Chemoselective hydrogenation of furfural to furfuryl alcohol on ZrO$_2$ systems synthesized through the microemulsion method

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Abstract

Different solids consisting in hydrous zirconia were synthesized by the water in oil microemulsion technique (ME series). For comparative purposes, diverse solids were also obtained by the conventional sol-gel method (P-series). The solids were tested for liquid-phase selective hydrogenation of furfural to furfuryl alcohol, using propan-2-ol as the hydrogen donor (Meerwein-Ponndorf-Verley process). The best results corresponded to catalysts calcined at 200ºC which consisted in amorphous solids with surface areas of ca 200m^2/g. The presence of some surfactant remaining from the synthetic process in solids obtained through the microemulsion technique favored selectivity to furfuryl alcohol with values ≥98%. Results were explained by the steric hindrance of furfural by the surfactant molecules in micelles thus favoring the interaction of the substrate with hydroxyl groups in hydrous zirconia through the C=O group. Application of microwave irradiation accelerated the reaction (15-30 times) as compared to conventional heating.

Keywords: microemulsion technique; sol-gel; furfural hydrogenation; furfuryl alcohol; Meerwein-Ponndorf-Verley reaction

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1. Introduction

Nowadays, biomass valorization is one of the most interesting research topics in the context of sustainable chemistry [1]. Biomass can be used as an energy source [2-4]. There is, however a unique feature of biomass as compared to other renewable energy sources: it can also provide chemicals [5-7]. Furfural and furfural derivatives are among the so-called platform molecules obtained from biomass which can be used for the synthesis of chemicals and fuels [8,9]. Furfural selective hydrogenation can lead to furfuryl alcohol, which has important applications in the production of resins, fibers or as a solvent, just to cite some of them [10, 11].

Copper-based solids are the most widely used catalysts for furfural hydrogenation into furfuryl alcohol [10, 11], though some other non-noble (Fe, Co, Ni) [12-14] or noble metals (Pt, Pd, Au, Ru) [15-18] have also been described. Hydrogenation is normally conducted using molecular hydrogen. Nevertheless, carbonyl groups can also be reduced to the corresponding alcohol through hydrogen transfer from an alcohol (the so-called Meerwein-Ponndorf-Verley, MPV, reaction) [19-21]. The process, traditionally conducted in the homogeneous phase using aluminium alkoxides as the catalysts, has also been successfully described in the heterogeneous phase using a wide range of solids such as magnesia or zirconia [22-27]. In the present piece of research different zirconium-based systems were obtained through the microemulsion technique. For comparative purposes, the solids were also synthesized through conventional sol-gel process. The systems were tested for liquid-phase selective hydrogenation of furfural to furfuryl alcohol using propan-2-ol as the hydrogen donor (MPV process).

2. Experimental

2.1. Materials

Chloroform anhydrous $\geq$ 99% (Ref. 288306-2L), 2,2,4-Trimethylpentane anhydrous 99.8% (36006-1L), cetyltrimethylammonium bromide (CTAB) $\geq$98% (H5882-500G), 1-Butanol (360465-2.5L), ethanol (02860-2.5L), ammonium hydroxide solution (0.1N) (318620-2L), zirconium (IV) oxynitrate hydrate (346462), furfural (185914) and furfuryl alcohol (185930) were purchased from Sigma-Aldrich. Ammonium hydroxide solution (5.0N) (318612-2L) and hydrochloric acid solution (318949-2L) were purchased from Fluka analytical. Milli-Q water was used for preparation of solutions.

2.2. Synthesis of the solids

2.2.1. Precipitation method (P series)

A 0.4M zirconium (IV) oxynitrate hydrate solution was dropwise added to a 200 mL solution of NH_4OH (pH 10, prepared from NH_4OH 5 N). pH 10 was kept during the whole process adding NH_4OH 5N or HCl 0.2M using a Syrris Atlas pump, with constant agitation (500 rpm). Once the addition had finished, typically after 1hour, the solution was aged overnight. Then the white precipitate was filtered and dried overnight at 120°C. Afterwards, the solid was calcined at the desired temperature (200, 300, 400, 500, 600 or 700°C) for four hours with a temperature ramp of 5°C/min under synthetic air flow (50 mL/min). Finally, the solids were ground and sieved (particle size <0.149 mm). The nomenclature used for the solids was P-Zr-X, where X indicates the calcination temperature.

2.2.2. Microemulsion method (ME series)

For the synthesis of zirconium systems through reverse (water in oil) microemulsion, two microemulsion systems, ME1 and ME2, for NH_4OH and the Zr precursor, respectively, were prepared.

Under optimized conditions, the composition of microemulsions (ME) was surfactant: CTAB (15 wt%), oil: 2,2,4-trimethylpentane (53%), co-surfactant: butan-1-ol (12%), water solution: 20 wt%. In the case of ME1, water solution contained 5M NH_4OH whereas for ME2 0.4M $ZrO(NO_3)_2 \cdot xH_2O$ was used.

Similarly as for precipitation method, ME2 was dropwise added to ME1 at a stirring rate of 500 rpm. In order to ensure complete precipitation of zirconium precursor, the used amount of NH_4OH was three times that stoichiometrically required.

Once both microemulsions had been mixed, a white precipitate was observed, which was kept aging overnight under constant agitation. The precipitate was then filtered and divided into two parts. One portion was washed 5 times with 200 mL of a 50/50% chloroform/ethanol mixture, with the intention to remove the residual surfactant. The solid was then dried in an oven at 120°C overnight.

The other portion was directly dried in an oven at 120°C overnight without washing.

The rest of the preparation procedure was analogous to that described for the precipitation method: after the drying process, all solids were calcined at the desired temperature (200, 300, 400, 500, 600 or 700 °C) for 4 hours (ramp temperature of 5°C/min under 50mL/min synthetic flow). Catalyst nomenclature is ME-Zr-X- Y were X denotes the calcination temperature and Y whether the solid was washed (W) or unwashed (UW).

2.3 Characterization

Thermogravimetric analyses (TGA–DTA) were performed on a Setaram SetSys 12 instrument. An amount of 20 mg of sample was placed in an alumina crucible and heated at temperatures from 30 to 1000ºC at a rate of 10ºC/min under a stream of synthetic air at 50 mL/min in order to measure weight loss, heat flow and derivative weight loss.

Surface areas of the solids were determined from nitrogen adsorption–desorption isotherms obtained at liquid nitrogen temperature on a Micromeritics ASAP-2010 instrument, using the Brunnauer–Emmett–Teller (BET) method. All samples were degassed to 0.1 Pa at 120ºC prior to measurement.

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 1400 microscope. All samples were mounted on 3 mm holey carbon copper grids.

X-ray diffraction (XRD) of all catalysts were performed on a Siemens D-5000 X-Ray diffractometer using a cobalt source, Co Kα, and a graphite monochromator. The voltage and current intensity were 20 kV and 25 mA, respectively. Scans were performed at 0.05º intervals over the 2θ range from 10º to 70º.

Surface acidity in the catalysts were determined by thermal programmed desorption (TPD) of a pre-adsorbed probe molecule, pyridine (Py) monitored by TCD. An amount of 50 mg of sample was placed under a He stream flowing at 75 mL/min in a reactor 10 mm in diameter that was placed inside an oven. He stream was used to clean the solids by heating to 350∘C (200ºC in the case of solids calcined at 200ºC) at a rate of 10∘C/min and then cooling to 50∘C. At that point, the surface of the solid was saturated with the Py for 30 min. Pyridine was supplied by bubbling the He stream through liquid pyridine at room temperature over the samples. After saturation, excess physisorbed Py was removed increasing the temperature up to 50∘C and passing a He stream at 75 mL/min for 60 min. Then temperature was increased up to 400∘C (200ºC in the case of solids calcined at 200ºC)

at 10∘C/min, holding the final level for 30 min. Desorbed pyridine was quantified against a calibration graph previously constructed from variable injected volumes of pyridine. Additionally, Raman analyses of solids pre-saturated with pyridine were performed in order to determine the type of surface acid sites. First the solids were cleaned by heating up until 120°C during 30 min under nitrogen flow. Then temperature was cooled down to 50 °C and the pyridine was saturated for 1 hour. Physisorbed pyridine was removed by heating up to 120 °C for 1 hour under nitrogen flow. Finally, the Raman spectra were recorded at 300mW using a portable Raman spectrometer EZRaman-N series 785-B, (Manufactured by TSI, Irvine CA, USA) with an excitation laser of 785nm.

2.4 Catalytic tests

The solids were tested for selective hydrogenation of furfural to furfuryl alcohol using propan-2-ol as the hydrogen donor. Catalytic test were conducted in two reaction systems:

a) Multi-reactor (conventional thermal heating)

A Carrusel Reaction Station TM multi-reactor (Radley Discovery Technologies) with twelve 50mL vials was used. The reaction mixture consisted in 1mL furfural, 9 mL isopropanol and 50 mg catalyst. Temperature and stirring rate were adjusted at 100ºC and 1000 rpm, respectively. The top part of the vials was always refrigerated at 5ºC thus preventing lost in the reaction volume as a result of evaporation.

b) Microwave oven

Microwave assisted reactions were carried out in a computer-controlled CEM Discover microwave reactor. Reactions were performed in a closed 10 mL vial at 100ºC,

with a maximum pressure of 200 psi. The reaction mixture consisted in 0.5 mL furfural, 2.0 mL isopropanol and 25mg catalyst (i.e. same substrate/catalyst ratio as for conventional heating).

After the reactions, the solids were filtered using a PTFE syringe filter 0.45µm and the liquid phase was analyzed by gas chromatography, GC-FID (Agilent Technologies 7890, with a Supelcowax-10 capillary column) with confirmation by GC-MS (CP-3800 Gas Chromatograph connected to a Varian 1200 QuadrupoleMS). Quantification of furfural and furfuryl alcohol was performed using the corresponding calibration curves.

