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Silver Modified η -Al₂O₃ Catalyst for DME Production

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Abstract

Herein, an in-situ DRIFT technique was used to study the reaction mechanism of methanol dehydration to dimethyl ether (DME). Moreover, the effect of silver loading on the catalytic performance of η -Al₂O₃ was examined in a fixed bed reactor under the reaction conditions where the temperature ranged from 180-300 °C with a WHSV= 48.4 h⁻¹. It was observed that the optimum Ag loading was found to be 10% Ag/ η -Al₂O₃ with this novel catalyst also showing a high degree of stability under steady-state conditions and this is attributed to the enhancement in both the surface Lewis acidity and hydrophobicity.

1. Introduction

Air pollution and global warming due to the combustion of carbon-based non-renewable resources for transportation are two major global challenges. The production of clean biofuel such as dimethyl ether (DME) is an attractive alternative for pollution mitigation. DME is an environmentally friendly fuel with clean-burning and smoke-free emissions¹. The attractive combustion properties are due to it is containing neither sulphur nor nitrogen which leads to the absence of SO_x emissions and the possibility of the absence of NO_x emissions at low combustion temperatures. Usually, at high combustion temperatures, the release of NO_x emissions comes from nitrogen and oxygen of the air. The lack of direct carbon-to-carbon bonds means it does not generate particulate matter (PM) emissions. DME can be produced by two main routes; either from syngas using a bi-functional catalyst (Equation 1) or via the dehydration of methanol over solid catalysts such as Al₂O₃ (Equation 2), according to the following reactions¹⁻⁵:-



The synthesis of efficient and commercially attractive, robust catalysts has become increasingly challenging due to the both increased demand for DME production and the catalytic process required for methanol to DME process (MTD). Alumina is a cost-efficient material that can be tailored to unique textural properties including high surface area and high porosity. Therefore, optimizing Al₂O₃ as a catalyst for this process remains a topic of great importance⁶. Extensive studies were performed on γ -Al₂O₃ for MTD reaction, however, in our previous publication⁷; we showed that η -Al₂O₃ catalyst is more active than that of γ -Al₂O₃. Few publications have studied the mechanism and the kinetic modelling of η -Al₂O₃ in MTD reaction, therefore, this area requires further examination.

The dehydration reaction occurs over a solid acid catalyst where its acidity plays a big role in product distribution. Over very strong acidic sites, further dehydration will take place producing olefins. In order to suppress the dehydration to olefins reaction and increase the selectivity towards the DME, weak or moderate acidity catalysts are desirable as in the Al₂O₃. Methanol dehydration is known to take place on

Lewis acid-base pair sites and its rate increases as the surface Lewis acidity increases⁸. It was well reported that γ - Al_2O_3 , a typical Lewis acid catalyst and also the η - Al_2O_3 used in the study, can catalyse dehydration of methanol to DME⁷. Several reaction mechanisms have been presented for methanol dehydration on acid catalysts⁸⁻⁹. Either Brønsted acid sites or Lewis acid-base pair sites are believed to play a role in such reaction and, generally, the stronger the acid sites the more active the catalysts, however, it should be remembered that as far as Brønsted sites are concerned, their strength and the reaction temperature should be controlled to avoid hydrocarbons formations⁷. The mechanism based on the Lewis acidity, on the other hand, requires adjacent acid-base pair sites to provide the reaction between the adsorbed alcohol molecule on an acidic site and an adsorbed alkoxide anion on a basic site⁸.

The most widely used catalyst for the MTD reaction is Al_2O_3 however; modifications are needed to increase the weak acidity of alumina along with the water deactivation due to its superhydrophilic properties. To enhance the acidity, group 11 elements such as Cu, Ag and Au were used to improve the Lewis acidity as they act as electron acceptors. In a recent study by Camposeco et al.¹⁰, they studied the effect of Ag loading on the acidity of titania nanotubes by using FTIR analysis of adsorbed pyridine on the support. They found that after Ag loading, the Lewis acidic sites on the TiO_2 support increased. Gora-Marek et al.¹¹ also reported an increase in the Lewis acidity of different supports with Ag loadings and reported that silver cations act as strong electron acceptors which can also be considered as Lewis acids. Furthermore, they used the same catalyst ($\text{Ag}/\text{Al}_2\text{O}_3$) for selective ammonia oxidation and mentioned that the high catalytic performance of 10 wt. % $\text{Ag}/\text{Al}_2\text{O}_3$ was related to the specific interaction between the Ag and alumina support along with the high Ag dispersion over the surface of the alumina support.

Furthermore, in the MTD process water is produced which also has a significant effect on catalyst deactivation¹²⁻¹⁵ as Al_2O_3 is super-hydrophilic¹⁶, and facilitates strong water adsorption. Both water and methanol compete for adsorbing on the active sites of Al_2O_3 with water being adsorbed more strongly¹². It is possible to increase the hydrophobicity of the support thereby reducing the deactivation by water. Several techniques can be employed for this purpose; for instance, Zhao et al.¹⁷ used the electrodeposition

of silver aggregate to prepare superhydrophobic surfaces with water contact angle (CA) of 154°. An electroless galvanic deposition method was used by Feng et al.¹⁸ to fabricate superhydrophobic Ag nano-coatings with a CA of 156.4°, where the coatings showed a high thermal stability; the CA did not change with heating up to 200 °C for 2hrs. Li et al.¹⁹ prepared a superhydrophobic coating of silver-doped titania @ polycarbonate with a CA >160°. Wu et al.²⁰ demonstrated a convenient solution dipping method to make self-healing superhydrophobic materials using Ag nanoparticles that prepared from silver nitrate solution with a CA of 159 °. Recently, copper was used to prevent the strong binding of H₂O-Al₂O₃ by enhancing the surface hydrophobicity with CA =12° for 6% Cu/Al₂O₃ catalyst that was used for the MTD reaction²¹. Jo et al.²² reported that the addition of Si to η -Al₂O₃ by using TEOS (tetraethyl orthosilicate) enhanced the MTD conversion.

Ag/Al₂O₃ catalyst is commonly used in the catalytic reduction of NO_x reaction²³⁻²⁷. To the extent of the authors' knowledge, no research has been done using that catalyst in the methanol dehydration reaction to produce DME. The above discussion highlights the necessity of understanding the mechanism of MTD over η -Al₂O₃ catalyst along with the kinetic modelling study. Furthermore, the modifications of η -Al₂O₃ catalyst in term of the acid site strength and water deactivation need to be studied more closely. This suggests that the addition of a metal onto the support could modify the properties of the catalyst surface, for instance, the addition of silver to the alumina surface could decrease the water adsorption by changing the hydrophobicity of the surface, leading to an increase in activity. However, high Ag loadings could partially block the pore volume of the alumina support. The balance between these two effects suggests that an optimum loading exists where it is recognised that this will likely be a function of the original support. Herein, we studied the mechanism of the MTD reaction using the DRIFTS (Diffuse Reflectance Infrared Fourier Transform) technique along with the kinetic modelling. Moreover, we investigated the potential benefits of loading of Ag onto η -Al₂O₃ for the production of DME via the MTD reaction in term of dispersion, acidity and hydrophobicity.

2. Experimental

2.1 Materials and methods

The chemicals used in the present study were all of analytical grade and supplied by Aldrich, UK. The chemicals included aluminium nitrate nonahydrate $[\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, silver nitrate (AgNO_3 , >99%), Triethoxy(octyl)silane (TEOOS, $\geq 97.5\%$) and ammonia solution (35%). The commercial $\gamma\text{-Al}_2\text{O}_3$ (BET = $117 \text{ m}^2/\text{g}$, pore size = 1.035 nm) was prepared by crushing $\gamma\text{-Al}_2\text{O}_3$ pellets (Alfa Aesar). The He, H₂ and air gases were purchased from BOC with purity 99.99%.

