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The Synthesis and Evaluation of Up-scalable Molybdenum Based Ultra Dispersed Catalysts: Effect of Temperature on Particle Size

**John Thompson · Alejandro Vasquez ·
Josephine M. Hill · Pedro Pereira-Almao**

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Abstract Unsupported molybdenum (Mo) micro/nano-particle size range catalysts have been synthesized via precursor salts dissolved within a water-in-oil emulsion and online injected to a decomposition zone simulating processing conditions. The particles were characterized via DLS, reactivity tests and SEM. The effect of decomposition temperature on particle sizes was studied in both a horizontal reactor and vertical reactor configuration.

Keywords Mo catalyst · Nanocatalyst synthesis · Hydroprocessing · Hydrotreating · Sub-micron catalyst synthesis · Water-in-oil emulsion · Nanoparticle

1 Introduction

Heavy oils are starting to play a significant role in the world energy market as the demand for transportation fuels increases, and the reserves of conventional oil decrease. These oils are more viscous than conventional oils and also contain a significant amount of impurities including sulfur, nitrogen and metals (such as nickel and vanadium). These impurities deactivate the catalysts used in typical processing operations. Thus, in order to produce and refine heavy oils, more advanced technologies, including more efficient catalysts for hydroprocessing, are required [1].

Molybdenum (Mo) based catalysts have been widely used in the petroleum industry for the hydroprocessing of heavy oil fractions [2]. Typically, commercial hydroprocessing catalysts are supported on alumina and used in a fixed or ebullated bed reactor. These catalysts are prone to deactivation because carbonaceous materials or metals deposit at the mouth of the pores of the alumina, causing pore-mouth plugging [3]. As an alternative to supported catalysts, unsupported catalysts have been developed and in particular UD catalysts are of great interest for the processing of heavy feedstock [4]. These catalysts can be discarded when the proportion of catalyst to product needed is extremely low and when the catalyst remaining with the products no longer has a significant impact on the product specifications or quality. These catalysts can also be recycled depending on the process economics. UD catalysts have particular advantages in the upgrading of heavy oil feedstock due to their greater surface area of accessible active sites leading to an increase in the reactive site-to-mass ratio, thereby allowing large complex molecules (i.e. heavy hydrocarbons) to reach active sites rather than plugging pores as is the case in supported catalysts. The methods that have been used to produce materials of nanometer structure include acidification of organometallic compounds [5], thermal decomposition of organometallic compounds [6], metal evaporation [7], the reduction of metal salts [8], and sonochemical decomposition of metal carbonyl compounds [9]. With respect to the decomposition of organometallic compounds from oil-in-water emulsion mediated routes, there are a limited number of oil-soluble Mo compounds, and these compounds have limited solubility with high associated costs. Under a thermal treatment, less expensive water-in-oil emulsions can be easily decomposed to give rise to a slurry of fine submicron solid particles, which can be successfully used in the upgrading of heavy feeds [10].

J. Thompson · A. Vasquez · J. M. Hill · P. Pereira-Almao (✉)
Schulich School of Engineering, Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada T2N 1N4
e-mail: ppereira@ucalgary.ca

Prior to the 21st century there was little published research on Mo-based nanoparticle synthesis for hydroprocessing reactions from the decomposition of water-in-oil emulsions. Recently however, studies have been performed that have indicated that decomposition temperature, residence time, water-to-oil ratio, and surfactant concentration all have an effect on the size of the molybdenum oxide particles produced for such reactions [11–13].

This paper examines the effect of decomposition temperature on particle size for molybdenum oxide catalysts synthesized from a water-in-oil emulsion method. These catalysts were prepared in a continuous mode designed for online application to conventional above-ground hydroprocessing facilities or to in situ upgrading, whereby the reservoir itself acts as a reactor. For the purposes of establishing preparation and characterization procedures, catalysts were prepared in the less active oxide form (MoO_x) and were not presulphided (MoS_x) before use, as would be the case for industrial hydrotreating processes. Two preparation units were designed. The first unit featured a horizontally positioned reactor (HR) and the second was constructed with a reactor, which was vertically positioned (VR) in order to study the influence of the flow dynamics regime on particle synthesis. The texture (i.e. size and shape), crystalline structure, surface area and particle size were determined using scanning electron microscopy, X-ray diffraction, nitrogen physisorption and dynamic light scattering, respectively. Catalysts from the HR runs, JMT-026 (synthesized at 498 K) and JMT-028 (synthesized at 598 K), were tested for their reactivity in the conversion of toluene to hydrodearomatized products. The emulsions were formulated with high boiling point lubricant base oil whose gas fraction may be neglected at the temperature range studied and the experiments were all performed at a constant emulsion flow rate.