3. Results and discussion

TGA-DTA profiles of P-Zr, ME-Zr-W and ME-Zr-UW gels are represented in Fig. 1. From that figure it is evident that weight loss is significantly higher in the case of ME series, especially for the unwashed system, due to the presence of surfactant (weight losses percentages of 17.0, 36.9 and 72.5%, for P-Zr, ME-Zr-W and ME-Zr-UW, respectively). As for the heat flow profiles, in the case of P-Zr (Fig. 1A), there are two main peaks. The first endothermic peak centered at ca. 106ºC corresponds to the loss of water whereas the sharp exothermal peak at ca. 453ºC (the so-called glow exotherm) is attributed to the crystallization of zirconia [24, 28]. For solids synthesized through microemulsion method, combustion of CTAB (which occurs in the 300-550ºC for pure CTAB, see dotted line in Fig. 1C) tends to mask the glow exotherm, though it can be seen at 477ºC in ME-Zr-W solid (Fig. 1B) thus evidencing that zirconia crystallization is retarded in the presence of the surfactant.

Fig. 2 represents the evolution of surface area (as determined by the BET method) as a function of the calcination temperature of the solids. Results are consistent with TG-DTA profiles: for calcination temperatures below 200ºC, BET surface area of the solids of ME

series are very low as compared to P-Zr system as a result of the presence of a high amount of surfactant. As the temperature rises, zirconia crystallizes which results in BET area dropping. However, in the 200-400ºC range, the catalysts synthesized through microemulsion, especially unwashed solids, exhibit higher BET area values than those of the P series which can be ascribed to the retardation in zirconia crystallization evidenced in the heat flow profile of Fig. 1B. All in all, the highest surface areas (200-250 m^2/g) correspond to solids synthesized in the 200-300ºC range.

BET isotherms (see Figure S1A) are of the H2b type according to IUPAC nomenclature [29], associated to mesoporous materials. In fact, average pore sizes are in the 3-9 nm for P-Zr and ME-Zr W solids, whereas ME-Zr UW systems exhibited larger pores (4-15 nm). (Figure S1B). Pore sizes are smaller for lower calcination temperatures. Nevertheless, they are always in the range of mesopores whereas furfural molecular size is 5.7 Å (0.57 nm) which ensures the absence of diffusion problems [30, 31].

XRD patterns (Fig. 3) evidenced that solids calcined at temperatures below 400ºC are amorphous and confirmed the retardation in the crystallization in the presence of residual surfactant. From TEM micrographs (Fig. S2), it seems that the presence of CTAB also resulted in more separation between particles. Moreover, crystallite particle size, as determined from XRD through Scherrer equation, is significant lower for the microemulsion method as compared to conventional sol-gel precipitation (Fig. 3).

At 400 and 500ºC zirconia is present in the tetragonal phase mainly (JCPDS Card No. 42-1164) whereas subsequent calcination at 700ºC results in monoclinic (JCPDS Card No. 37-1484) being the predominant phase for P-Zr and ME-Zr-W solids. On the contrary, tetragonal is still the major phase in ME-Zr 700 UW system which suggests that surfactant could somehow contribute to the stabilization of such a phase on calcination.

Determination of the surface acidity of the solids is difficult, especially at the lowest calcination temperatures, since catalysts structure of hydrous zirconia can vary under experimental conditions and the presence of surfactant in the ME series can interfere in the measurement. Nevertheless, in order to have a comparison of acidity of solids, pyridine TPD profiles of the systems calcined at 200, 400, 500 and 700ºC were recorded (Fig. 4). All three series present quite similar acidities which in the case of solids calcined at 400ºC correspond to 250, 217 and 237 µmol py/g for P-Zr 400, ME-Zr 400 W and ME-Zr 400 UW, respectively. Additionally, some Raman spectra of pre-adsorbed pyridine were recorded (Fig. S3). Liquid pyridine exhibits a Raman band at ca. 990 cm^{-1} (symmetric ring breathing), the position of this band being sensitive to the interaction with the catalyst surface through hydrogen bonds (996-1008 cm^{-1}) or chemisorption at Brönsted (1007-1015 cm^{-1}) or Lewis acid sites (1018-1028cm^{-1}) [32].

From Figure S3, it is evident that P-Zr-200 solid exhibits such hydrogen bonds or Brönsted sites. For solids obtained through microemulsion, their colored nature made the analysis difficult though in the case of ME-Zr-200 UW those signals seem to be present.

3.3. Catalytic activity

Initially, solids were tested for selective reduction of furfural to furfuryl alcohol in the multi-reactor system under conventional heating. Results achieved for solids calcined at 120, 300, 500 and 700ºC are summarized in Fig. 5 expressed as conversion, selectivity to furfuryl alcohol (FA) and furfuryl alcohol yield after 3, 6 and 20 h. The main by-product identified by GC-MS was a C13 compound resulting from the condensation of acetone with two furfural molecules [25]. In the absence of a standard, the response factor was calculated considering the so-called effective carbon number [33].

In general, conversion values decrease with calcination temperature. This is especially dramatic in the case of P-Zr solids which are not active at temperatures ≥500ºC whereas ME-Zr W and ME-Zr UW still exhibit some conversion.

The generally accepted mechanism for MPV reaction on hidrous zirconia is represented in Fig. 6A [24, 27]. As can be seen, surface OH groups play an important role in the reaction as anchoring groups for propan-2-ol which adsorbs onto OH groups as 2-propoxide via dehydration. As calcination temperature rises, the number of surface OH groups decreases thus resulting in a drop in conversion. The presence of surfactant retards ZrO_2 crystallization and consequently surface dehydration thus accounting for the observed higher activity in ME series at high temperatures as compared to P-Zr solids.

It is also worth noting that solids synthesized through microemulsion technique exhibit higher selectivity to furfuryl alcohol than those obtained by conventional sol-gel method, especially at low calcination temperatures. Meric et al [34] studied chemoselective reduction of citral on supported paladium systems synthesized through the microemulsion method. The authors reported a change in product selectivity (citronellal or dihydrocitronellal) depending on palladium being under microemulsion conditions or outside the microemulsion. The authors explained the differences in terms of the specific environment of the "micelle enclosed" Pd particles. The steric hindrance of the citral molecule by the surfactant molecules adsorbed on the Pd particle favored the interaction through the C=O group. This could also be the case in our work, and explain the high selectivity observed to furfuryl alcohol (Fig. 6B). An excessive amount of surfactant could be detrimental to the adsorption, thus accounting for the higher selectivity to FA observed on ME-Zr 120 W as compared to ME-Zr 120 UW. For ME solids, calcination results in the progressive loss of the surfactant, thus resulting in a drop in selectivity to furfuryl alcohol.

All in all, the highest furfuryl alcohol yields obtained at this first screening corresponded to ME-Zr 120 UW (21.8% yield to FA at 24.7% conversion for t=20h).

From this first screening it is evident that the most active solids are those calcined at low temperatures. In principle, in order to conduct selective hydrogenation of furfural to furfuryl alcohol on hydrous zirconia, the optimum catalysts to achieve a high conversion should be those with a high density of surface OH groups and exhibiting a relatively high surface area. In this sense, the calcination temperature of 200ºC could be a good choice since all three systems (P-Zr-200, ME-Zr-200 UW and ME-Zr-W 200) are still amorphous (Fig. 3) and exhibit surface areas in the 213-232 m^2/g range (Fig. 2). Moreover, selectivity to FA could be enhanced by the presence of a certain amount of the surfactant which has not been completely eliminated (evidenced by TG-DTA in Fig. 1). Catalytic results obtained for solids calcined at 200ºC in the multi-reactor system are summarized in Fig. 7. As can be seen, despite exhibiting similar BET surface areas, conversion values follow the sequence ME-Zr 200 UW >ME-Zr 200 W> P-Zr 200 which is also that expected considering that ME retards crystallization and thus results in more surface OH groups. As for the selectivity, again, the system synthesized by microemulsion but with a lower amount of surfactant as a result of the washing (ME-Zr-200 W) exhibits the highest values (ca. 98%) whereas solids obtained by conventional sol-gel method (P-Zr 200) or containing a larger amount of surfactant (ME-Zr 200 UW) present selectivities in the 70-89% range. Yields to FA on the solids synthesized by the microemulsion method are ca. 53-57% after 120h of reaction. Some additional studies (not shown) were performed doubling the catalyst/substrate ratio which resulted in conversion rate almost being doubled whereas selectivity to furfuryl alcohol remained almost the same (e.g. 48.2% conversion and 98.1% selectivity to furfuryl alcohol over ME-Zr-200 W for t=24h).

Finally, in a new attempt at decreasing reaction times, the solids calcined at 200ºC were tested in the microwave oven (Fig. 8). Such a Figure confirms results observed by conventional heating in terms of higher conversion and selectivities to FA for similar reaction times for solids synthesized through microemulsion and the particularly high selectivities on ME-Zr-200 W. Moreover, the reaction is indeed accelerated under these conditions (15-30 times for ME solids, compare Figs. 7 and 8). The question on whether acceleration of chemical reactions by microwaves is a result of the thermal heat generated by the microwave or any specific effect of microwave heating ("specific microwave effect") continues to be a matter of debate [35, 36]. In the latter case, basically the two ways to increase the reaction rate according to Arrhenius equation ($k = A\ e^{-\Delta G\ddagger/RT}$) are: i) affecting preexponential factor through increasing molecular vibrations; ii) altering free energy of activation, $\Delta G^{\ddagger}$. From the practical point of view, many reactions are accelerated, especially when polarity increases during the reaction.