2.2 Catalyst preparation

2.2.1 Pure catalyst:

The preparation of alumina supports has been described elsewhere ⁷. It was prepared from aluminium nitrate nonahydrate that was then precipitated by ammonia solution, the resulting precipitate was calcined at 550°C and designated as $\eta\text{-Al}_2\text{O}_3$.

2.2.1 Hydrophobic catalyst:

The preparation of the hydrophobic alumina was carried out using triethoxy(octyl)silane (TEOOS). Firstly, 5g of the $\eta\text{-Al}_2\text{O}_3$ catalyst was sonicated in 100 mL of toluene for 1 hr, afterwards, 3 mL of TEOOS was added then the whole solution was refluxed for 3hrs. Subsequently, a centrifugation at 4500 rpm was performed to recover the precipitated powder, followed by washing several times with toluene to remove the un-reacted TEOOS. Finally, the resulted powder was dried overnight at 120°C and designated as H- Al_2O_3 .

2.2.3 Silver metal loadings on $\eta\text{-Al}_2\text{O}_3$:

Silver loaded catalysts were prepared by wet impregnation with the aid of sonication. Pure $\eta\text{-Al}_2\text{O}_3$ was loaded with x% (wt/wt) of silver (where x = 1, 10 or 15%). Calculated amounts of silver nitrate were

dissolved and/or dispersed with a known amount of support, in ~ 5 mL deionized water. This was sonicated at 80 °C (Crest ultrasonic bath model 200 HT), at a frequency of 45 kHz, resulting in a homogeneous paste. All mixtures were then evaporated to dryness. Herein, catalysts loaded with 1, 10, and 15% which were then calcined 550 °C are denoted as follows: X%Ag/ η -Al₂O₃ where X is the weight percentage of Ag.

2.3 Catalyst Characterization

In-situ DRIFTS study of methanol dehydration over pure η -Al₂O₃ sample was performed during a temperature ramp from 50 to 250°C under reaction feed. The DRIFTS study was performed in order to investigate the adsorption/desorption properties of the catalyst surface towards methanol dehydration and to elucidate some aspects of the reaction mechanism over this catalyst, using a Bruker Vertex 70 FTIR Spectrometer equipped with a liquid N₂ cooled detector. Before exposure to the reaction feed, the pre-treated catalyst surface was taken as the reference and was subtracted as the spectra's background.

Powder X-ray diffraction (XRD) analyses of the catalysts were carried out using a PANalytical X'Pert Pro X-ray diffractometer. This diffractometer was equipped with a CuK α X-ray source with a wavelength of 1.5405 Å. Diffractograms were collected from 15° to 80°. The X-ray tube was set at 40 kV and 40 mA. Once the scan had finished, the main peaks were selected and compared to diffraction patterns from the software library. The pattern with the highest percentage match was used. The particle size was calculated according to the Scherrer equation.

Brunauer-Emmett-Teller (BET) analysis was performed using a Micromeritics ASAP 2010 system. The BET surface areas and pore volumes were measured by N₂ adsorption and the desorption isotherms at liquid nitrogen temperature (-196 °C).

TPD-pyridine was used to determine the total surface acidity of the catalyst using the adsorption of pyridine as a probe molecule. Small portions (50 mg) of each sample were pre-heated to 250 °C for 2 hrs in air before exposure to the probe molecule (pyridine) in a sealed desiccator for two weeks. The pyridine-covered samples were subjected to Thermogravimetric (TG) analysis on heating up to 600 °C at heating

rate of 20 °C.min⁻¹ in dry N₂ (flow rate = 40 ml.min⁻¹). The weight loss due to desorption of pyridine from the acidic sites was determined as a function of total surface acidity as sites.g_{cat}⁻¹ ⁷.

Temperature-programmed reduction (TPR) was used to investigate the reducibility of the catalysts using a Micromeritics Autochem 2910 apparatus with the H₂ uptake monitored by a TCD. The catalyst sample (0.1 g) was placed in a quartz tube and Ar flowed over it until the temperature decreased to 30 °C. 5% H₂/Ar with a flow rate 30 mL min⁻¹ was then passed over the catalyst until a stable baseline was obtained after which the sample was heated at 10 °C min⁻¹ up to 700 °C.

XPS was performed in a Kratos AXIS ULTRA spectrometer using monochromatic Al K α radiation of energy 1486.6 eV. High-resolution spectra of Ag 3d, O 1s and Ag MNN were taken at a fixed pass energy of 20 eV, 0.05 eV step size and 100 ms dwell time per step. Surface charge was efficiently neutralized by flooding the sample surface with low energy electrons. Core level binding energies were corrected using C 1s peak at 284.8 eV as charge reference. For construction and fitting of synthetic peaks of high-resolution spectra, mixed Gaussian-Lorentzian functions with a Shirley type background subtraction were used.

The relative strength of the Lewis acid sites was determined by DRIFT analysis of adsorbed pyridine using a Bruker Vertex 70 FTIR Spectrometer equipped with a detector cooled with liquid N₂. Prior to these measurements, samples were pre-treated by outgassing at 120 °C for 0.5 h under an Ar atmosphere. Subsequently, the samples were saturated with pyridine at 50 °C then the physisorbed pyridine was removed by flushing at ~25 °C with Ar gas for 0.5 h. Fresh samples (catalyst without pyridine) were used to record the IR background under Ar flow at 300 °C. Then, the pyridine (Py) adsorbed samples were placed in the DRIFT cell at 40 °C. The samples were heated under Ar at a flow rate of 50 cm³/min and the *in situ* DRIFT spectra were recorded at a resolution of 4 cm⁻¹ and with an accumulation of 56 scans every 30 s. The spectra after pyridine desorption were subtracted from those measured before pyridine adsorption (fresh samples) to observe the bands corresponding to Lewis and Brönsted acidic sites.

The static contact angle of the catalyst pellets with water was measured using a contact angle meter equipped with a CCD camera (FTA1000 Drop Shape Instrument- B Frame system). The morphology of the catalysts' surface was characterized by transmission electron microscopy (TEM) using a FEI Tecnai F20 at 200 kV using bright field TEM, selected area electron diffraction (SAED) and high angle annular dark field (HAADF) scanning TEM (STEM).

Scanning electron microscope (SEM) images were obtained on a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT microscope Control software.

2.4 Catalyst activity

Catalyst activity tests were conducted in an isothermal fixed-bed reactor made of stainless steel (6 mm OD). The catalyst bed consisted of 50-200 mg (250-425 μm) of a catalyst placed between two plugs of quartz wool. Aera mass flow controllers were used to control the flow of gases to the reactor. The liquid methanol was injected *via* a Cheminert® M Series liquid handling pump. A stable flow of methanol vapour to the reactor was established by passing the combined flow of He and methanol through a saturator system, with the evaporation chamber maintained at 150 °C. To prevent condensation, all lines were heated to \sim 150 °C. This mixture was then fed to the fixed bed reactor. The reaction conditions used were different % MeOH in the kinetic experiments and 20% MeOH in the Ag/ η -Al₂O₃ experiments under atmospheric pressure over a temperature range from 180 to 300 °C. The total flow rate was 100 cm³.min⁻¹. Before the reaction, the catalyst was activated in a stream of pure He at 325 °C for 3 h under atmospheric pressure. Then, the methanol and He mixture were fed to the reactor and samples analysed by on-line gas chromatography (Perkin-Elmer 500) equipped with a TCD and a Flame Ionisation Detector (FID). A Hayesep DB column was used for the separation of CO, CO₂, DME, MeOH, CH₄, C₂H₄, C₂H₆, ethanol, propanol, and butanol. Each data point was repeated 5 times to determine the reproducibility of the data for the products

