its structure. The peaks observed at around 2930 cm^{-1} were attributed to the stretching vibration of C-H (alkane) and the pair of the bands at and 2770 cm^{-1} and 2810 cm^{-1} are attributed to the stretching vibration of aldehyde C-H. The two peaks at 1450 cm^{-1} and 1369 cm^{-1} could be attributed to the bending vibration of methylene and methyl groups. The bands located between 1000 cm^{-1} and 1310 cm^{-1} are attributed to the stretching vibration of C-N. They could also represent the stretching vibration of C-O and the possible presence of esters and anhydrides. The lack of the band related to the stretching vibration of N-H in the region from 3500 to 3200 cm^{-1} suggests that Amberlyst A21 contains tertiary amine functional groups. The vibrations at 860 cm^{-1} and 800 cm^{-1} represent the bending vibration of CH out-of-plane. No major peaks in FT-IR spectra for magnesium oxide were detected and therefore no graph is presented for this catalyst.

3.2. Catalytic Isomerization of Glucose to Fructose

3.2.1. Performance of Different Solid Base Catalysts

The results for the effects of different catalysts on glucose isomerization are presented in Fig. 7. These samples were taken two hours after reaching steady state condition. All of

the experiments were performed at 100 ^{o}C with initial glucose concentration of 100 mg/ml, feeding flow rate of 0.5 ml/min and 4 g catalyst loading (WHSV = 0.75 hr^{-1}) and no detectable soluble by-product was found in HPLC analysis.

Comparison of the results in Fig. 7 shows that MgO had the highest glucose conversion (36.3%) and fructose yield (22.8%), while the highest fructose selectivity (78.1%) was obtained by HT-C-R catalyst. The conversion, selectivity and yield in the presence of MgO catalyst and fructose selectivity and yield in the presence of HT-C-R catalyst were even higher than those of commercial catalysts (HT MG30 and HT MG30/K_2CO_3). The obtained fructose yields follow the trend of MgO > HT-C-R > HT MG30 > HT MG30/K_2CO_3 > Amb A21. Amberlyst A21 with the lowest glucose conversion of 6.4% and fructose yield of 3.8% was found to be the least effective base catalyst for glucose isomerization reaction. The lowest activity of Amberlyst A21 for glucose isomerization might be due to lower amount and strength of basic sites. Furthermore, this catalyst is an ion exchange polystyrene resin whose catalytic activity depends on its swelling property in the solvent and the pH. At neutral pH, adsorption of Amb. A21 is characterized with non-ionic interactions with lower adsorption capacity, which would lead to its low activity for glucose isomerization [19].

These results indicate that the BET surface area may not be a key indicator of the catalyst performance in glucose isomerization reaction. According to BET results (Table 1), MgO had the lowest BET surface area while it was the most active catalyst for this reaction in terms of glucose conversion and fructose yield. In addition, despite the large BET surface area of the commercial hydrotalcite catalysts, they did not show a superior activity in isomerization reaction. The activity of a catalyst is mostly determined by the type of the material which might tune the features of the accessible basic sites (number and strength) [4]. The high activity of MgO in glucose isomerization reaction could be due to the unique characteristics of the strong base sites on the surface of this catalyst [18]. However, the fructose selectivity of this catalyst is still lower than that of activated hydrotalcite (HT-C-R). High fructose selectivity in the presence of HT-C-R catalyst could be attributed to the formation of abundant and selective surface base sites during the rehydration process [11]. Therefore, MgO and HT-C-R were identified as the

catalysts with highest conversion and selectivity for glucose isomerization, respectively and selected for further investigations.

3.2.2. Effects of Reaction Temperature

Fig. 8 shows the activities of MgO and HT-C-R catalysts at different reaction temperatures. For both catalysts, glucose conversion and fructose yield improved with increasing reaction temperature while the fructose selectivity dropped. Conversion and selectivity were found to be more sensitive to the reaction temperature for MgO catalyst. The fructose selectivity for HT-C-R remained almost constant with a slight increase from 72.3% at 80 ^{o}C to 78.1% at 100 ^{o}C. The decrease in selectivity and darkening of the product solution indicates the formation of undesired organic by-products (mainly humins) as a result of self-polymerization and condensation of glucose and fructose by increasing temperature. [8] Therefore, it could be concluded that even at higher temperatures less undesirable products were formed when HT-C-R was used as a catalyst compared to MgO.

Fructose yield was enhanced for both catalysts as a result of temperature rise to 120 ^{o}C and reached the maxima of 19.5% and 25.1% for HT-C-R and MgO, respectively. This is a considerable fructose yield in a continuous-flow reactor using heterogeneous catalyst when compared with other reported catalytic isomerization of glucose in batch reactors or homogeneous catalysts. 25% fructose yield is equivalent to around 60% of the thermodynamic yield achieved in the enzymatic isomerization reaction after long reaction times as glucose isomerization into fructose is an equilibrium controlled reaction and maximum attainable degree of glucose conversion is governed by the thermodynamic equilibrium [4]. Further increase in temperature to 140 ^{o}C for HT-C-R resulted in an increased glucose conversion to 41.9% (compared to 28.2% at 120 ^{o}C), but the corresponding fructose selectivity dropped to 47.6% (compared to 68.9% at 120 ^{o}C). However, increasing temperature from 120 to 140 ^{o}C did not change the fructose yield significantly. As such, 80-120 ^{o}C appeared to be a good range of reaction temperature for fructose production using HT-C-R catalyst because of the higher selectivity.