In our case, an additional factor to be considered, given the low calcination temperature of the most active solids, is the possibility that microwaves affected catalyst structure during the reaction. To cast further light on that, some experiments were performed on ME-Zr-200 UW system: two portions of fresh catalyst were re-suspended in isopropanol and submitted to conventional and microwave heating, respectively, for 30 min. Then, the solvent was eliminated and N_2 adsorption-desorption isotherms were registered. Results showed that in all three cases (fresh catalyst, catalyst submitted to conventional heating or to microwaves), BET surface areas were in the 200-215 m^2/g range and pore size distribution hardly changed. Therefore, the catalysts synthesized at 200ºC are stable under working conditions.

3. Conclusions

Different zirconium-based systems were obtained from zirconium (IV) oxynitrate via microemulsion (ME) water in oil technique. Once nanoparticles had been precipitated, one portion was washed with chloroform/ethanol mixture to partially eliminate the surfactant prior to calcination whereas another portion was not washed. For comparative purposes, other solids were also synthesized by conventional sol-gel process (P series). The presence of surfactant remaining from the synthetic procedure retarded ZrO_2 crystallisation (as evidenced by TGA-DTA) and resulted in higher surface areas in the 300-400ºC range as compared to P-series. Moreover, average particle sizes (XRD) in ME solids are comparatively smaller than those of the systems belonging to P series. The solids were tested for liquid-phase selective hydrogenation furfural to furfuryl alcohol using propan-2-ol as the hydrogen donor, under conventional heating and microwave irradiation. The optimum calcination temperature was about 200ºC which ensured that hydrous zirconia was still amorphous with a high amount of OH surface groups to catalyze the Meerwein-Ponndorf-Verley process and a high surface area (ca. $200m^2/g$). Moreover, the presence of some surfactant from the synthetic procedure in solids synthesized through the microemulsion process favored the selectivity to furfuryl alcohol. The steric hindrance of furfural molecule by the surfactant molecules surrounding zirconium nanoparticles could somehow favor the interaction through the C=O group. Nevertheless, the amount of surfactant residues should not be too high, as evidenced by the fact that ME series solids submitted to a washing process prior to calcination led to better results in term of selectivity to furfuryl alcohol than unwashed systems.

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Caption to figures

Fig. 1. Thermal study of P-Zr (A), ME-Zr-W (B) and ME-Zr-UW (C) systems by TGA–DTA.

Fig. 2. Evolution of BET surface area of P-Zr, ME-Zr-W and ME-Zr-UW systems as a function of calcination temperature.

Fig. 3. X-ray diffractograms of different systems. Symbols indicate the main signals for tetragonal (circle) or monoclinic (triangle) zirconia. Crystallite particle sizes, as determined from XRD through Scherrer equation, are also given.

Fig. 4. TPD profile of pre-adsorbed pyridine for solids calcined at 200, 400, 500 and 700ºC.

Fig. 5. Reaction in multi-reactor under conventional heating. Results obtained for liquid-phase selective hydrogenation of furfural to furfuryl alcohol on different solids expressed as conversion, selectivity to furfuryl alcohol (FA) and FA yield. Reaction conditions: 1mL furfural, 9 mL isopropanol and 50 mg catalyst. Reaction temperature: 100ºC.

Fig. 6. A) Mechanism suggested by Chuah et al. [27] for MPV reaction on zirconia systems, highlighting the importance of surface OH groups and the proposed six-membered ring similarly as for reactions in the homogeneous phase. B) Interaction of carbonyl group in furfural with micelles which could explain the high selectivity to furfuryl alcohol.

(We used Fig. 8A in a previous Catalysis Today paper [24]. So, we ask for permission from Elsevier to reproduce it).

Fig. 7. Reaction in multi-reactor under conventional heating. Results obtained for liquid-phase selective hydrogenation of furfural to furfuryl alcohol on the solids calcined at 200ºC expressed as conversion, selectivity to furfuryl alcohol (FA) and FA yield. Reaction conditions: 1mL furfural, 9 mL isopropanol and 50 mg catalyst. Reaction temperature: 100ºC.

Fig. 8. Reactions in the microwave oven. Results obtained for liquid-phase selective hydrogenation of furfural to furfuryl alcohol on the solids calcined at 200ºC expressed as conversion, selectivity to furfuryl alcohol (FA) and FA yield. Reaction conditions: 0.5 mL furfural, 2.0 mL isopropanol, 25 mg catalyst. 100ºC and 200 psi as the maximum pressure.

Supplementary material

Fig. S1A. Nitrogen adsorption–desorption isotherms obtained at liquid nitrogen temperature for different catalysts belonging to P-Zr, ME-Zr W and M-Zr UW series.

Fig. S1B. Pore size distribution in the different solids obtained from N_2 adsorption-desorption isotherms.

Fig. S2. TEM micrographs of different solids belonging to P-Zr, ME-Zr W and ME-Zr UW series.

Fig. S3. Raman spectra of adsorbed pyridine on the solids calcined at 200ºC.
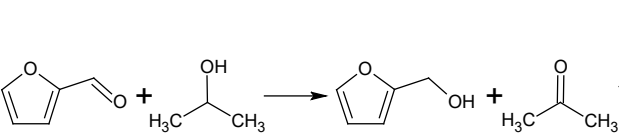
Meerwein-Pondorf-Verley reaction