As shown in Eq. 3, the methanol conversion (X_{MeOH}) was calculated on the basis of the molar flow rate of methanol in the feed ($F_{MeOH, in}$) and in the outlet stream ($F_{MeOH, out}$):

$$X_{MeOH} = \frac{F_{MeOH, in} - F_{MeOH, out}}{F_{MeOH, in}} \quad (3)$$

DME formation rate (r_{DME}) was determined using Eq. 4, which represents the actual moles of the produced DME per unit time ($F_{DME, actual}$) per gram of the catalyst:

$$r_{DME} = \frac{F_{DME, actual}}{wt. of the catalyst} \times 100\% \quad (4)$$

The selectivity for DME (S_{DME}) was determined using Eq. 5 as the ratio (expressed in mole%) between the content of carbon in the product DME and the sum of carbon content corresponding to all observed organic products which are present in the reactor outlet stream:

$$S_{DME} = \frac{2F_{DME}}{F_{CO_2} + F_{CO} + 2F_{DME} + \sum_i n_{Ci}F_i} \times 100\% \quad (5)$$

Here, F_{DME} , F_{CO_2} and F_{CO} are the molar flow rates of DME, CO_2 and CO respectively in the outlet stream, n_{Ci} is the number of carbon atoms for each of the hydrocarbons (byproducts) and F_i is the molar flow rate of these hydrocarbons²⁸.

3. Results and Discussion

3.1 Mechanism study of pure alumina using DRIFTS technique:

Figure 1 shows the DRIFT spectra of η - Al_2O_3 sample obtained during the exposure to the reaction feed with a stepwise increase in the reaction temperature. The spectrum obtained at 50°C is characterised by negative bands in the (3800–3500 cm^{-1}) region and bands at 3260, 2943, 2870, 2830, 2600, 2070 and 1450 cm^{-1} . The negative bands (i.e. 3763 and 3740 cm^{-1}) are attributed to the loss of hydroxyl groups initially present on the Al_2O_3 surface due to the formation of hydrogen bond between surface hydroxyl groups and the adsorbed methoxy species^{9, 29}. The broad peak around 3260 cm^{-1} is attributed to the stretching mode of these hydrogen-bonded hydroxyl groups^{9, 29}. The bands located at 2943, 2870 and 2830 can be attributed to the symmetric $\nu(CH_3)$ stretching mode of adsorbed methoxy groups produced due to the dissociative adsorption of methanol on the η - Al_2O_3 catalyst surface^{9, 29-31}. The band at 2600

cm^{-1} can be assigned to a combination band of two different modes (methyl rock and methyl deformation) of the adsorbed methoxy species ^{9, 29-31}. The band at 2070 is likely due to adsorbed CO which may form as a result of the decomposition of formate species while the band at 1450 cm^{-1} can be attributed to carbonate–carboxylate species ^{29, 32-33}. The formation of CO and carbonate–carboxylate species can be correlated to the occurrence of side reactions that are not involved in the dehydration reaction of methanol ⁹. The stepwise increase in the temperature of the reaction feed results in a progressive decrease in the intensity of the bands at 3260, 2600, 2070 and 1450 cm^{-1} . A progressive decrease in the intensity of the surface hydroxyl negative bands is observed by increasing the temperature which indicates a partial restoration of hydroxyl groups on the alumina surface ^{9, 29}. This is due to the desorption of some of the adsorbed methoxy species that form hydrogen bonds with these hydroxyl groups which is confirmed by the accompanying decrease in the intensity of the bands at 3260 and 2600 cm^{-1} . In addition, bands at 1599, 1390 and 1375 cm^{-1} corresponding to surface formate species started to appear at 200°C and became more intense by increasing the temperature up to 250°C ^{9, 29, 33-34}. Apart from the observed decrease in the intensity of some bands and the increase in the intensity of the others, there is no notable change in the band positions can be observed as temperature increases.

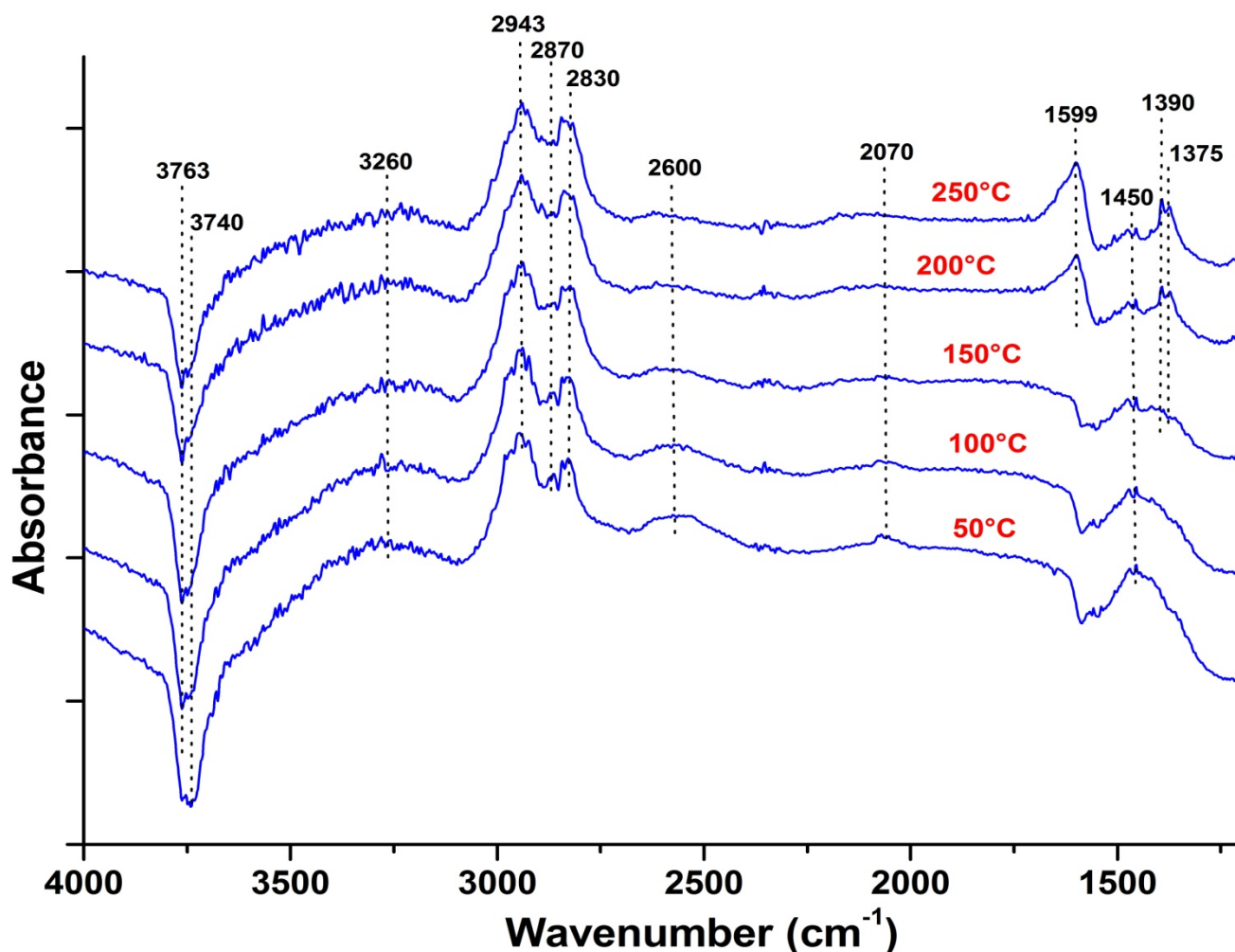


Figure 1: In-situ DRIFT spectra obtained over the pure η - Al_2O_3 catalyst during the interaction under reaction feed (20% MeOH+ He gas as an inert in the feed) at 50°C for 20 min followed by a stepwise heating to the indicated temperatures under the same reaction feed.