3.2.3. Effects of Calcination Temperature on Hydrotalcite Catalytic Activity

As HT-C-R catalyst showed more than 70% fructose selectivity in the experiments, the possibility of enhancing its catalytic activity for glucose isomerization reaction was then evaluated by quantifying the effects of calcination temperature on its activity. Calcination temperature of hydrotalcite is known to affect the catalytic activity of this catalyst as it effectively destroys the hydrotalcite structure [9,20]. Hydrotalcites are usually calcined at temperatures between 300-500 ^{o}C [9]. As a comparative study herein, hydrotalcite was activated at two different temperatures, 350 ^{o}C and 450 ^{o}C, followed by rehydration. It was then used in the continuous-flow reactor at the reaction temperature of 110 ^{o}C for isomerization of glucose to fructose. The results are shown in Fig. 9.

Slightly higher activity for the HT-C-R catalyst in terms of glucose conversion and fructose selectivity and yield was observed for the higher calcination temperature of 450 ^{o}C. This could be attributed to the change in basicity of hydrotalcite as a result of the activation at higher temperature. Hydrotalcites are reported to have the maximum basicity when calcined at temperatures between 400 and 600 ^{o}C and the increase in basicity could be expected to correlate with an improvement in the catalyst activity [10].

3.2.4. Stability of the Catalysts with Time

Fig. 10 shows the activities of MgO and HT-C-R catalysts at 120 ^{o}C that was monitored for 4 hours continuously on stream. They are the indicators of catalyst stability. Little drop in conversion was observed for both catalysts, and fructose yield remained almost constant while selectivity was improved over time. All these results indicate that HT-C-R and MgO were stable during 4-hour continuous experiments for glucose isomerization reaction in the continuous-flow reactor. The slight decrease in conversion could be attributed to the deposition and accumulation of the insoluble organic materials as the condensation by-products (mainly humins) on the surface of the catalyst particles, which consequently resulted in deactivation of the catalysts.

3.3. Characterization of Used Catalysts

Fig. 11 shows the TGA and DTG graphs for fresh and used MgO and HT-C-R catalysts in the experiments at 120 ^{o}C after 4 hours of continuous time on stream. These results

allow us to study the catalyst deactivation mechanism. All used catalysts were dark brown, likely due to deposition of insoluble organic by-products (mainly humins) with high molecular weights [8], as evidenced in Figs. 11a and 11b. There was a weight loss of 15.5% compared to no weight loss for the fresh catalyst. The deposited insoluble organic by-products were burned in the air between 300 to 400 ^{o}C and resulted in a sharp peak in DTG curve at 380 ^{o}C. According to Figs. 11c and 11d, both fresh and used HT-C-R catalysts showed the same two stages of weight loss. It suggests that this catalyst retains its double layered structure after being used at 120 ^{o}C continuously for 4 hours. The used HT-C-R catalyst showed 43.5% weight loss compared to 38.5% for fresh catalyst. The increased weight loss (5%) is resulted from the deposition of insoluble organic by-products on the surface of the catalyst. Comparing the difference between the weight losses of the used and fresh MgO (15.5%) with that of the used and fresh HT-C-R (5%) shows that in the presence of MgO more insoluble organic by-products were produced compared to HT-C-R in the same operating conditions. This result is in agreement with lower selectivity of MgO compared to HT-C-R in glucose isomerization reaction, which was already discussed.

4. Conclusions

The present work compared the performance of calcined and rehydrated hydrotalcite, magnesium oxide, Amberlyst A21, PURAL MG30 and PURAL MG30/K_2CO_3 commercial hydrotalcites for isomerization of glucose into fructose in a continuous-flow tubular reactor, and obtained the following conclusions.

1) Despite the large BET surface area of the commercial hydrotalcite catalysts, they did not show a superior activity in glucose isomerization reaction. Thus BET surface area could not be considered as a key indicator of the catalyst activity for the glucose-to-fructose isomerization reaction. MgO was the most active catalyst for the reaction with the glucose conversion of 62.7% and the fructose yield of 25.1% at 120 ^{o}C. Whereas, the highest fructose selectivity (78.1%) was obtained with HT-C-R catalyst at 100 ^{o}C.

2) Increasing the reaction temperature from 80 ^{o}C to 120 ^{o}C led to increased glucose conversion and fructose yield in the presence of MgO and HT-C-R catalysts. However,

the selectivity of these catalysts decreased by increasing temperature, and the drop in selectivity was greater for MgO compared to HT-C-R. Both these catalysts demonstrated good stabilities in the continuous-flow reactor.

3) TGA analyses of the used MgO and HT-C-R catalyst showed obvious deposition of insoluble organic by-products (mainly humans) on the surface of the catalyst particles, and the insoluble organic by-products deposition was severer on the used MgO than that on the used HT-C-R. This result is in agreement with lower selectivity of MgO compared to HT-C-R for glucose isomerization.