2 Experimental Section

2.1 Catalyst Preparation

Unsupported molybdenum catalysts were prepared via flashing and decomposition of water-in-oil emulsions consisting of the non-ionic surfactant sorbitan monooleate (Sigma-Aldrich Span 80), base oil (Imperial Oil MCT 10, IBP 623 K), ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Strem Chemicals, 99.98% Mo), and distilled water. All experiments were conducted at atmospheric pressure and all emulsions were prepared using 150 g of oil and 16.8 g of water (corresponding to 10% by wt.). 9 g of surfactant was added to each mixture to reduce the interfacial tension between the continuous oil phase and water droplets. The mixtures were blended in a homogenizer (IKA Ultra-Turrax T25 Basic) for 6 min at a speed of 24,000 rpm to produce the inverse micelle emulsions. A high surfactant concentration was used due to the inherent instability of the emulsion at lower concentrations. The high boiling point translucent base oil was selected as the continuous phase to enable particle size measurement via dynamic light scattering.

Figure 1 is a schematic of the process showing the HR and VR preparation units used to study the behaviour of emulsion decomposition and particle synthesis. The first set of experiments was generated by pumping the prepared emulsions through the HR unit while the second batch was carried out using the VR unit. The reactors were heated to temperatures ranging from 498 to 598 K (experiments conducted in 25° increments) using insulated heating tapes, while being monitored and controlled using a 3-point type-K temperature probe and a PID temperature controller (OMEGA) with solid-state relays (Model SSRL240DC10, OMEGA Engineering Inc.). The reactors used in the decomposition of the emulsion consisted of 9.5 mm (0.375 in.) diameter, 0.0889 mm (0.035 in.) wall thickness and 381 mm (15 in.) long stainless steel tubes, heated in two sections with ribbon heating tapes.

Using a precision high pressure dual-syringe pump (Teledyne ISCO, Electric Valve Dual Pump), blank emulsions (with no dissolved salt) were pumped through the reactors at constant flow rates of 250 $cm^3\ h^{-1}$ (for HR unit) and 200 $cm^3\ h^{-1}$ (for VR unit) until steady-state temperatures were achieved. Once steady state was achieved, and the remaining blank emulsion pumped into the system, the second of the two pumps was activated and the metal-based emulsion was injected at flow rates mimicking the blank emulsion settings to avoid temperature fluctuation in the decomposition zone. Experiments between the HR and VR configurations were conducted to determine if the flow type affected the results. The liquid product from either set-up was collected at the exit of the flash separator for DLS analysis, and for separation in a high-speed (6,000 rpm) centrifuge (MPW-350/110 V, MPW Instruments), followed by solvent washing and drying to obtain a solid product free of most hydrocarbon.

Figure 2 illustrates an example of temperature control achieved during experimentation using LabView 7.0 (National Instruments). The slight disturbance in the temperature profile, which appears within the first few minutes of the recording is attributed to switching over from pumping the blank-emulsion to the molybdenum-emulsion. Following this transition, steady-state temperatures are observed.