The mechanism of MTD over alumina catalysts may take place by two possible routes⁹: In the first route, the adsorbed methoxy species interacts with un-dissociated or molecularly adsorbed methanol, while in the second route, the reaction takes place between two adsorbed methoxy species. In the present study, the DME production started at temperatures higher than $\sim 200^\circ\text{C}$, which supports the second route, as only methoxy species and not un-dissociated methanol are present on the catalyst surface at this temperature or at higher temperatures.

4. Silver modification η - Al_2O_3

4.1 Catalyst characterisation

The XRD patterns of η -Al₂O₃ catalyst along with silver modifications at different levels of loadings (1, 10 and 15 wt. % Ag) are shown in Figure 2. The diffraction lines corresponding to the η -Al₂O₃ phase decreased with increasing the Ag loading, due to the metal coverage onto the η -Al₂O₃ support with increasing the silver metal loadings which is in agreement with the work done by Yuan et al.³⁵. The catalyst 15% Ag/ η -Al₂O₃ with the highest Ag loading showed diffraction lines related to hexagonal Ag₂O (100) at 2θ = 33.6 and 38.39 (JCPDS no. 72-2108) and minor diffraction line for the metallic silver at 2θ = 77.30 Å (ICDD 76-1393)³⁶. It is worth noting that all catalysts showed amorphous structures with broad diffraction peaks.

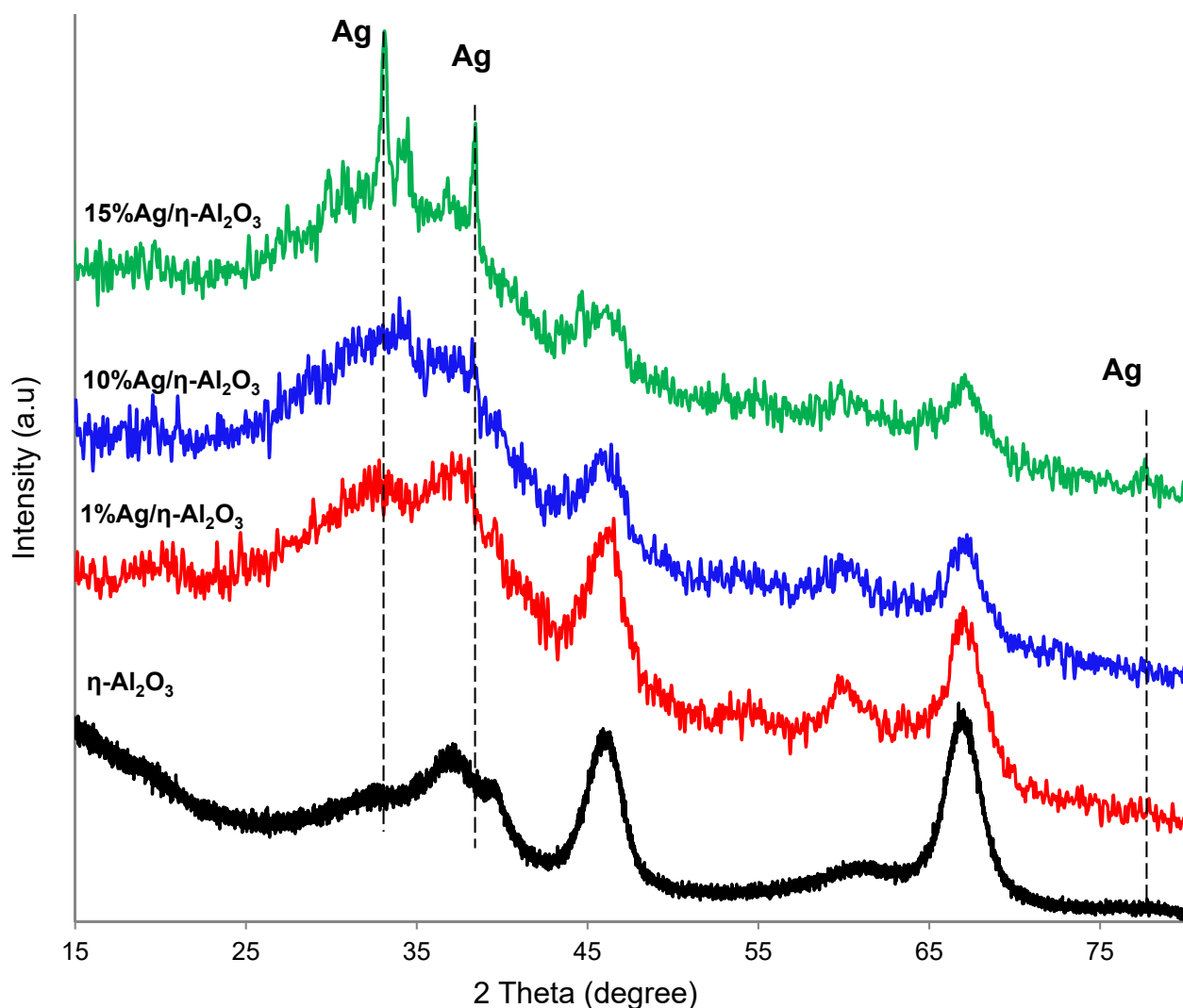


Figure 2: XRD patterns of η -Al₂O₃ catalyst along with silver modifications at different levels of loadings (1, 10 and 15 wt. % Ag).

Table 1: Surface area, pore volume, total acidity and acid density along with the EDX results of pure and Ag modified η -Al₂O₃ catalyst.

Support / Catalyst	S _{BET} (m ² g ⁻¹)	Cryst. size (nm)	Pore volume (cm ³ g ⁻¹)	Total acidity ^a , A(sites/g)	Acid density ^b , B(sites/m ²)	EDX results			XPS results	
						Al	O	Ag	I _{Ag} /I _{Al}	%C
η -Al ₂ O ₃	223	5.5	0.5	8.56	3.8	51.9	48.1	--	--	
1% Ag/ η -Al ₂ O ₃	222	3.1	0.33	8.76	3.95	43.5	55.5	1	0.01	10.2
10% Ag/ η -Al ₂ O ₃	218	3.8	0.27	9.80	4.5	32.5	57.5	10	0.07	13.7
15% Ag/ η -Al ₂ O ₃	202	4.2	0.26	9.82	4.8	33.3	51.0	15.7	0.11	14.5

^a Total acidity = A x 10²⁰, measured by TPD-Pyridine.

^b Acid density = B x 10¹⁸, , measured by TPD-Pyridine.

The Nitrogen adsorption-desorption isotherms of silver modified catalysts with different loadings (1, 10 and 15 wt. % Ag) on η -Al₂O₃ acidic support catalyst showed type IV isotherm of mesoporous structures implying a mesoporous structure. It is obvious that there is a slightly small difference in the pore volume after loading the Ag, where the pore volume decreased from 0.33 to 0.26 cm³/g at % loading of 1 and 15% Ag, respectively as seen in Figure S1. Furthermore, the surface area also declined from 222 to 202 at the same metal loadings as seen in Table 1. It is obvious that the total surface acidity and the acid density are increasing with increasing the Ag loadings.

The surface structure of the modified catalyst using the scanning electron microscope with both BSED (Back-Scattered Electrons Detector) and ETD detectors (Everhart-Thornley Detector) are shown in Figures 3 and S2, respectively. Elements of higher atomic number appear brighter in the image due to a large number of back-scattered electrons (BSE) ³⁷. It is apparent from Figure 3 that images of 15% Ag/ η -Al₂O₃ catalyst appeared with far more lighter spots than that of 1% Ag/ η -Al₂O₃ catalyst. Catalyst 10% Ag/ η -Al₂O₃ showed good pellet particle size distribution where at low loading (1 wt. %) Ag is hardly distinguished over the surface of the catalyst and at the highest loading (15 wt. %) Ag formed a separated island with big clusters that can be confirmed using the ETD detector as seen in Figure S3. However, the orientation of particles towards the detector plays also a significant role. So, image interpretation based on brightness is arbitrary unless it is a flat sample.