High selectivity to furfuryl alcohol
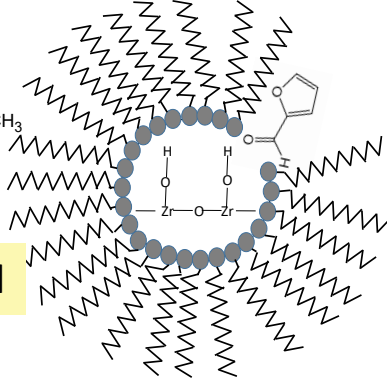
FIGURE 1
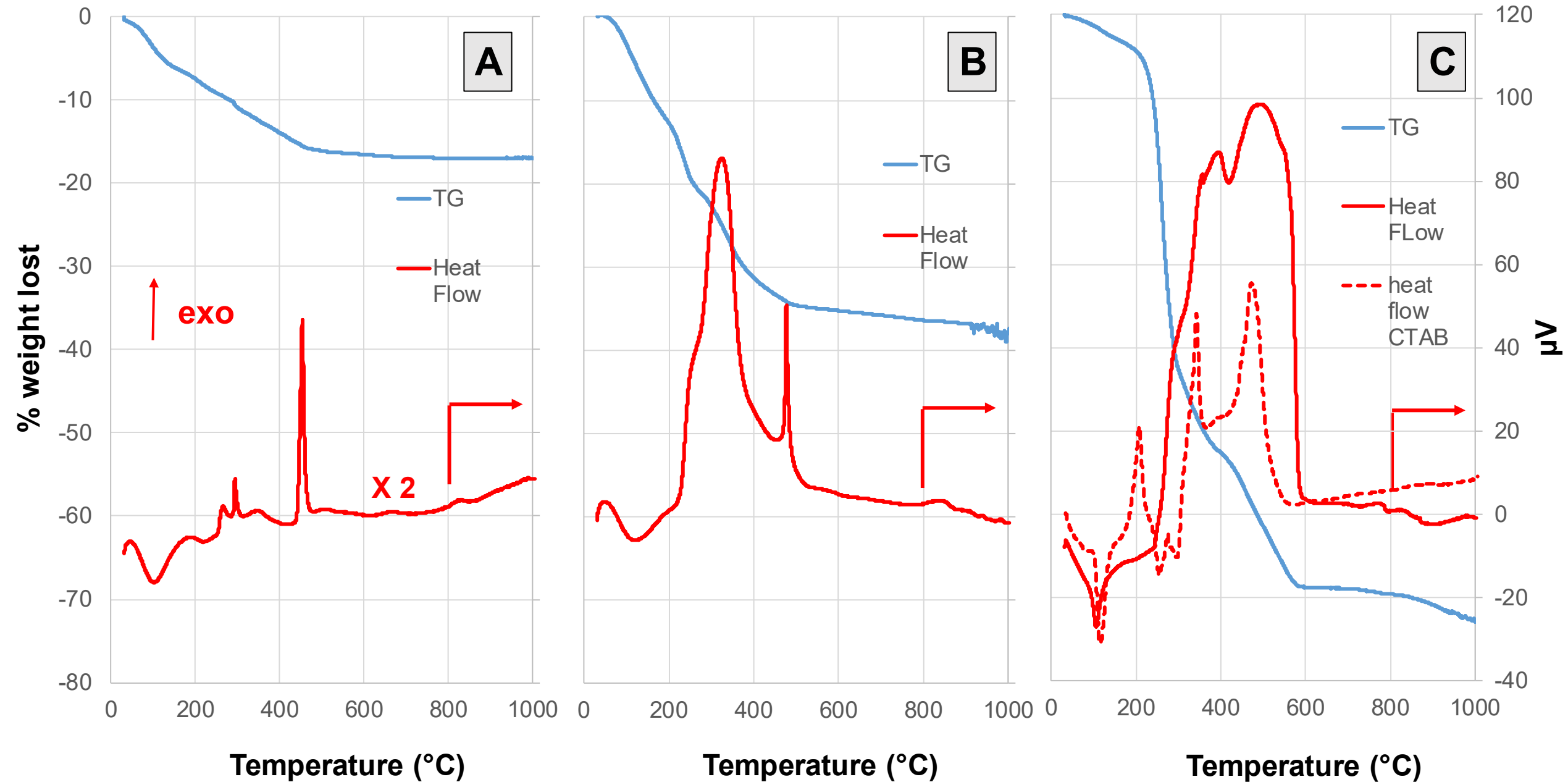
FIGURE 2
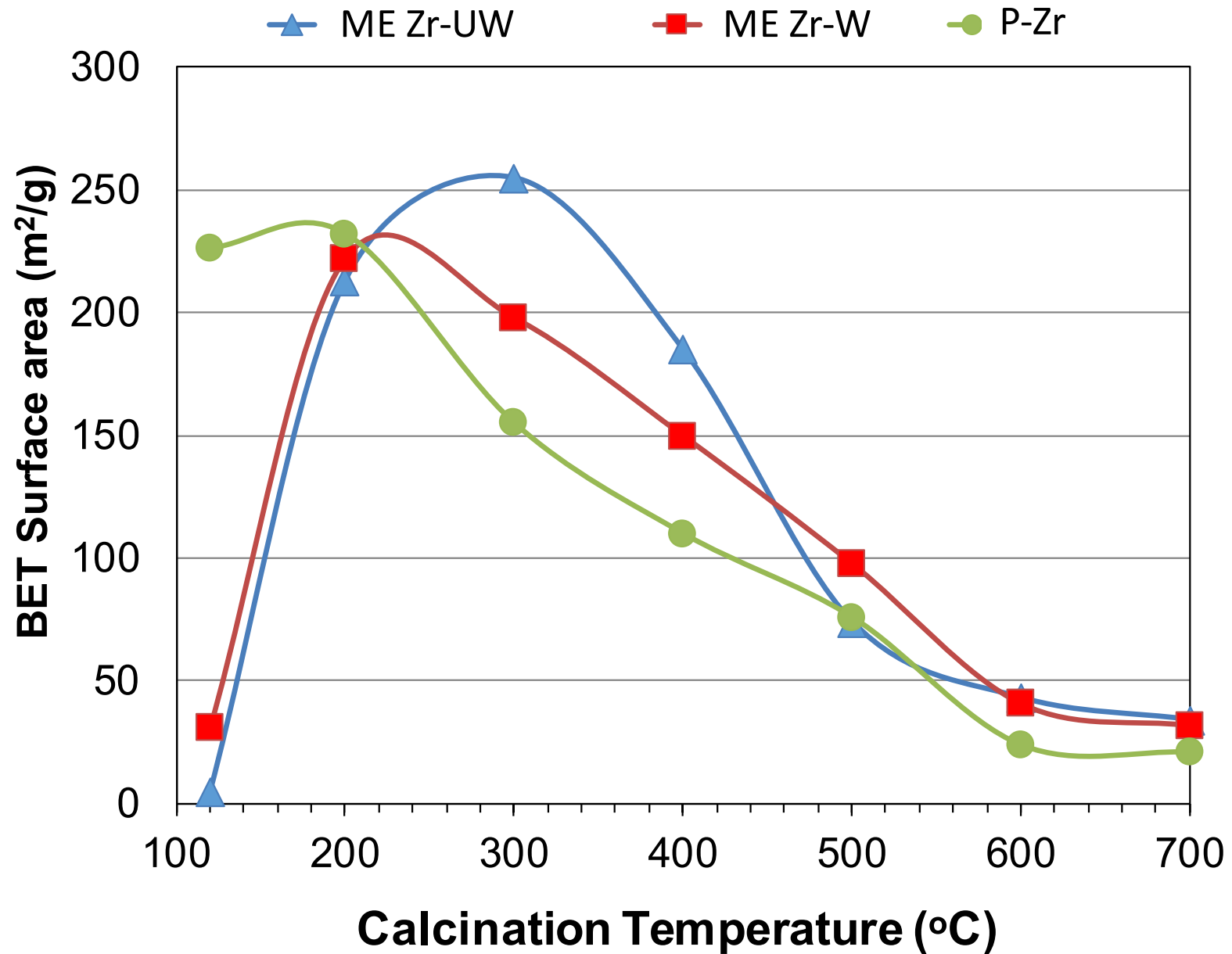
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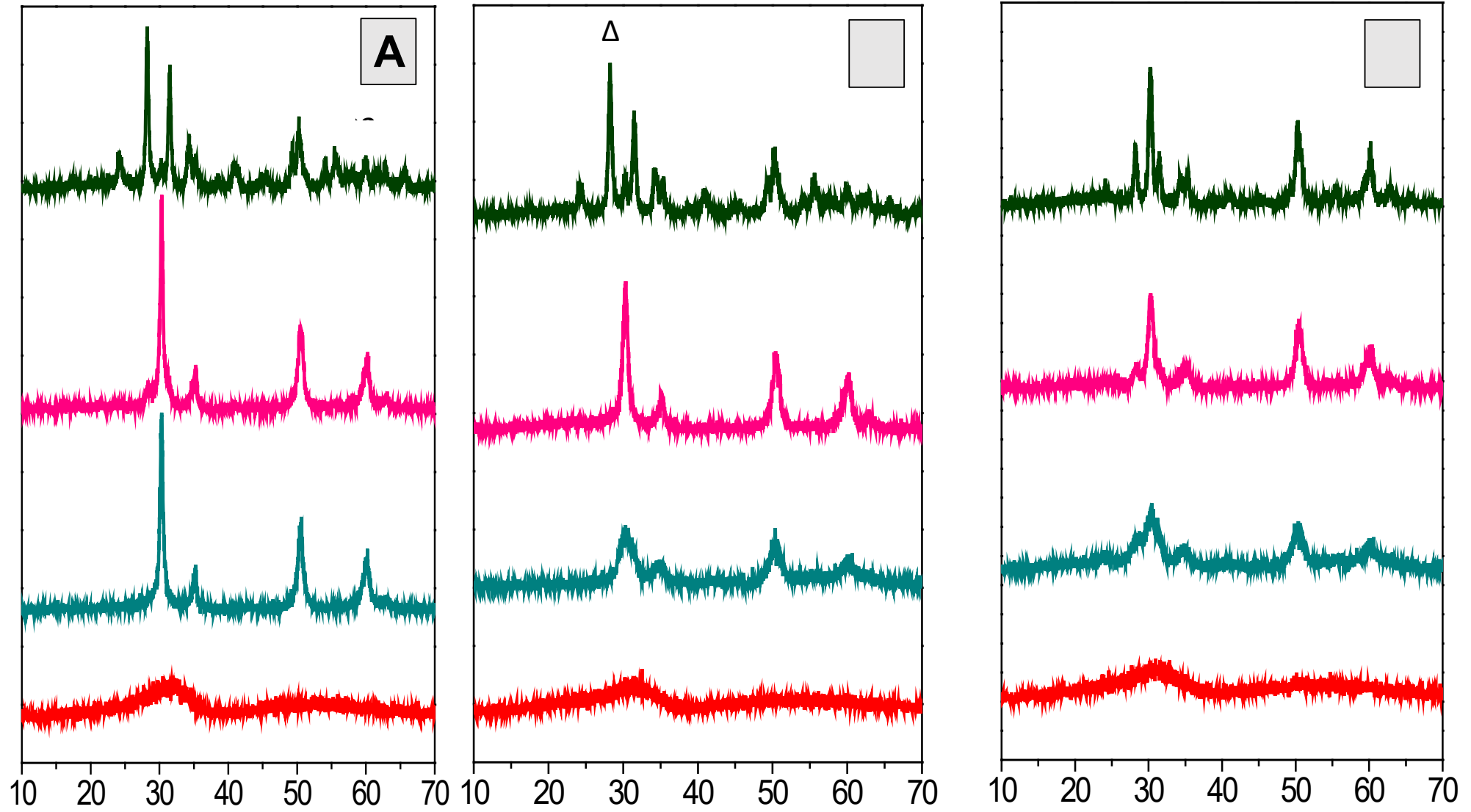