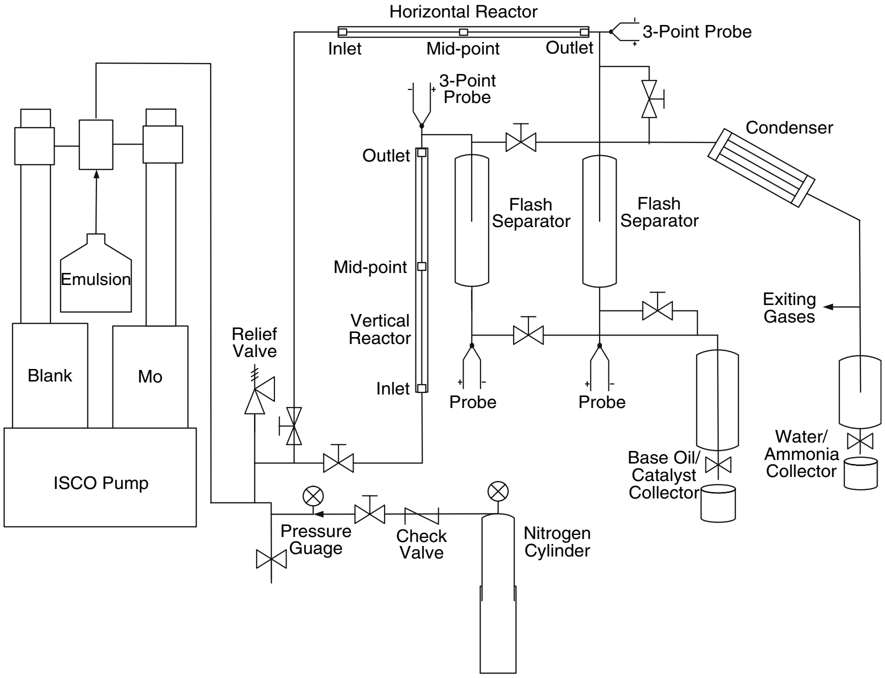


Fig. 1 Schematic of catalyst preparation unit

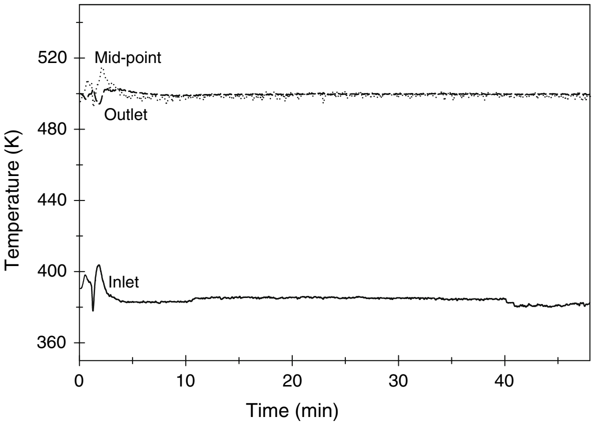


Fig. 2 Typical temperature profile achieved during catalyst synthesis in HR at 498 K

2.2 Catalyst Characterization

2.2.1 Particle Size Determination

Particle size of UD catalysts is an extremely important parameter because it is the essential parameter in determining the surface area, assuming internal porosity within the catalyst particles is either very small or negligible for large molecules of heavy hydrocarbon fractions. Due to the submicron nature of the manufactured catalyst particles produced in the oil media for these experiments, the diameters of the Mo particles produced were determined using a dynamic light scattering (DLS) technique with a Zetasizer Nano S (Malvern Instruments). The DLS instrument was equipped with a 4.0 mW He–Ne laser (633 nm) and operated at an angle of 173° and a temperature of 298 K to obtain the particle size distribution width (i.e. polydispersivity) and average particle size (i.e. *Z*-Ave) of the suspended particles.

In organic media an ion charge layer (i.e. stern layer) is not present reducing the interaction of the particles with the solvent media, thus not affecting the direct measurement of the DLS. Particles suspended in oil tend to both agglomerate and settle. Sonication before the measurement disperses the particles. However, there is a critical time in sonication beyond which re-agglomeration occurs. A sonication time of 10 min for each sample was used to disperse the sub-micron particles as it was found that sonication periods under 10 min did not completely re-disperse the particles and periods greater than 20 min resulted in re-agglomeration of the particles [11].

Particle concentration is an important parameter in DLS analysis. A high particle concentration results in increased particle sizes due to the effects of agglomeration. These particle sizes can be increased to degrees beyond the measurement limitations of the instrument ($\geq$10μm). DLS results are only comparable with other techniques if the samples are monomodal (i.e. only one peak), spherical and monodispersed (i.e. no width to the distribution), and the samples are prepared in the correct dispersant [14]. The width parameter is known as the polydispersity index (PDI). PDI values below 0.1 correspond to reasonably narrow monomodal samples suitable for such comparison. High particle concentrations also lead to high sample opacities which also prevent the instrument from providing meaningful measurements. For these reasons, the catalyst particle/oil products produced from the preparation unit were dispersed with additional fresh (i.e. 'particle-free') base oil to obtain reasonable signal to noise ratios. Two dilution ratios were used to demonstrate the effect of increasing the particle concentration on the particle size measurement: 1 part catalyst/oil product plus 9 parts fresh base oil and 1 part catalyst/oil product plus 2 parts fresh base oil. The samples were transferred into 12 ml screw-cap glass vials and shaken for 5 min using a Burrell Model 75 Wrist Action Shaker (Burrell Scientific) before being placed in the sonication bath prior to DLS analysis.