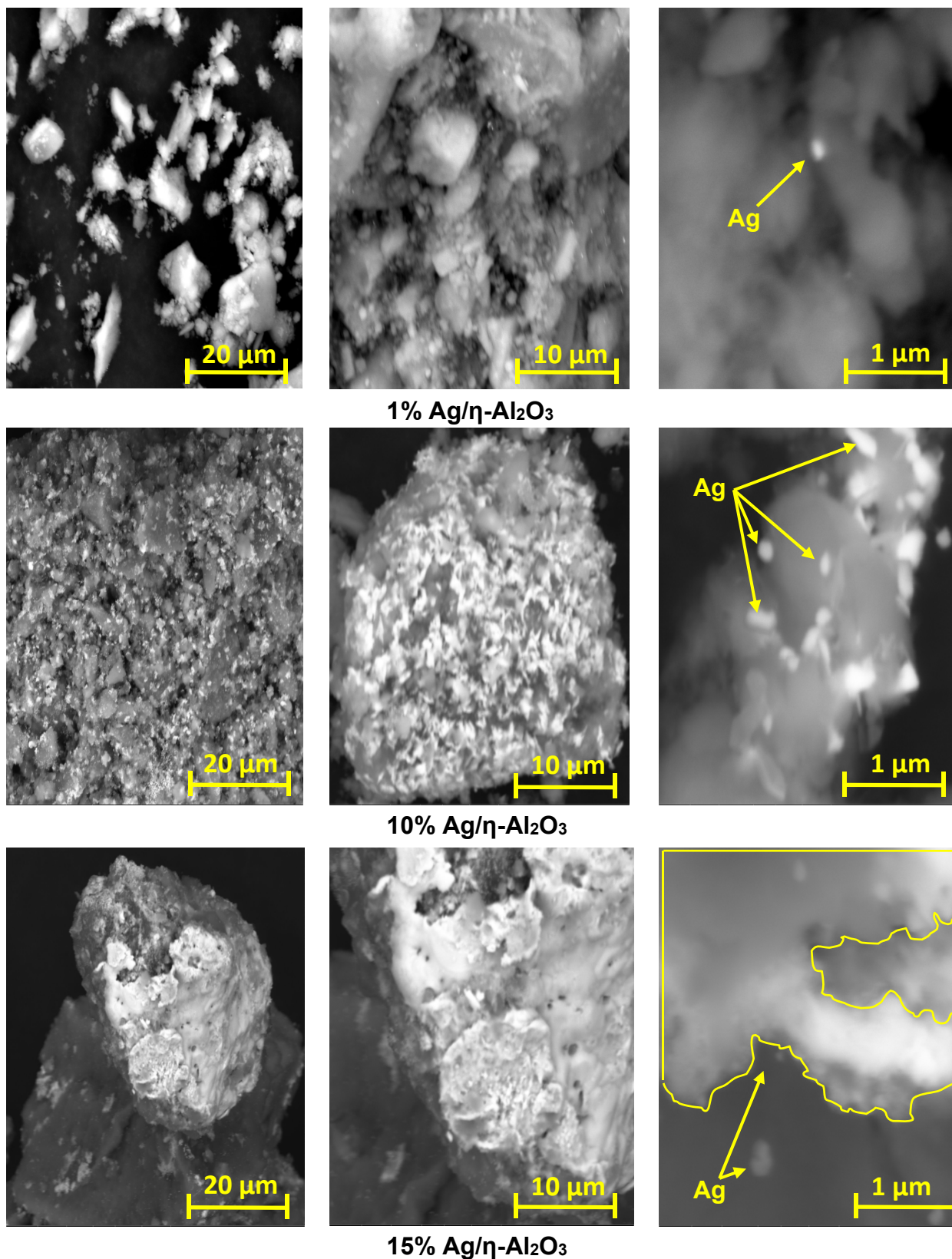


Figure 3: SEM images of 1% Ag/ η - Al_2O_3 , 10% Ag/ η - Al_2O_3 and 15% Ag/ η - Al_2O_3 catalysts at a different level of magnifications using the BSED detector where the Ag element is shown as bright areas on the image.

The EDX maps for the modified catalyst are shown in Figure 4. It is not surprising that catalyst 1% Ag/ η -Al₂O₃ showing the fewest spots of Ag over the surface of the catalyst. While 10% Ag/ η -Al₂O₃ catalyst showed good pellet particle size distribution among the series of the prepared catalysts. Further loading of Ag, 15% Ag/ η -Al₂O₃, apparently high concentration of Ag spots appeared with an isolated island formation along with darker spots i.e. less existence of alumina is observed over the Al maps as seen in Figure 4.

The elemental surface composition of the modified catalysts is shown in Figure S3 and Table 1. It is obvious that the wt. % of Ag increased with increasing the Ag loading with 1, 10 and 15.7 wt. % for 1% Ag/ η -Al₂O₃, 10% Ag/ η -Al₂O₃ and 15% Ag/ η -Al₂O₃, respectively. On the other hand, the wt. % of Al decreased from 43% to around 33% with increasing the Ag loading from 1 to 15 wt. %, respectively.