FIGURE 4
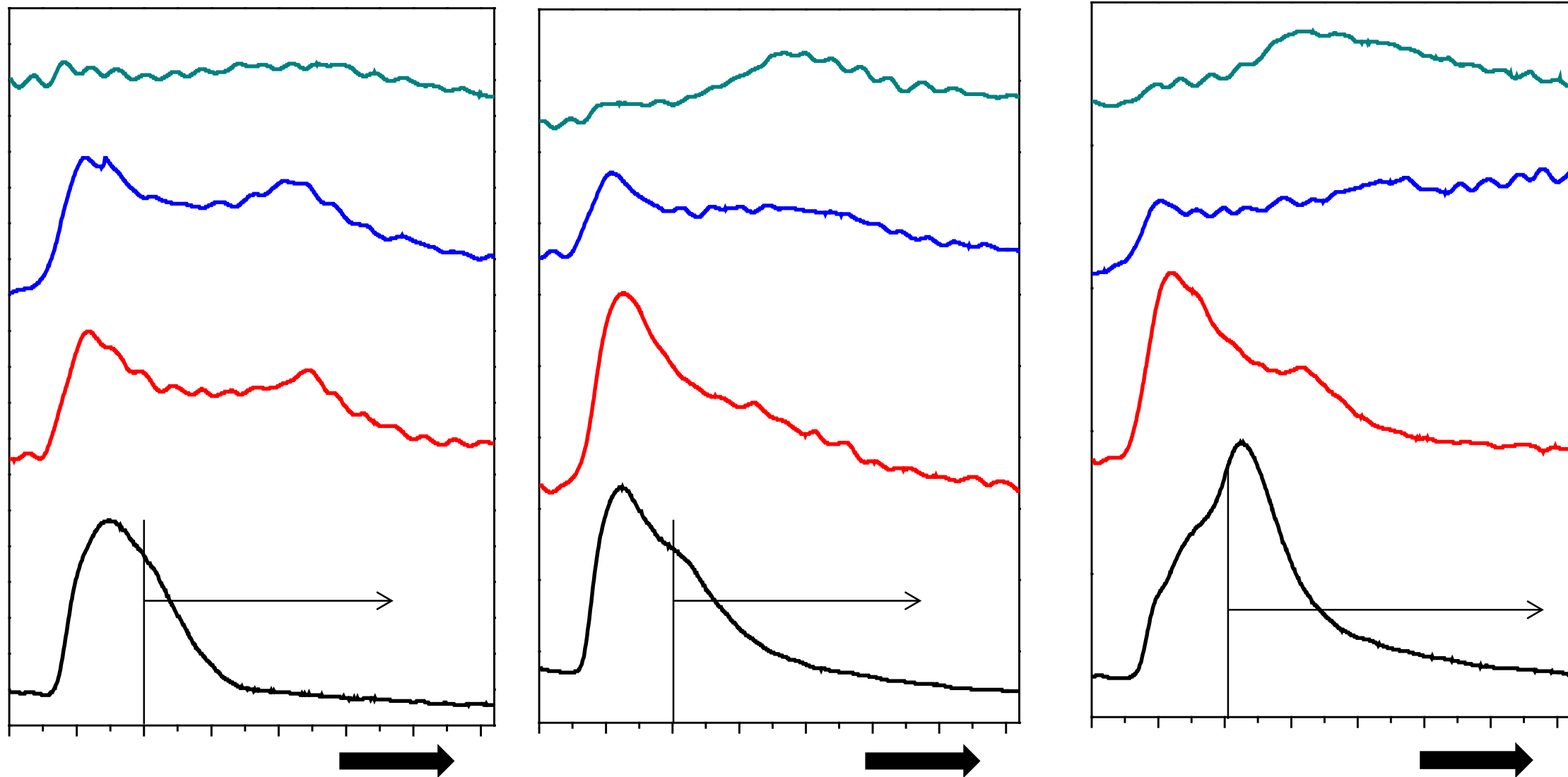
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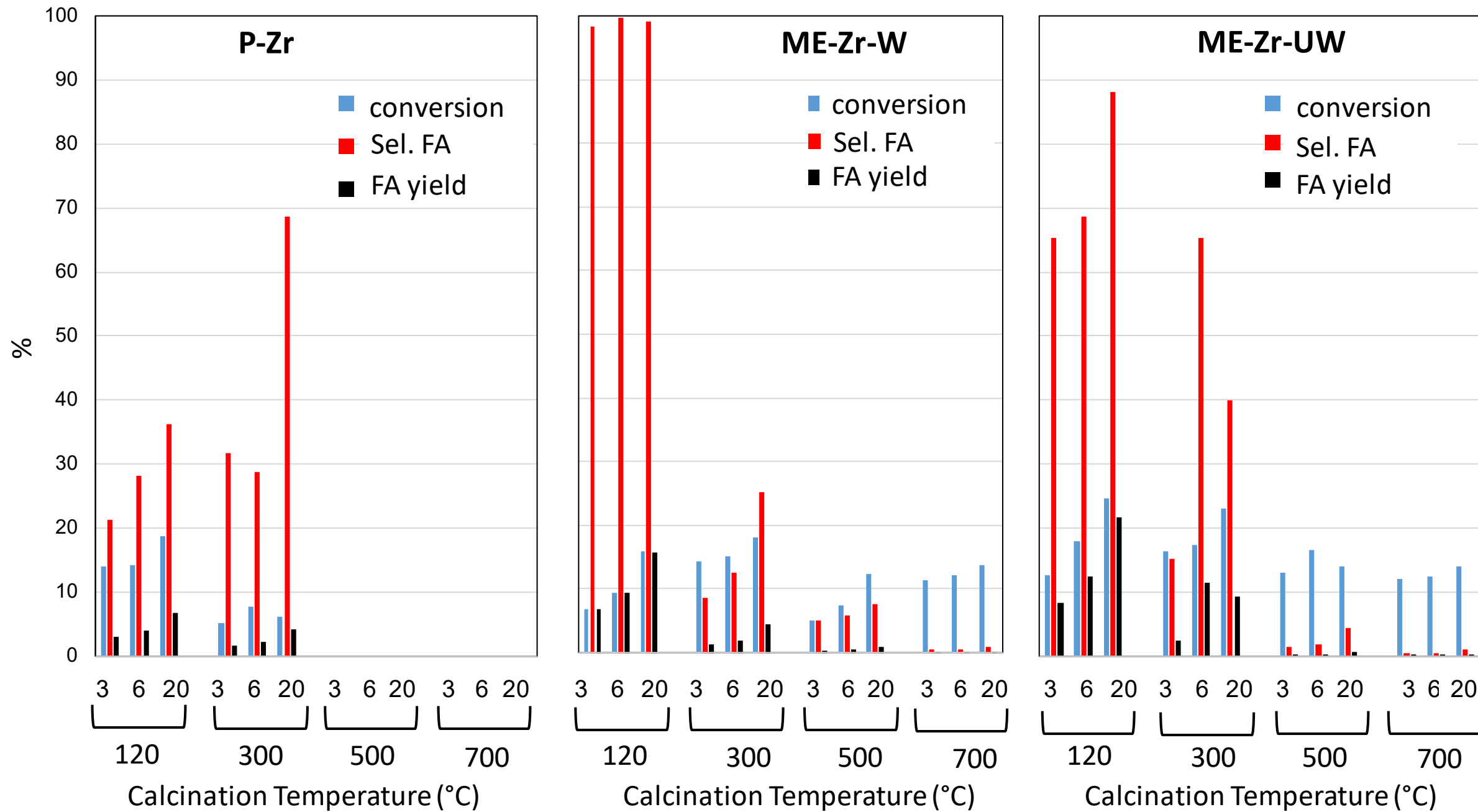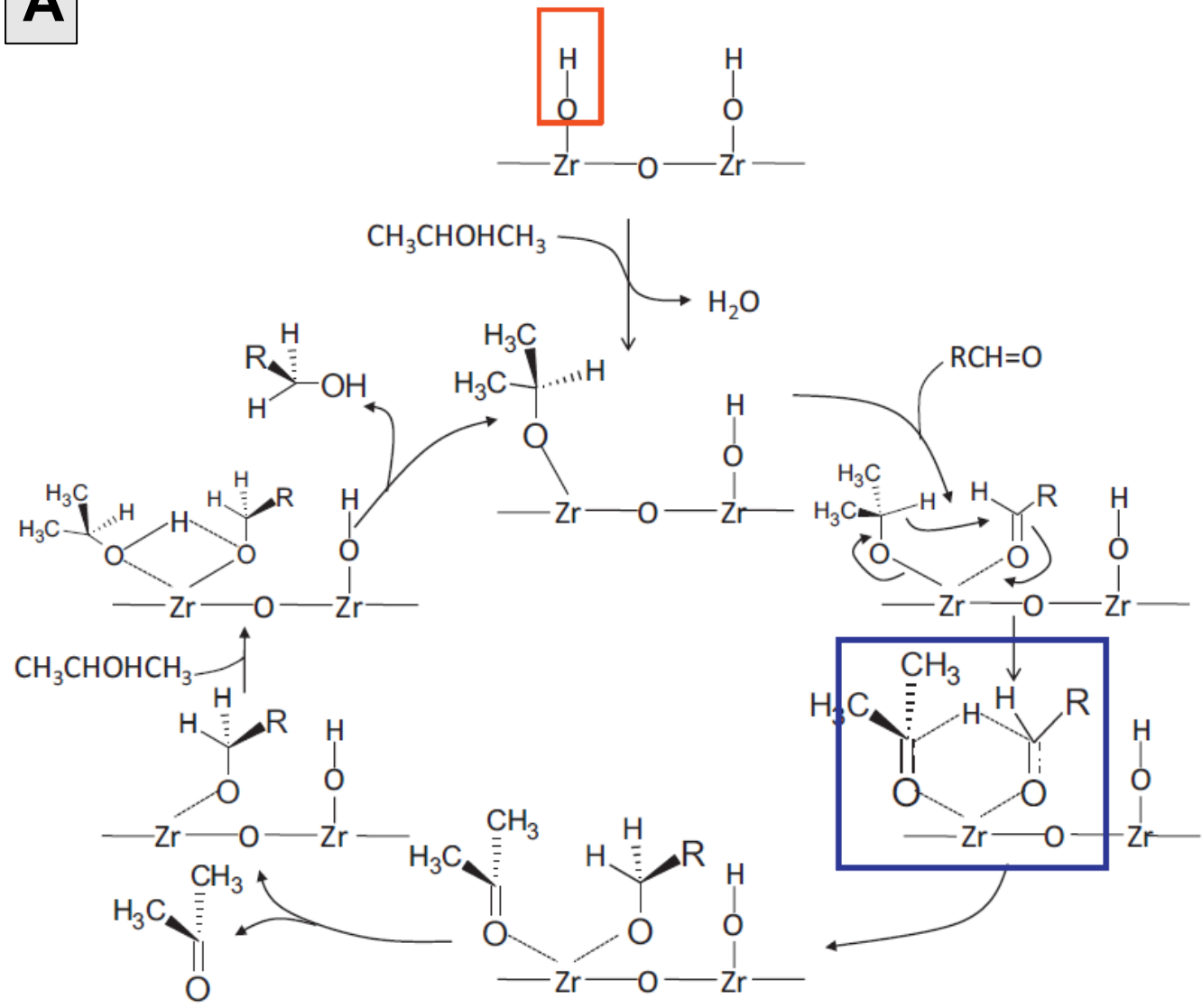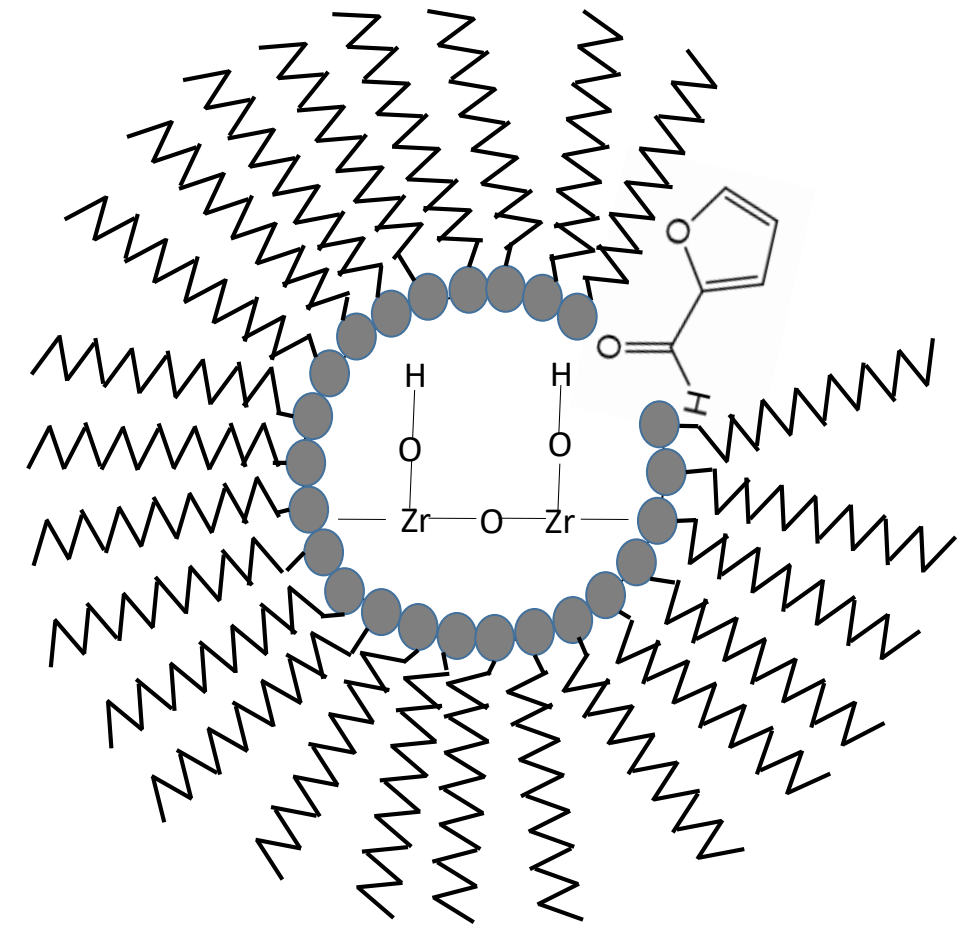
FIGURE 6