Scanning electron microscopy (SEM) images were captured using an environmental SEM (Phillips XL-30 ESEM). This technique was used to confirm the measured particle sizes and size distributions obtained through DLS and to examine the particle morphology. In preparation for SEM analysis, the particles were washed twice with toluene and then once with hexane and were allowed sufficient time to dry at room temperature in a fume hood. The particles were then pulverized as part of the preparation for SEM before being sputter coated with gold to improve their electrical conductivity to ensure image quality.

2.2.2 *Compositional Analysis*

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex X-ray diffractometer using Cu/Kα1 radiation ($\lambda = 1.54056$ Å) at 40 kV tube voltage and 40 mA tube current with a scanning speed of 2 °/min between 3° and 60° 2θ. The XRD patterns were referenced to the powder diffraction files (International Centre for Powder Diffraction PDF 2001) using the analysis software (JADE 6.5 Materials Data Inc.) for identification.

2.3 Reactivity

Reactivity tests were performed using a high pressure stainless steel catalytic reactivity test apparatus connected to a gas chromatograph (Hewlett Packard HP 6890 Series GC System) using hydrogen as the carrier gas. Toluene hydrodearomatization was used as a test reaction to allow estimation of both cracking as well as hydrogenating capabilities of the catalysts. Although the catalysts are ultimately intended to be used in an ultra-dispersed state, for the purposes of the reactivity testing they were centrifuged from the oil media, washed with toluene twice and hexane once, dried, and pressed at 6.895×10^7 Pa (10,000 psi) into pellets prior to being loaded in the reactor. Surface area analysis was performed on both pellets used for reactivity testing. Testing was performed in a continuous mode studying toluene conversion and product yields at two temperatures, namely 623 and 673 K.

3 Results and Discussion

3.1 Particle Size Determination

3.1.1 *Dynamic Light Scattering*

Figure 3 illustrates typical DLS output in measuring both the average polydispersivities and average particles sizes of a single experimental run at two distinct dispersant ratios, each measured four times in succession with intervals of 3 min between readings.

Figures 4 and 5 illustrate the effect of decomposition temperature on synthesized average particle size. Upon inspection, it is clear that the average particle size increases as the decomposition temperature increases for both HR and VR experiments.

For all tested decomposition temperatures it is also evident that the VR unit produced larger particles. However, it should be noted that the VR unit used an emulsion

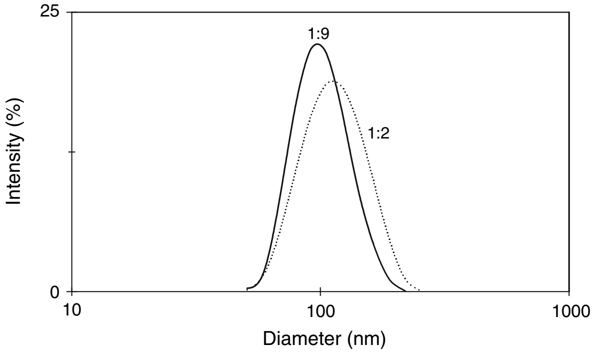


Fig. 3 DLS analysis of particles synthesized in HR at 498 K with product-to-base oil dispersant ratios of 1:9 and 1:2, corresponding to *Z*-averages of 98.5 and 110.4 nm, respectively and PDIs of 0.136 and 0.175, respectively