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Figures' Captions:

Figure 1. Reaction pathway for isomerization of glucose to fructose and by-products (modified from Ref. [3])

Figure 2. Schematic diagram of the continuous-flow tubular reactor system

Figure 3. XRD patterns of the catalysts

Figure 4. TGA graphs for hydrotalcites (a), Amb. A21 and MgO (b)

Figure 5. DTG graphs for HT-C-R (a), HT MG30 (b), HT MG30/K_2CO_3 (c) and Amb. A21 (d)

Figure 6. FT-IR spectra of the catalysts

Figure 7. Activity of solid base catalysts tested in glucose isomerization reaction at 100 ^oC (initial glucose concentration of 100 mg/ml, feeding flow rate of 0.5 ml/min)

Figure 8. Effects of reaction temperature on the activity of HT-C-R (closed symbols) and MgO (open symbols) catalysts in glucose isomerization reaction (initial glucose concentration of 100 mg/ml, feeding flow rate of 0.5 ml/min)

Figure 9. Effects of calcination temperature on the activity of HT-C-R catalyst in glucose isomerization reaction at 110 ^oC (initial glucose concentration of 100 mg/ml, feeding flow rate of 0.5 ml/min)

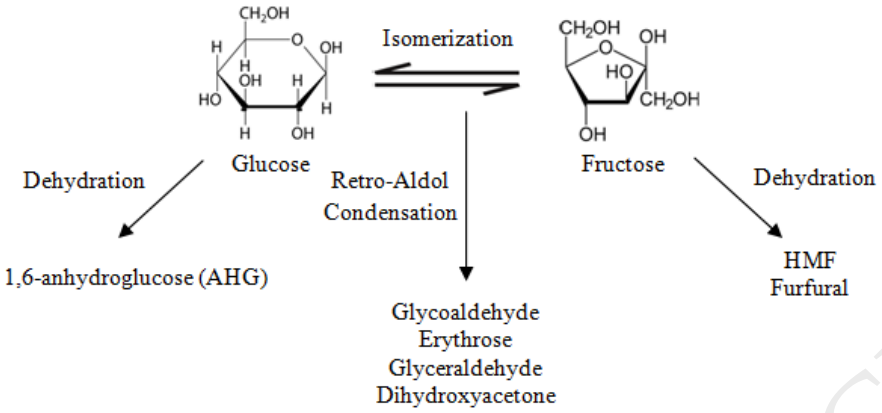
Figure 10. Effects of continuous time on stream on HT-C-R (closed symbols) and MgO (open symbols) activities in glucose isomerization reaction at 120 ^oC (initial glucose concentration of 100 mg/ml, feeding flow rate of 0.5 ml/min)

Figure 11. TGA and DTG graphs for the used MgO (a and b) and used HT-C-R (c and d) after experiments at 120 ^oC in comparison with the fresh catalysts

Tables' Captions:

Table 1. Textural properties of the catalysts

Table 2. TGA weight losses data for the fresh catalysts



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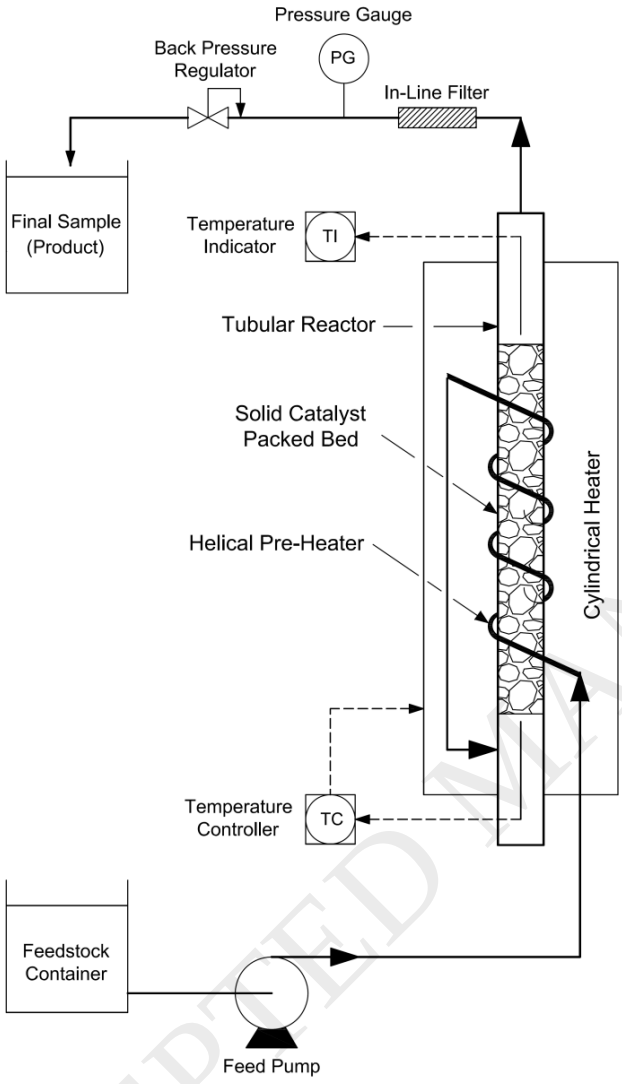