FIGURE 7

FIGURE 8

Legend: ■ Conv. ■ Sel. FA ■ FA Yield

P-Zr-200   ME-Zr-200 W   ME-Zr-200 UW

Reaction time (min)
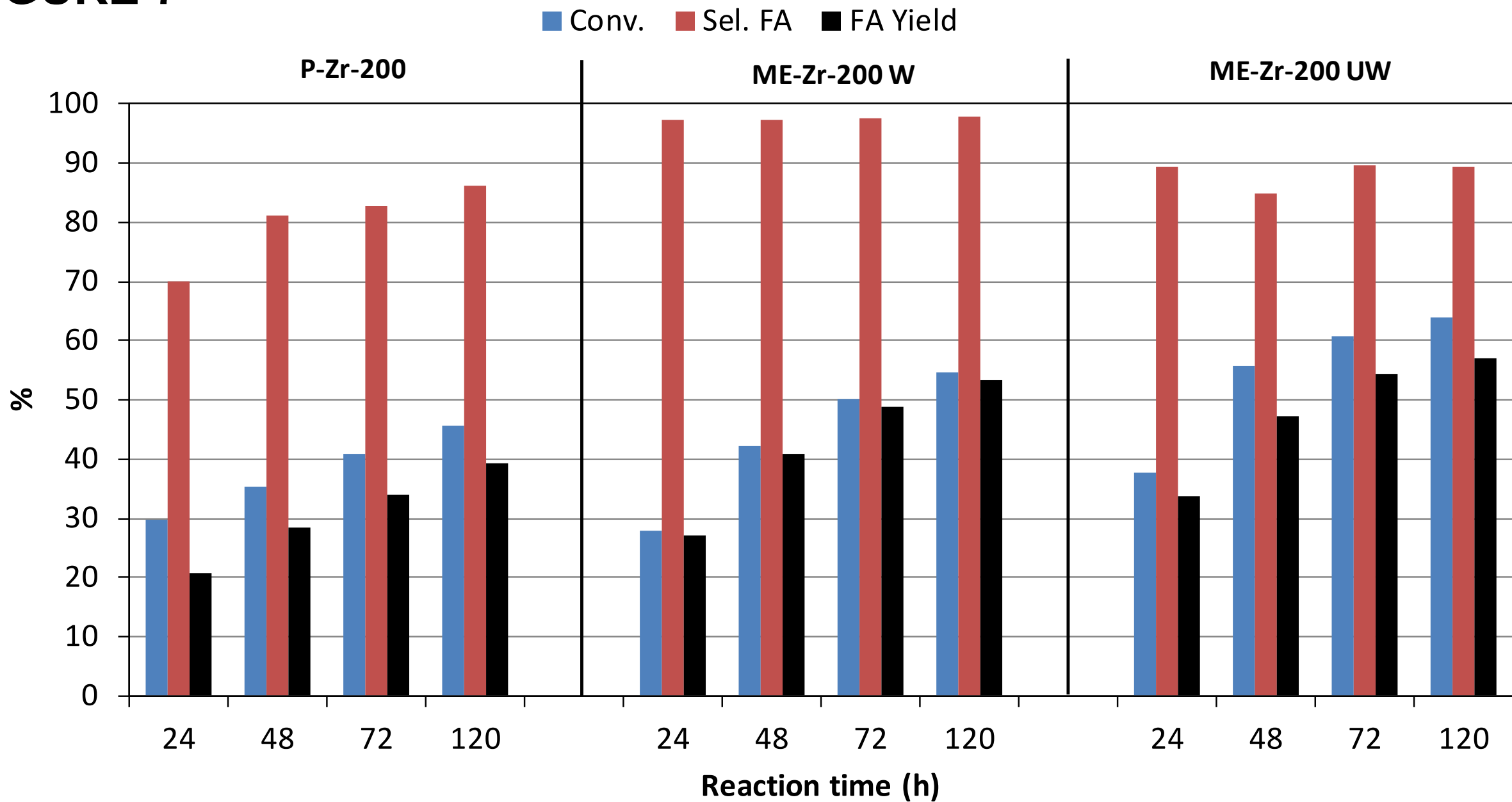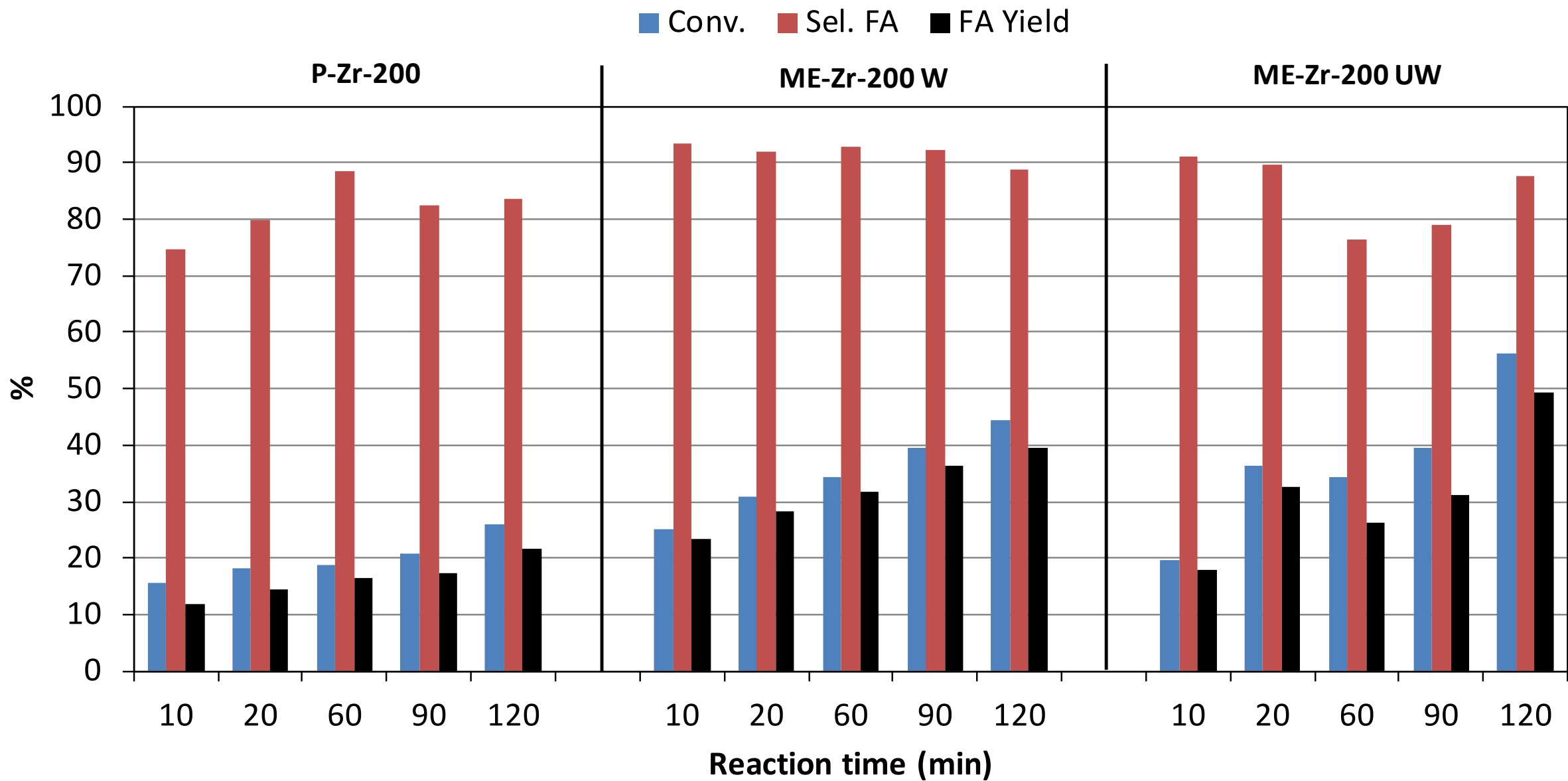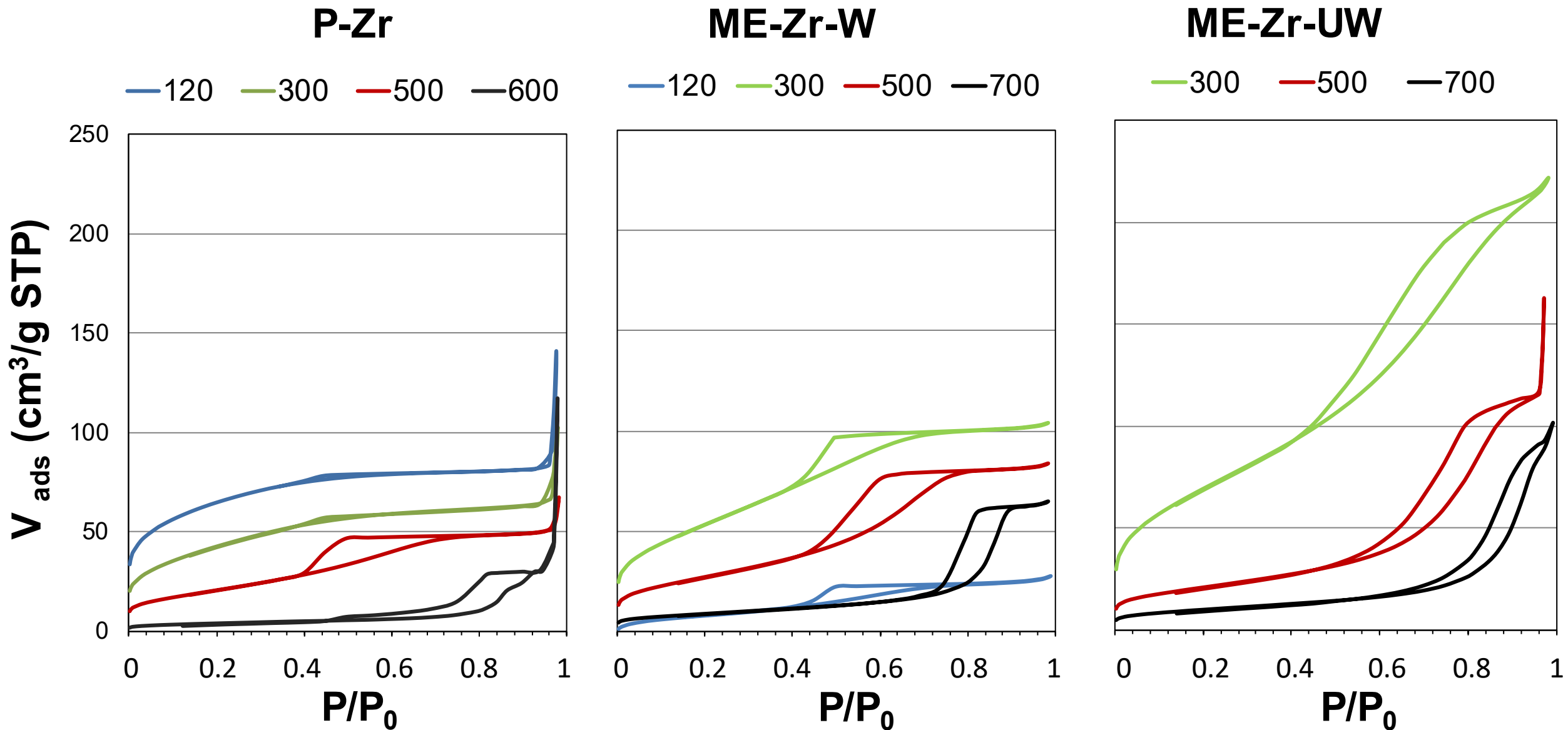