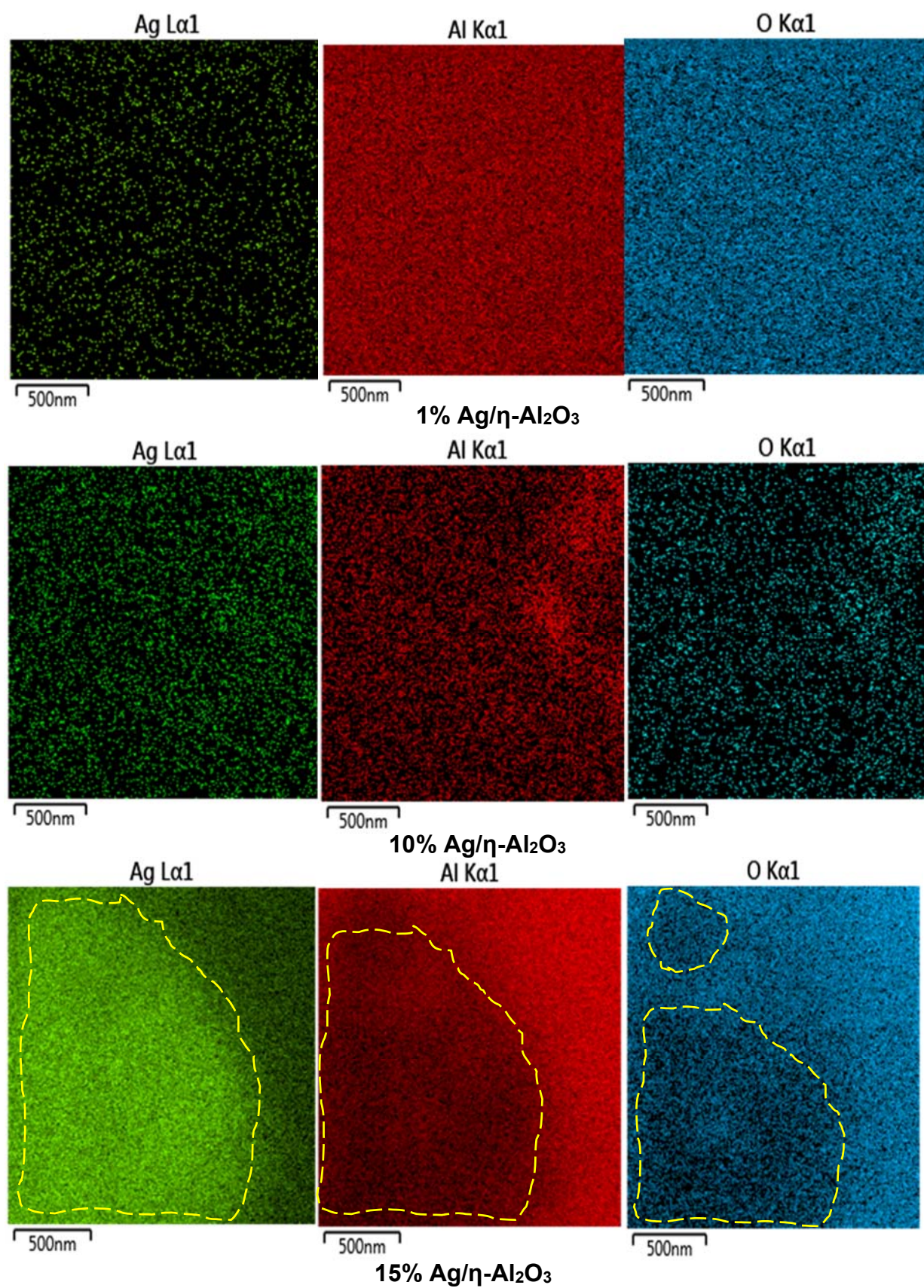


Figure 4: EDX maps of 1% Ag/ η -Al $_2$ O $_3$, 10% Ag/ η -Al $_2$ O $_3$ and 15% Ag/ η -Al $_2$ O $_3$ catalysts at the same level of magnification using the ETD detector.

The surface acidity of the pure and the modified catalysts were characterised using *in-situ* DRIFT-pyridine analysis as shown in Figure 5. The pure $\eta\text{-Al}_2\text{O}_3$ catalyst showed mainly Lewis acidic sites and the modified catalysts followed the same trend. The adsorption bands of pyridine at 1600 and 1445 cm^{-1} are ascribed to strong Lewis acidic sites while the band at 1582 cm^{-1} attributed to pyridine adsorbed on weak Lewis acidic sites. The adsorption band at 1482 cm^{-1} is attributed to pyridine adsorbed on both Lewis and Brönsted acid sites ⁷. The band intensities of pyridine on all sites were greater on the modified silver alumina catalysts showing a greater number of Lewis acidic sites than pure $\eta\text{-Al}_2\text{O}_3$. Apparently, the adsorption bands slightly increased with 1wt. % Ag loading, with a significant increase of Lewis acidic sites in 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ catalyst. These results in agreement with Camposeco et al.¹⁰ who investigated the surface acidity of Ag modified titania catalyst and showed that silver increases the Lewis acidic sites by forming Ag^{1+} ions on the surface of alumina catalyst. Silver increased the acidity of the pure support which may be attributed to the electronegativity. By adding more electron deficient element (Ag) with an electronegativity of 1.93 compared to the Al metal in the pure $\eta\text{-Al}_2\text{O}_3$ catalyst with an electronegativity of 1.61, then Ag will act as an electron acceptor due to its higher electronegativity. This hypothesis is in agreement with the work done by Gora-Marek et al. ¹¹ who reported an increase in the Lewis acidity of the supports with Ag loadings and reported that silver cations act as strong electron acceptors (higher electronegativity) which can also be considered as Lewis acids. The presence of Ag_2O species as confirmed by the XPS and XRD analyses along with the minor contribution of $\text{Ag}(0)$ increased the Lewis acidity, so in this case, the number and the strength of the acidic sites should be different from those of the pure $\eta\text{-Al}_2\text{O}_3$. The pyridine adsorption on Ag species was not excluded during the analysis.

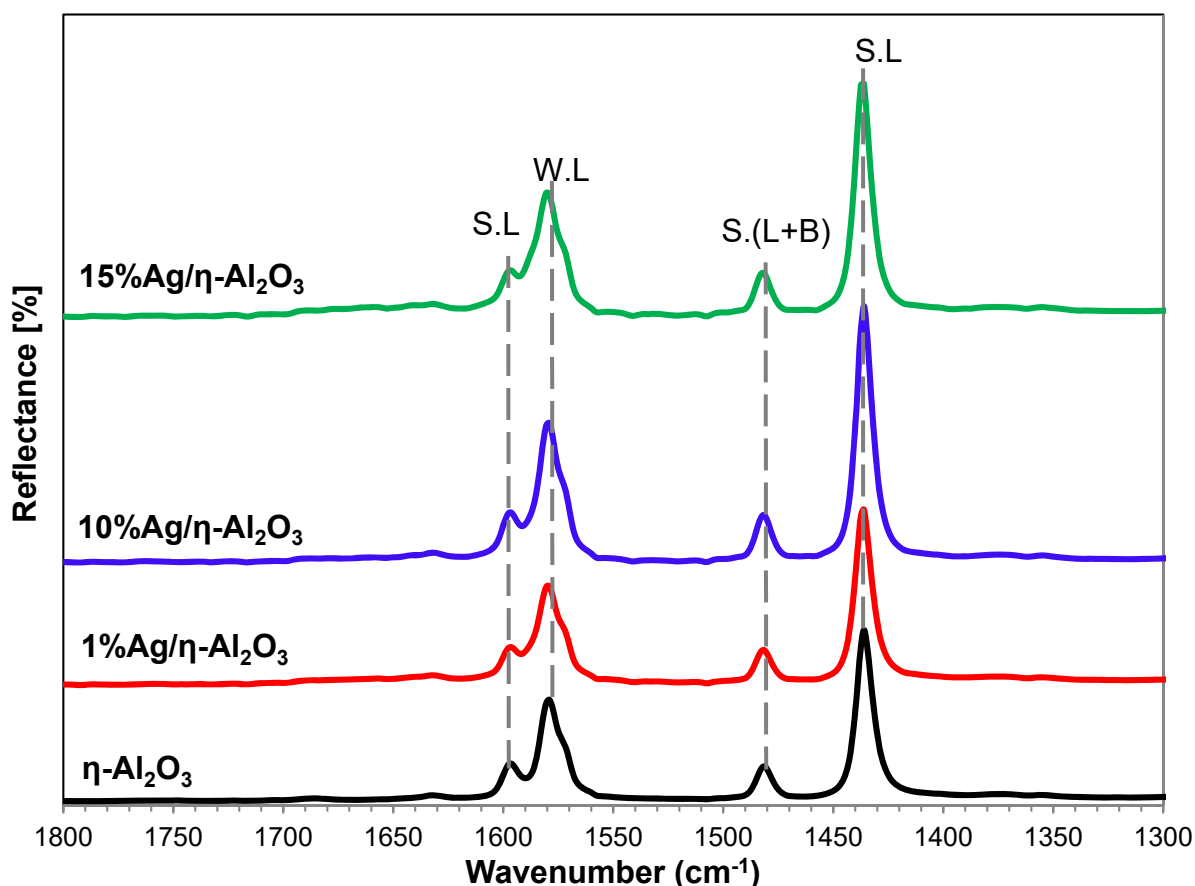


Figure 5: In-situ DRIFT spectra of pyridine adsorbed on the modified η - Al_2O_3 catalysts prepared from different loading of silver metal along with the pure η - Al_2O_3 catalyst.