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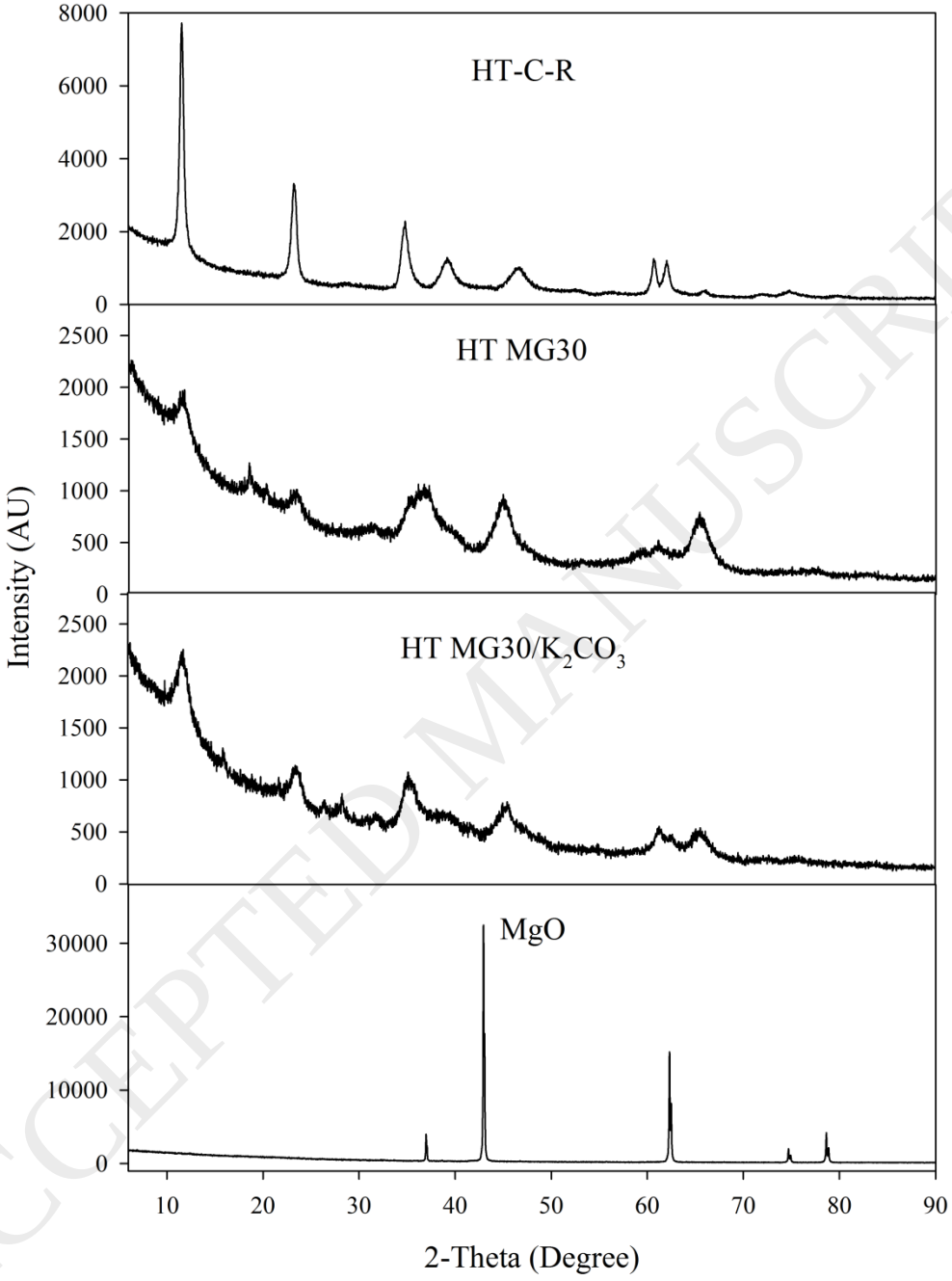

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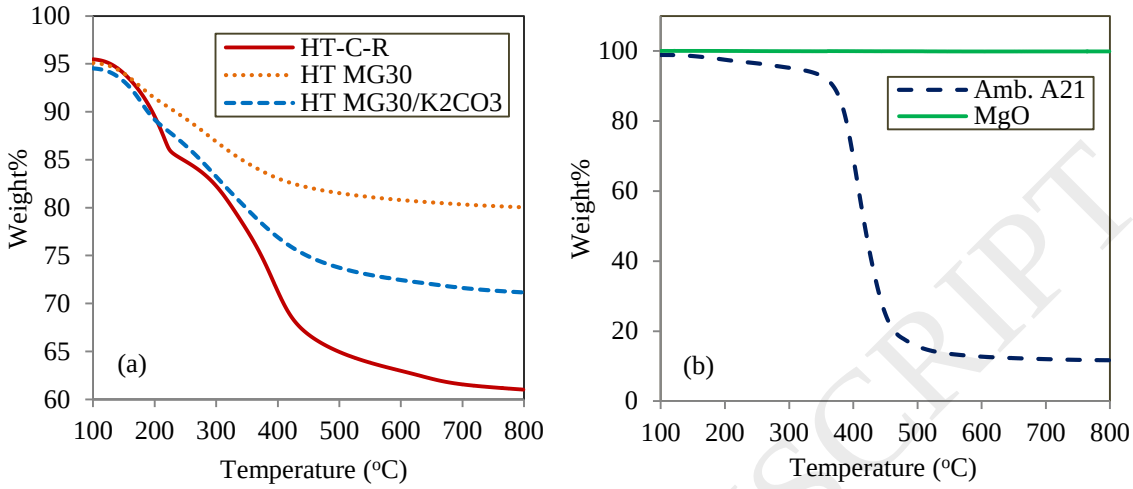