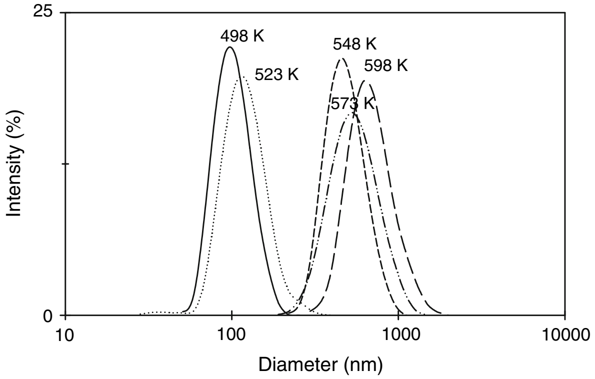


Fig. 4 Effect of temperature on DLS particle size and dispersivity for HR experimental runs with catalyst/oil product-to-fresh base oil dispersant ratio of 1:9

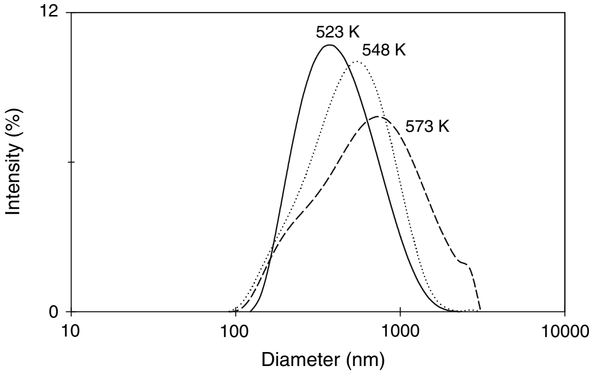


Fig. 5 Effect of temperature on DLS particle size and dispersivity for VR experimental runs with catalyst/oil product-to-fresh base oil dispersant ratio of 1:9

flow rate of 200 cm^3 h^{-1} resulting in a greater residence time of 5.2 min, compared to the residence time of 4.1 min for the HR set-up and previous work has shown that an increase in residence time leads to an increase in particle size [11]

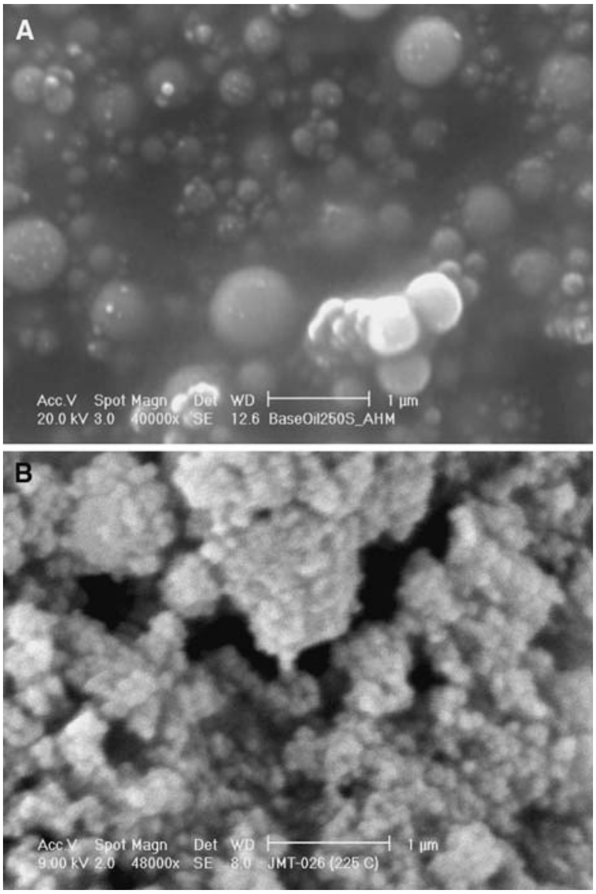


Fig. 6 Scanning electron microscope images of produced particles from VR at 523 K (**a**) and HR at 498 K (**b**)

3.1.2 Scanning Electron Microscopy

Figure 6 shows representative images of molybdenum-based particles from VR (a) and HR (b) configurations. These images indicate that primary or minimum particle sizes ranging between 50 and 70 nm have agglomerated into larger particles (several hundred nm). The spherical particle shapes observed suggest that the particles are suspended as a different phase (inorganic) within a liquid and possibly submitted to numerous collisions.