XPS was performed to analyse the surface chemistry of the pure and Ag modified catalysts. High-resolution spectra of Ag $3d$ and O $1s$ (531.5 eV) along with the adventitious carbon (C $1s$) are shown in Figure 6³⁸. The principle Ag $3d_{5/2}$ peak at approx. 368.2 eV is broad and symmetric; and energy loss features related to metallic silver is not observed on the higher binding energy side of the peak and therefore it is suggestive of the presence of Ag_2O . As expected, the relative intensity of silver increases with increasing Ag loading. The O $1s$ characteristic of η - Al_2O_3 shifts to lower binding energy with increasing silver loading. Silver oxide appears at lower O $1s$ binding energy and as the silver loading increases, the contribution from the silver oxide shifts the oxygen peak to lower binding energies i.e. the Ag loading facilitates the oxidation cycle.³⁹ Since the modified catalysts were left in the air, the C $1s$ spectra showed component peaks corresponding to adsorbed carbonaceous species (CO, CO_2 and CO_3) and with adventitious carbon C-C at 284.8 eV, adsorbed CO at 286.2 eV and O-C=O at ~288.6 eV (Figure 6 (c))⁴⁰

with 15% Ag/ η -Al₂O₃ catalyst showed slightly higher composition of surface carbon compared to the other two catalysts. Table 1 shows the IAg/IAI ratio which increased with increasing the silver loading from 0.01 to 0.07 and 0.11 for 1% Ag/ η -Al₂O₃, 10% Ag/ η -Al₂O₃ and 15% Ag/ η -Al₂O₃, respectively. It is worth noting that there is a probability of reduction of Ag⁺¹ under the reaction condition as the hydrogen in methanol is reductive, the reduction can be checked using XPS analysis (Ag MNN) for the fresh and the spent catalyst⁴¹, which will be discussed later.

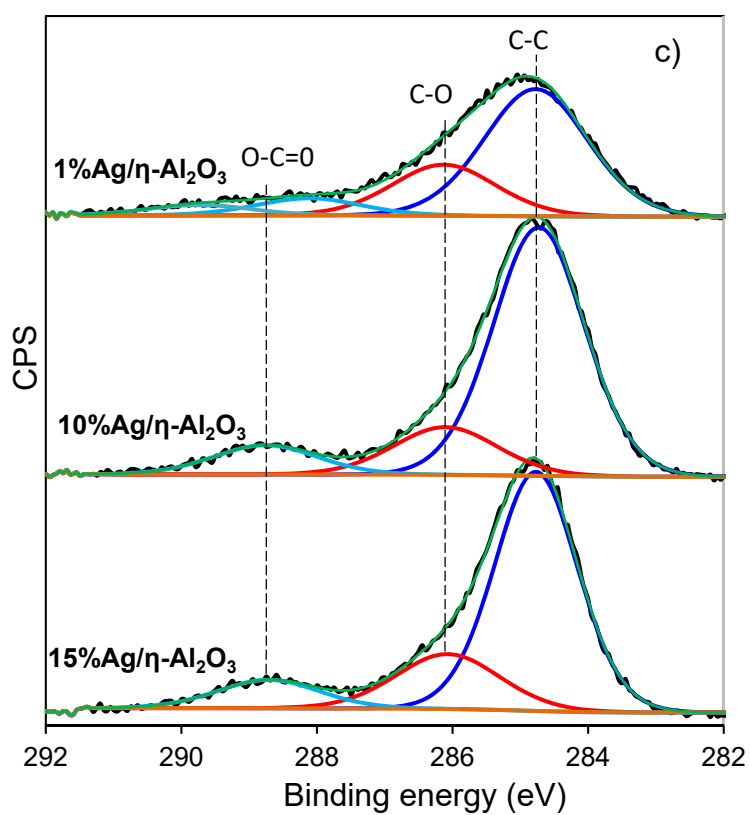
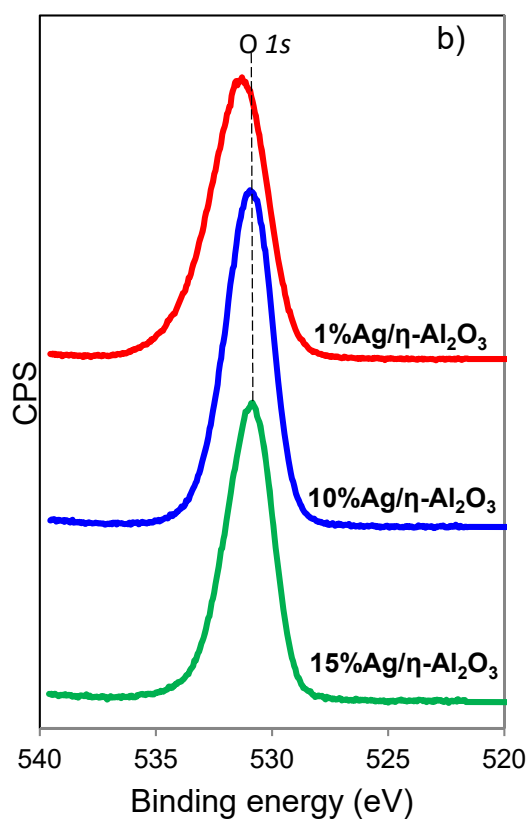
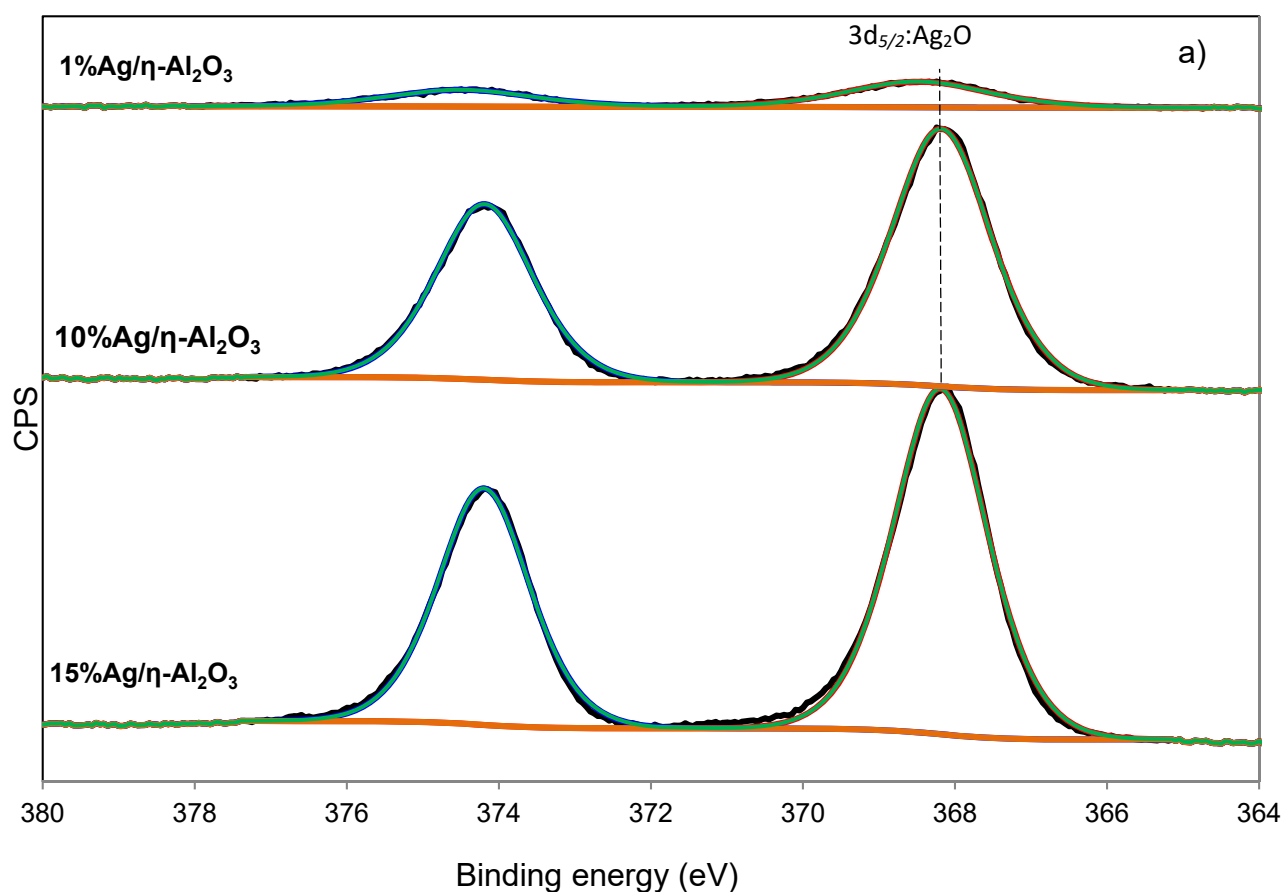


Figure 6: XPS of 1% Ag/ η -Al₂O₃, 10% Ag/ η -Al₂O₃ and 15% Ag/ η -Al₂O₃ catalysts for a) Ag 3d, b) O 1s and c) Adventitious carbon C 1s.