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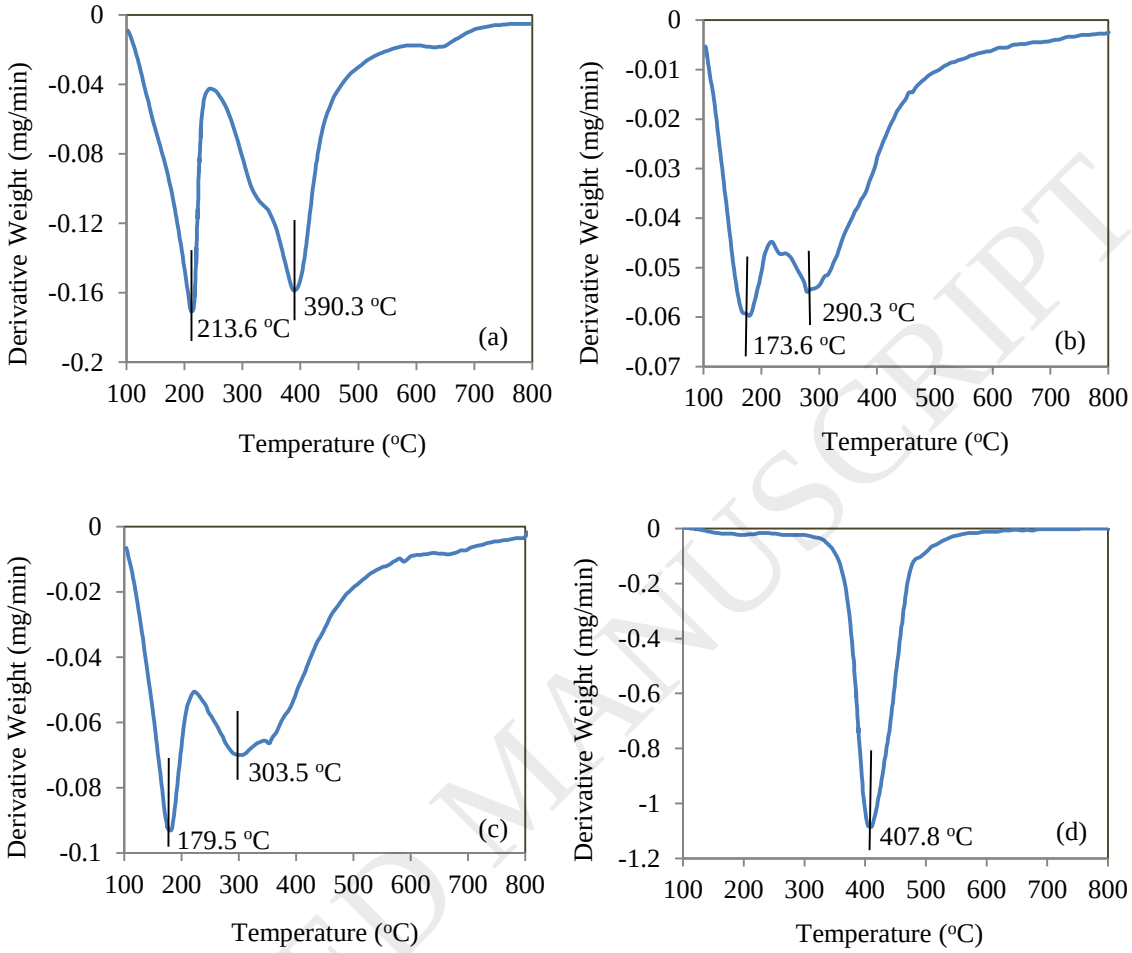
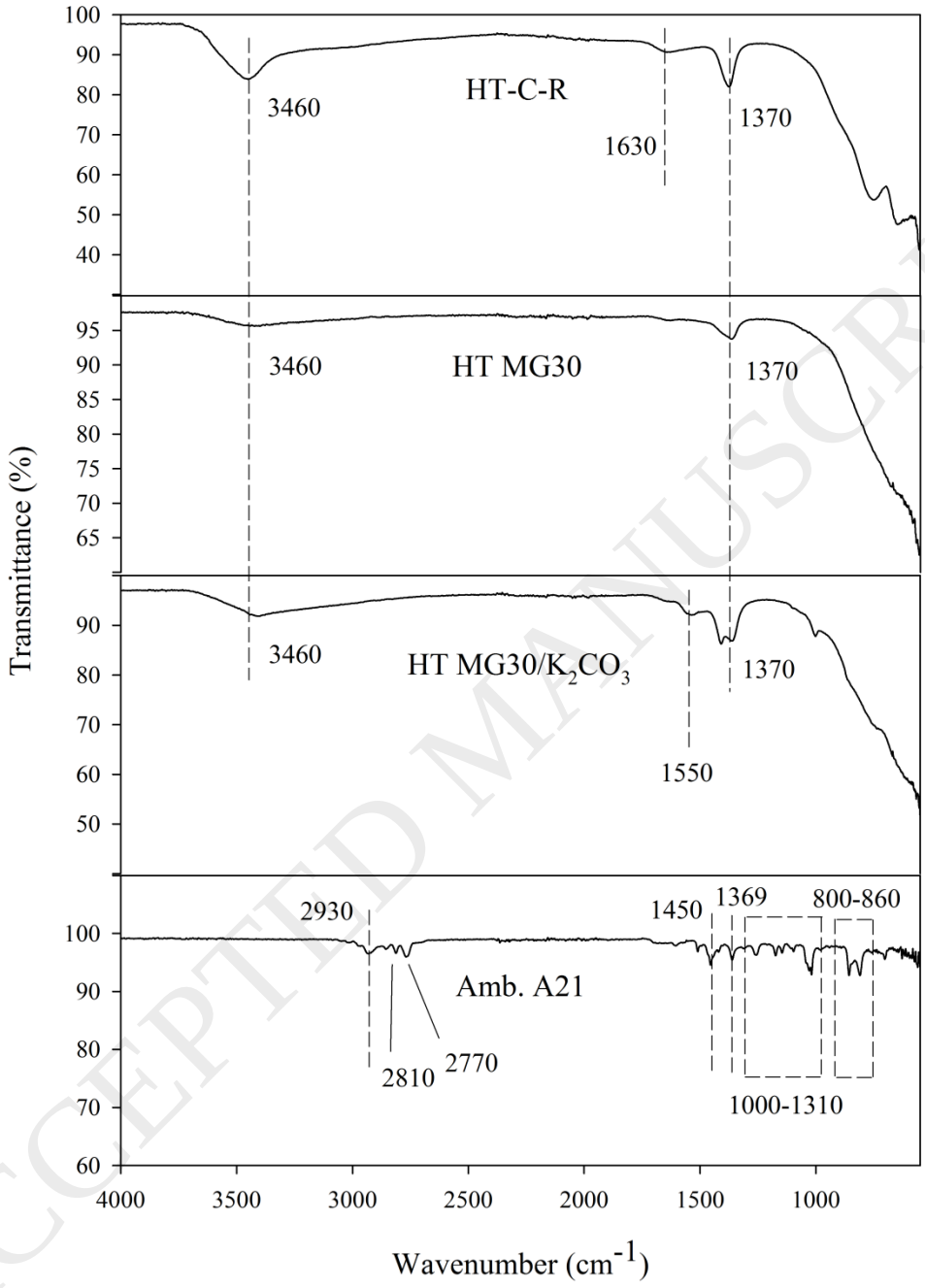