3.2 X-Ray Diffraction

All XRD diffraction patterns were amorphous, consistent with those obtained from the work of Wang, Hill and Pereira [11, 15]. Figure 7 illustrates that these patterns are also partially composed of MoO_2 and MoO_3 species. The sharp peak observed near 12 observed for the catalyst prepared at 473 K (denoted by ‘x’) demonstrates that the ammonium molybdate precursor salt did not fully decompose at this low temperature as this peak is representative of compounds containing molybdenum and ammonium (e.g. PDF#39-0035 > ammonia molybdenum oxide, PDF#18-0117 > ammonium molybdenum oxide, PDF#21-0571 > molybdenum oxide ammonia hydrate, PDF#47-0872 > molybdenum trioxide hydrate) [16].

Figure 8 presents the effects of reactivity on the crystal structure of a pelletized catalyst. For the catalyst before reaction, the broad amorphous peak spanning 25–30 , common to all experimental runs, spans the region that includes the predominant characteristic peaks corresponding to the MoO_2 and MoO_3 species. The peak near 40 for the catalyst after reaction closely corresponds to the published peak for the molybdenum carbide (Mo_2C) crystal structure (PDF#35-0787) [16].

3.3 Activation Energy of Agglomeration Process

To reveal the nature of particle agglomeration (being either a physical or chemical process), an investigation into its energetics was performed.

It follows that the concentration of particles in the system at any given time is inversely proportional to the average particle size (agglomerated) at any given time during the early stages of aggregation. This can be expressed as

$$[\phi_i] \sim \frac{1}{[\bar{\phi}_t]}. \tag{1}$$

It can be assumed that in a highly dispersed system of particles with small diameter and low concentration, the aggregation of particles can be treated like a simple chemical reaction:

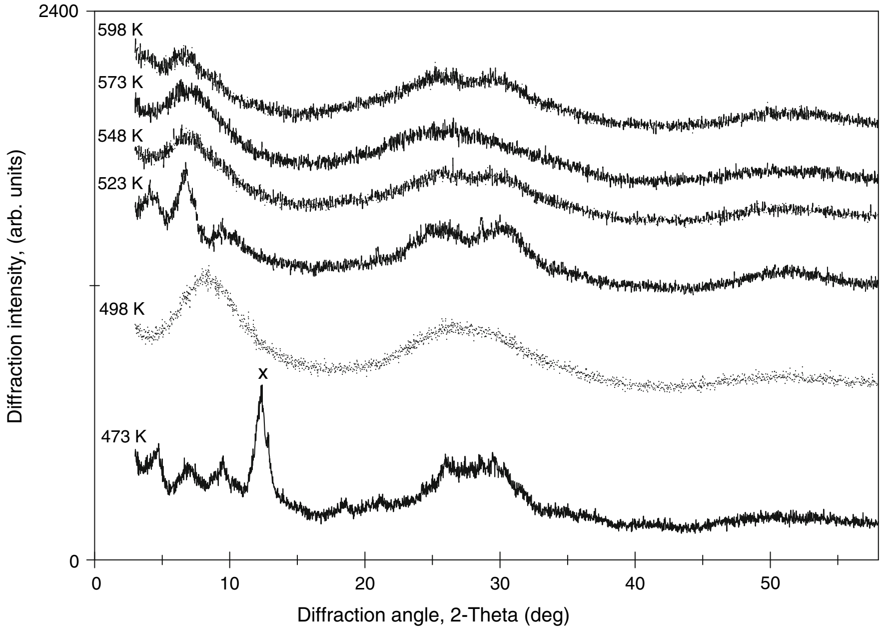
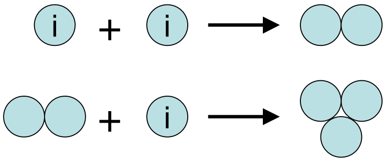


Fig. 7 XRD analysis of molybdenum-based particles produced from HR



Using a power law expression the following expression for the newly entitled ‘agglomeration reaction’ is obtained:

$$-\frac{\partial[\phi_i]}{\partial t} = k[\phi_i]^{\alpha}. \qquad (2)$$

From Eq. 1,

$$\partial[\phi_i] = \partial\left[\frac{1}{[\bar{\phi}_t]}\right] \quad \text{or} \quad \partial[\phi_i] = -\frac{\partial\bar{\phi}_t}{\bar{\phi}_t^2}. \qquad (3)$$