FIGURE S1A
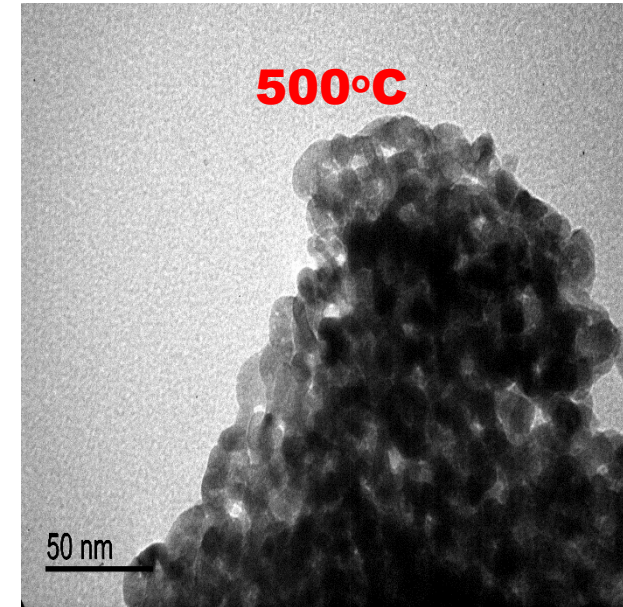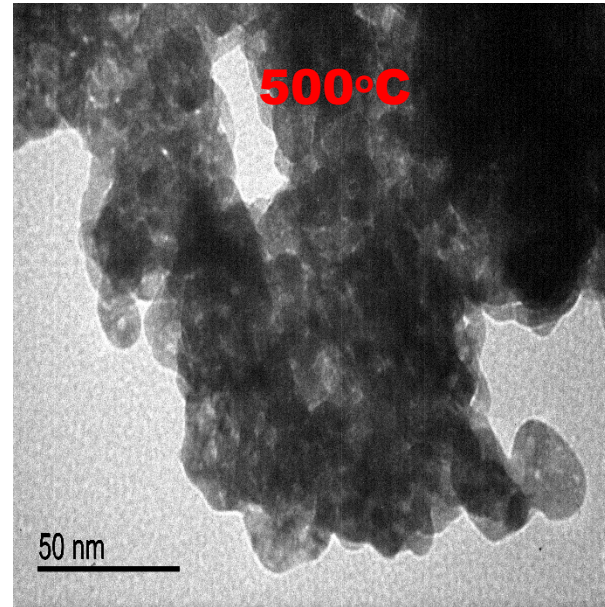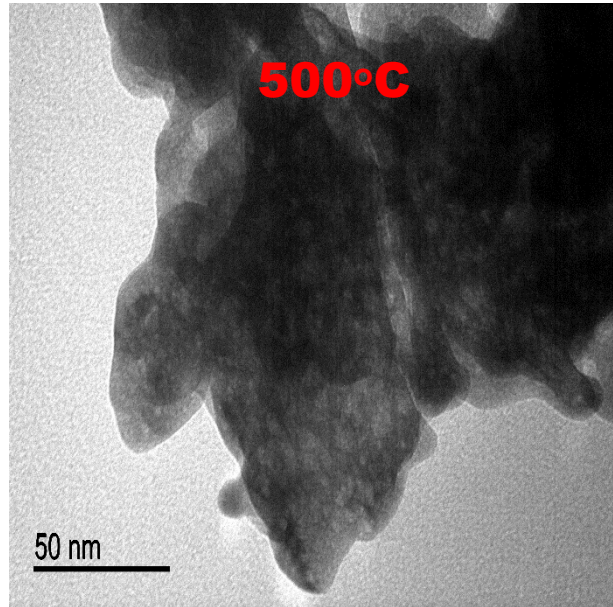
FIGURE S1B
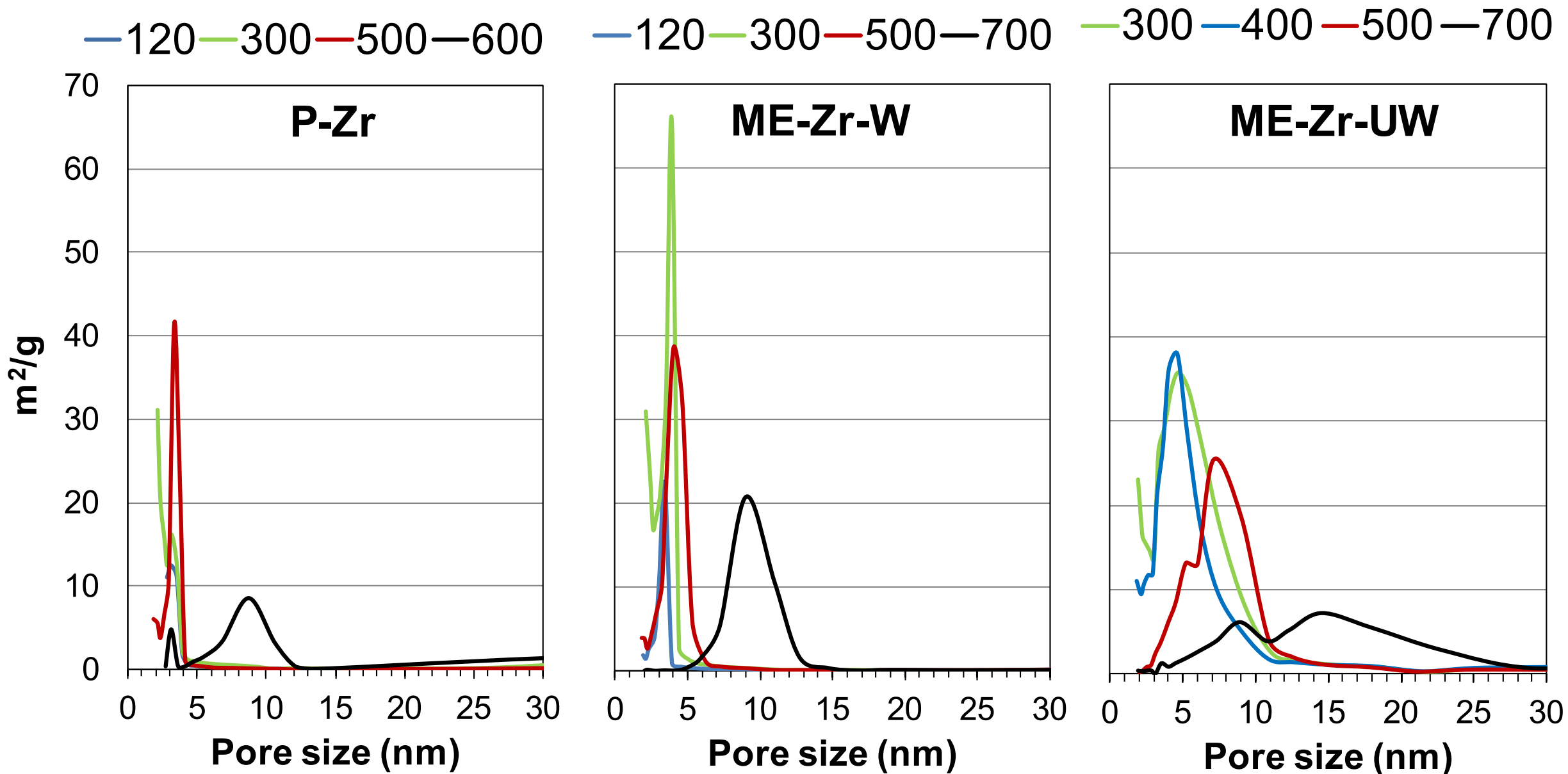
FIGURE S2
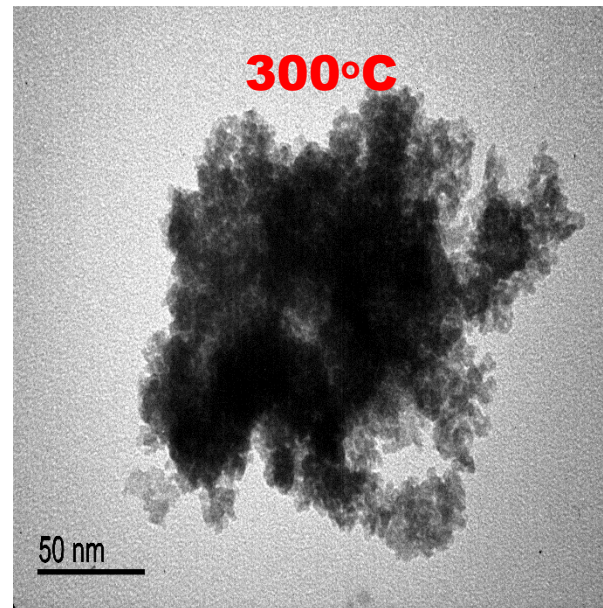