Figure 5. DTG graphs for HT-C-R (a), HT MG30 (b), HT MG30/K_2CO_3 (c) and Amb. A21 (d)



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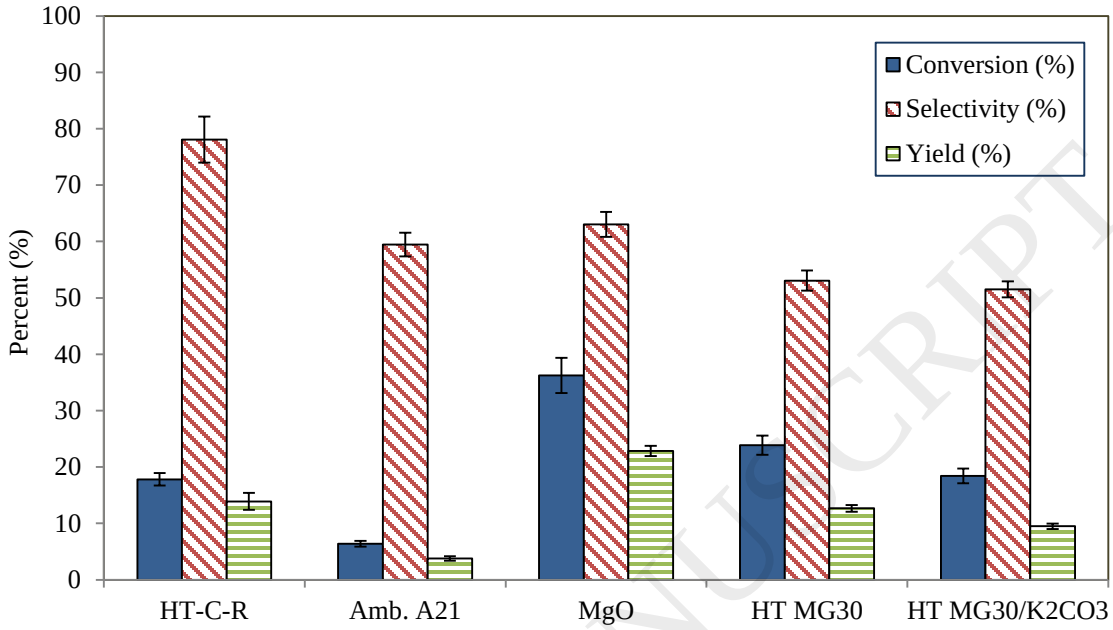