Substituting Eq. 3 into Eq. 2 provides:

$$\frac{\partial\bar{\phi}_t}{\bar{\phi}_t^2 dt} = k^1\left[\frac{1}{\bar{\phi}_t}\right]^{\alpha}.$$

If $\alpha = 1$ it follows a first-order reaction rate expression:

$$\frac{\partial\bar{\phi}_t}{\partial t} = k^1\bar{\phi}_t.$$

If $\alpha = 2$ it follows a zero-order reaction rate expression:

$$\frac{\partial\bar{\phi}_t}{\partial t} = k^1$$

where k^1 is a constant.

Figure 9 presents Arrhenius plots of the particle diameter versus decomposition temperature. The activation energy for the process of particle growth was calculated to be 52 and 36 kJ mol^{-1} for the HR and VR units,

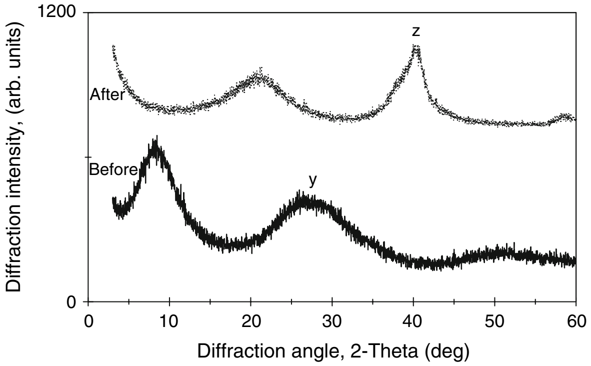


Fig. 8 XRD analysis of molybdenum-based catalyst particles synthesized at 498 K in the HR preparation unit before and after reactivity

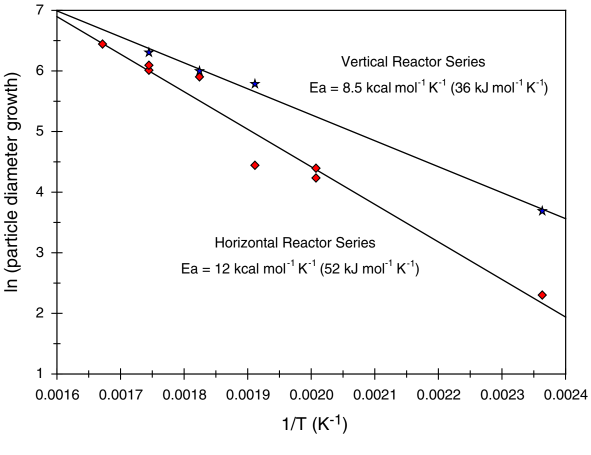


Fig. 9 Effect of decomposition temperature on particle size growth at atmospheric pressure for HR and VR units based on first order reaction kinetics

Table 1 Comparison of DLS results between HR and VR configurations using a catalyst/oil product to base oil dispersant ratio of 1:9

Decomposition temperature (K)	HR *Z*-Ave (nm)	VR *Z*-Ave (nm)
498	99	N/A
523	115	399
548	463	498
573	473	610
598	659	N/A

respectively, based on first order reaction kinetics using the data available in Table 1. It should be noted that the order does not have a significant impact on determining activation energy. It was assumed that the diameter of the first particles formed at an average value of 30 nm for the HR unit and 100 nm for the VR unit based on the smallest particle sizes measured through DLS (see Figs. 4 and 5); sizes which were confirmed through SEM analysis of the dried agglomerated particles (see Fig. 6). In the case of horizontal flow through the reactor at a temperature of 473 K, as previously stated, full decomposition of the precursor did not occur and is therefore not considered in the analysis of the agglomeration process.

The process of nanoparticle agglomeration may occur via reconstitution of large structural domains. For such a case the process would be of a chemical nature and it should be expected that with the formation of multiple bonds leading to stable solid larger particles that a highly exothermic reaction occur with a high activation energy value.

An activation energy of this low requirement (between 30 and 60 kJ/mol) is indicating that physical adsorption (resulting from simple Brownian collisions) with the participation of weak intermolecular forces, more than chemical binding, is the determining mechanism of agglomeration in the agglomeration process of nanoscale preformed catalytic particles. Both SEM and DLS analyses show that a distribution range of particle sizes is produced at every condition.