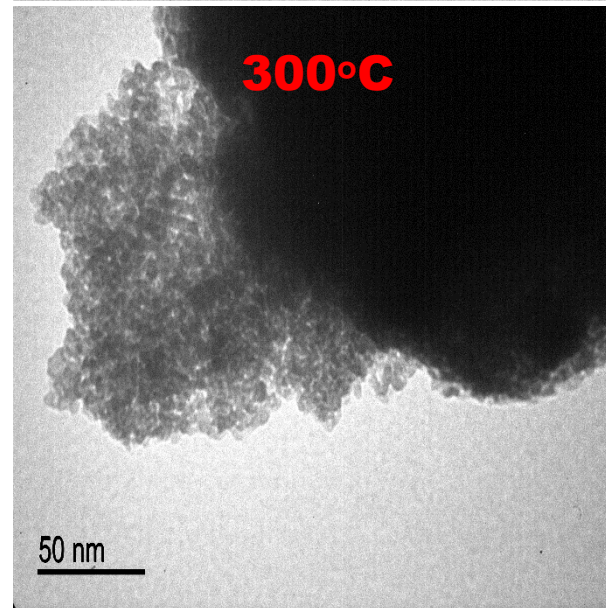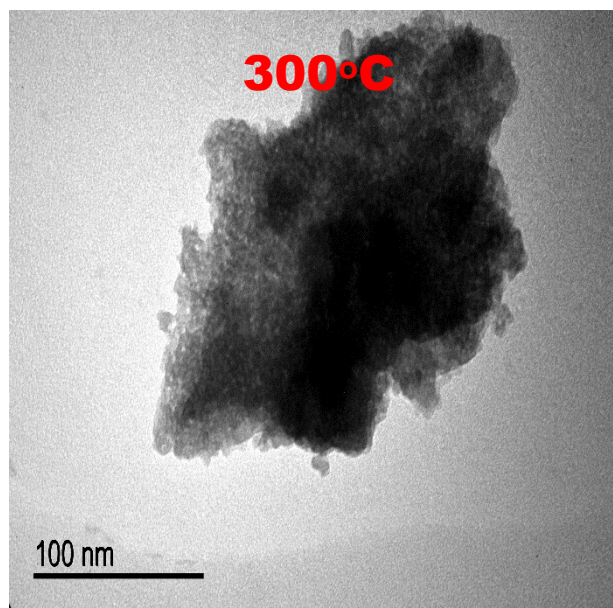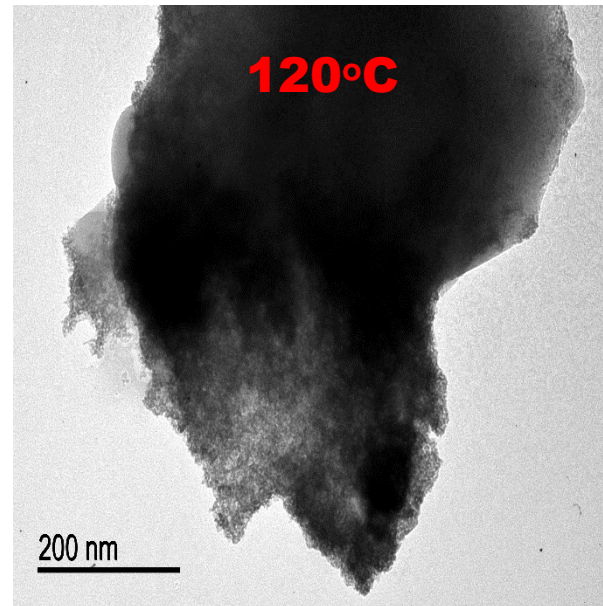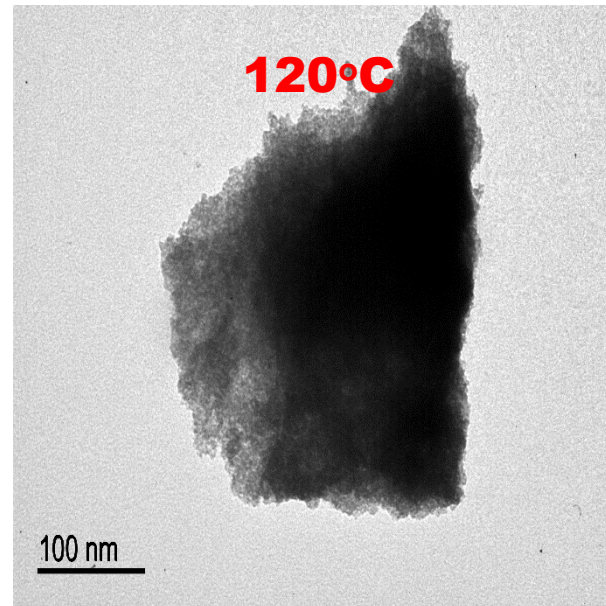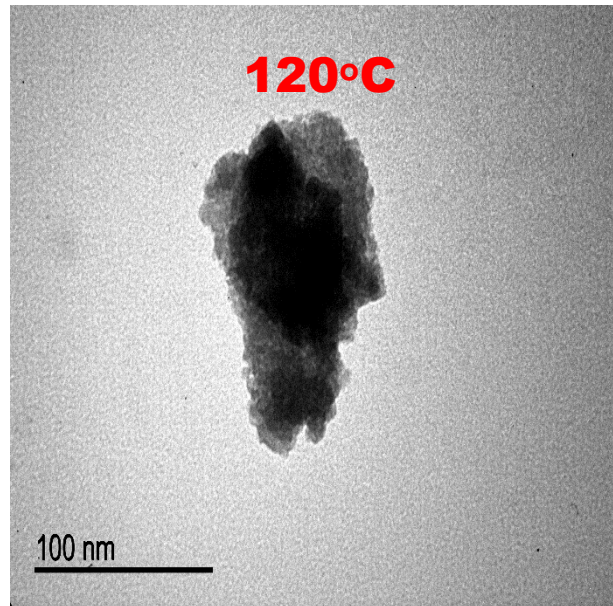
FIGURE S2 (cont)

P-Zr   ME-Zr-W   ME-Zr-UW

FIGURE S3