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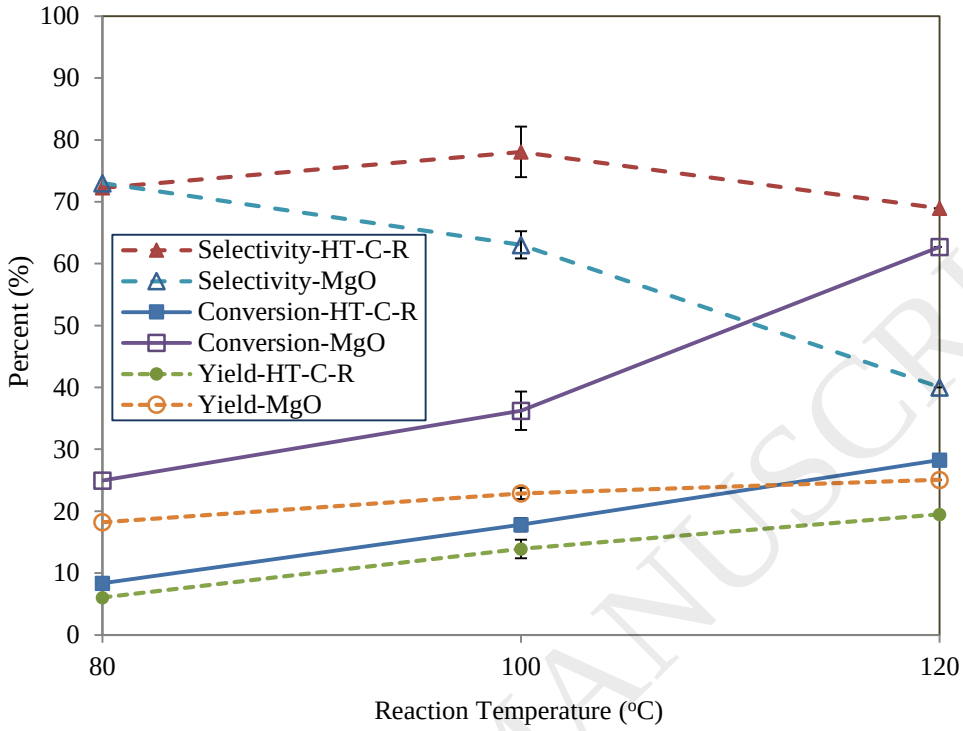

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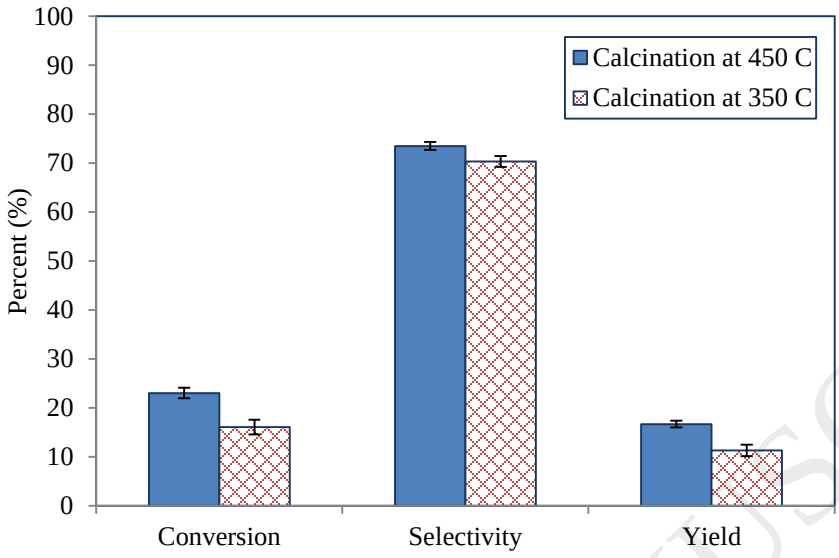

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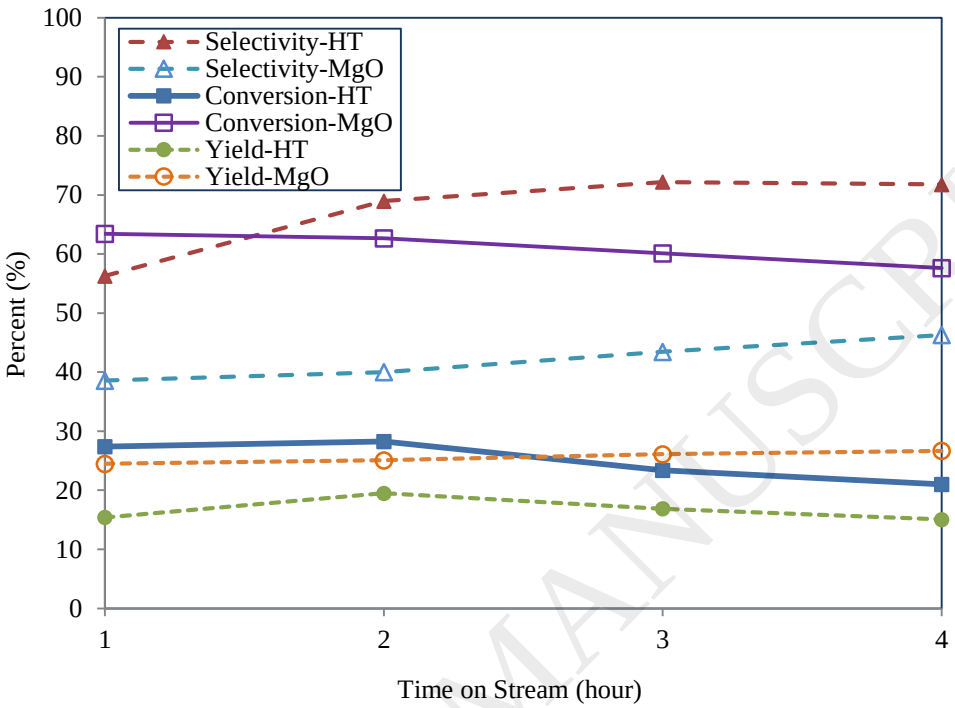