It is also assumed that these particles grow as a function of the concentration of particles, the residence time of the particles in the high temperature zone, the liquid nature and fraction in the decomposition zone, the geometry of that zone, and the temperature of the media. It is also expected that the viscosity of the media has an inverse effect on the particle growth. To keep these variables constant for evaluating the single effect of temperature is difficult, but it is presumed that, within a short range of temperature variation explored, these variables might not produce a significant impact to the qualitative conclusions derived from these results.

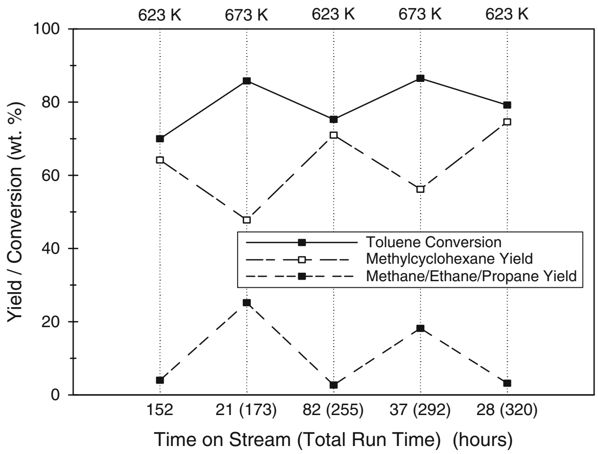


Fig. 10 Toluene conversion and product yields using 246 mg of catalyst (produced at 598 K), H_2 flow rate of 128 SCCM, WHSV of 3.4 h^{-1} and pressure of 6,000 kPa

3.4 Reactivity

Figure 10 presents the reactivity results, which confirm that the produced Mo-based particles are active catalysts. The reactivity experiment was performed in a continuum, i.e. the same catalyst sample was kept in the reactor for all (5) conditions of the run. Only temperature and time-on-stream (TOS) at each temperature were changed intentionally.

One conclusion that can be drawn from the results presented in Fig. 10 is that as TOS increases the catalyst becomes more active, which could signify the progressive formation or appearing of more active phases initially inexistent or veiled. A second observation is that increasing the reaction temperature increases the cracking of both toluene and methyl-cyclohexane in favour of methane. It also appears that the hydrogenation of aromatics improves with time. This may possibly be attributed to the bi-functionality of new active phases formed during the process, such as Mo_2C, apparently present in the catalyst as determined by X-ray diffraction analysis following reactivity testing (see Fig. 8). This argument is strengthened by reports that state molybdenum carbide is as active as noble metals (such as ruthenium) in liquid or gas hydrogenation reactions [17]. Another report describes transition metal carbides as having high hydrogenating properties [18].

It should also be noted that although no catalyst particles were evidenced downstream of the reactor vessel, approximately half of the weight of the catalyst was consumed during reaction for the reactivity test. This would increase the calculated WHSV values therefore providing less opportunity for toluene conversion. The weight loses may be associated to hydrocarbon moieties from the catalyst preparation stage that are progressively converted during the run time. Previous investigations regarding the catalytic performance of synthesized molybdenum oxide catalysts from water-in-oil emulsions list superior conversion of toluene into hydrodearomatized products in comparison to the results of this study [11, 15], however the WHSV used by Wang et al. was reported as being 0.7 h $^{-1}$, thus allowing the catalyst significantly greater time to convert the feedstock. Nevertheless, product distributions between the two studies were very similar.

4 Conclusions

The present study shows insight into the characterization of ultra-dispersed particles or nanocatalysts based on molybdenum for use as hydroprocessing catalysts. This ultra-dispersed solid has potential application for both in situ and ex situ upgrading of heavy oil. The particles were prepared via precursor emulsions, using inexpensive aqueous molybdenum salts in a continuous mode. The particles have average diameters in the nanosize range, as low as 30 nm. The activation energy estimate that was performed for both set-ups (horizontal and vertical positioned reactors), under a continuous mode, seem to reflect that simple collisions are at the basis of the agglomeration process regardless of reactor configuration.

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