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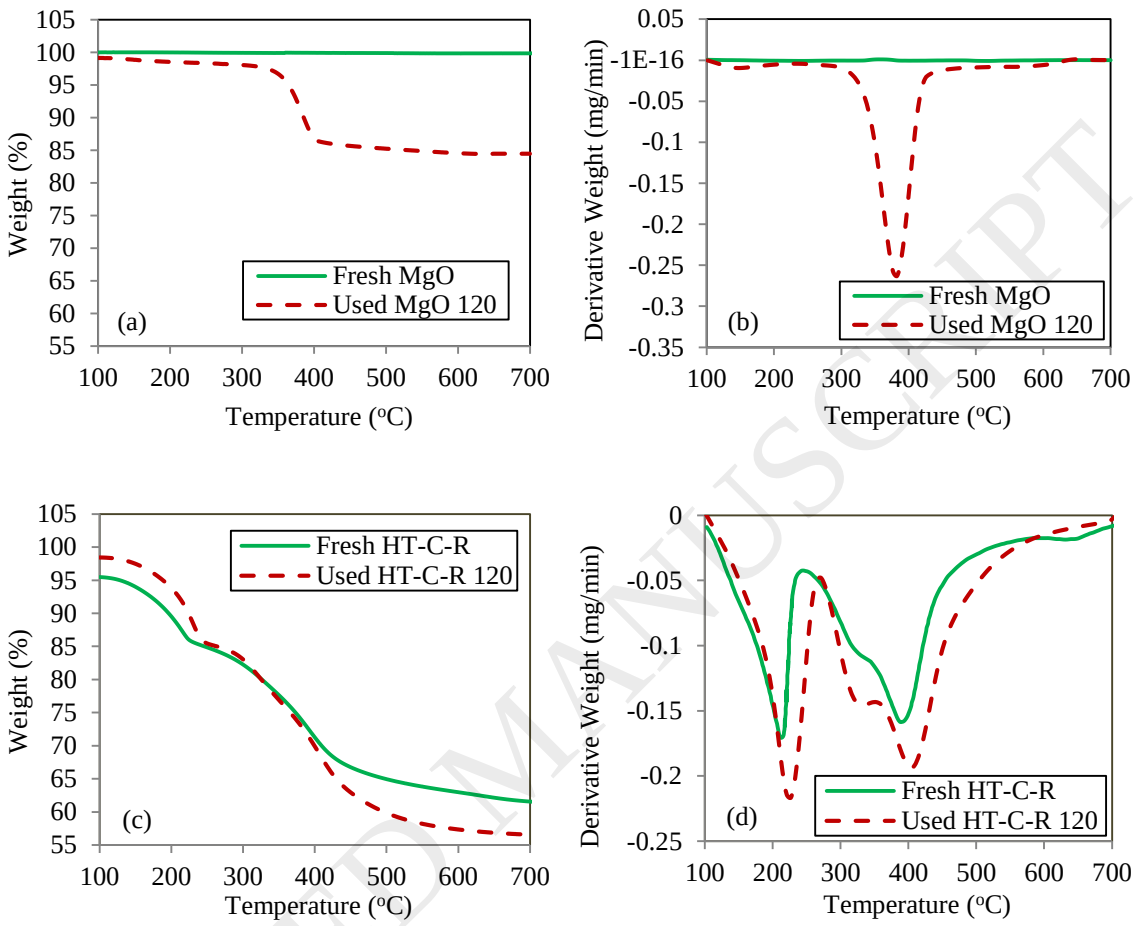

Figure 11. TGA and DTG graphs for the used MgO (a and b) and used HT-C-R (c and d) after experiments at 120 °C in comparison with the fresh catalysts

Table 1 *Textural properties of the catalysts*

Catalyst	BET Surface Area (m^2/g)	Average Pore Diameter (nm)	Total Pore Volume (cm^3/g)
HT-C-R	19.0	19.0	0.0902
HT MG30	171.2	7.3	0.3124
HT MG30/K_2CO_3	132.7	9.7	0.3215
Amb. A21	33.1	10.3	0.0853
MgO	0.2	6.8	0.0004

Table 2 *TGA weight losses data for the fresh catalysts*

Catalyst	First Weight Loss (%)	Second Weight Loss (%)
HT-C-R	15.15	23.30
HT MG30	8.57	11.10
HT MG30/K_2CO_3	10.82	17.57
Amb. A21	88.01	-
MgO	-	-