The surface hydrophobicity was measured according to the water contact angle (CA) as seen in Figure 7. The wettability of the catalyst surface, demonstrated by CA (θ) of a droplet of water, is assumed by Young's equation (Equation 15)

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (15)$$

Where, γ_{SV} , γ_{SL} and γ_{LV} stand for the interfacial surface tension of solid (S), liquid (L) and gas vapour (V). This equation is derived from the thermodynamic equilibrium of the free energy at the S-L-V interphase. The surface wettability is measured according to the CA and may be divided into four different categories; super-hydrophilic ($\theta < 10^\circ$), hydrophilic ($10 < \theta < 90^\circ$), hydrophobic ($90 < \theta < 150^\circ$) and super-hydrophobic ($\theta > 150^\circ$). It is well known that pure alumina catalyst is super-hydrophilic with CA approximately $\theta = 1.69^\circ$ as seen in Figure 7 (a). The CA increased to 20.7° with 1% the Ag loading and then significantly increased to 50.7° at 10% Ag loading. However, with further increasing of the Ag loading, the CA slightly decreased to 39° , this is may be attributed to the Ag loading over the surface of the η -Al₂O₃ catalyst, i.e. at low Ag loading (1% Ag) there was a small number of Ag atoms covering the surface of η -Al₂O₃, while at 10% Ag loading there was a uniform distribution of the silver atoms that prevent the water adsorption. Further loading of silver (15% Ag) shows a formation of big clusters as seen from the SEM images in Figure 3. The enhanced hydrophobicity with Ag loadings confirmed by the FTIR spectra in Figure S4, where the OH band at 3300 cm^{-1} disappeared at 10 and 15% Ag loading. Figure S4(b) shows the negative bands over pure η -Al₂O₃ and 10% Ag/ η -Al₂O₃ catalysts at 50°C due to the removal of surface hydroxyl groups. The negative band is due to the subtraction of the spectrum of the material before exposure to the reaction mixture. It is clear from Figure 5(b) that the negative band in case of 10% Ag/ η -Al₂O₃ is less deep than that in case of pure η -Al₂O₃ due to the increased surface hydrophobicity as a result of silver addition. This comes in accordance with the observation from figure S4(a) which shows a complete disappearance of the band at $3500\text{-}3100 \text{ cm}^{-1}$ corresponding to surface hydroxyl by increase the Ag loading from 1 to 10 and 15%.

Figure 7 (d) shows the CA of the H-Al₂O₃ catalyst, $\theta = 170.6^\circ$ i.e. super-hydrophobic materials. Schematic 1 depicts the superior enhancement in the hydrophobicity via the transformation of the super-hydrophilic η -Al₂O₃ ($\theta = 1.69^\circ$) into the super-hydrophobic alumina ($\theta = 170.6^\circ$) using the TEOOS reagent. Furthermore, the difference in the hydrophobicity is obvious as seen in video 1 of the water droplets on the surface of the super-hydrophilic and superhydrophobic alumina (η -Al₂O₃ and H-Al₂O₃) catalysts (using the yellow colour of ferric chloride for clarity) to illustrate the efficiency of the adopted approach used for the transformation of η -Al₂O₃ into H-Al₂O₃. On the other hand, during this transformation, most of the Lewis acidic sites were removed as seen in Figure S5 compared with the η -Al₂O₃ catalyst.

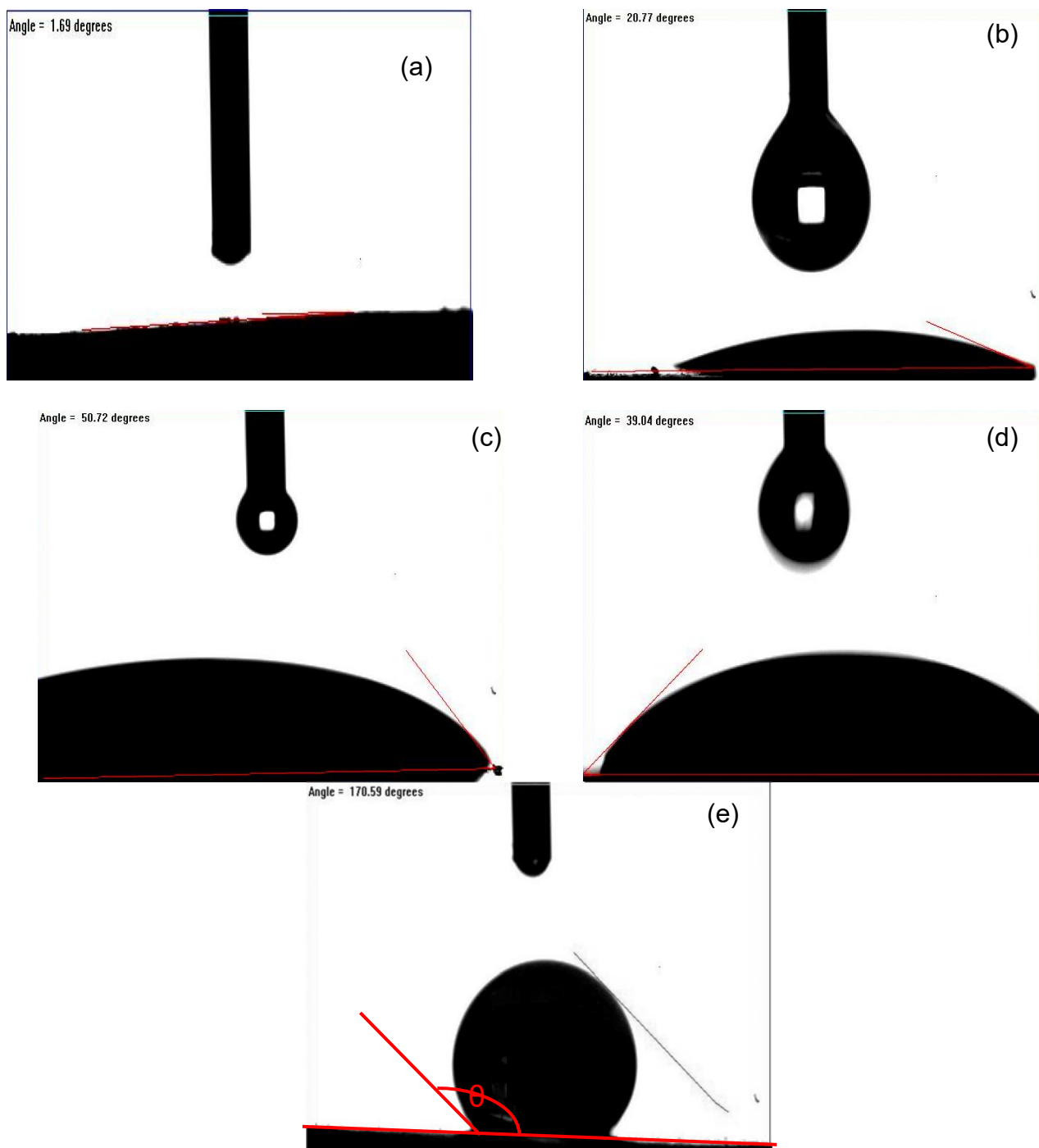
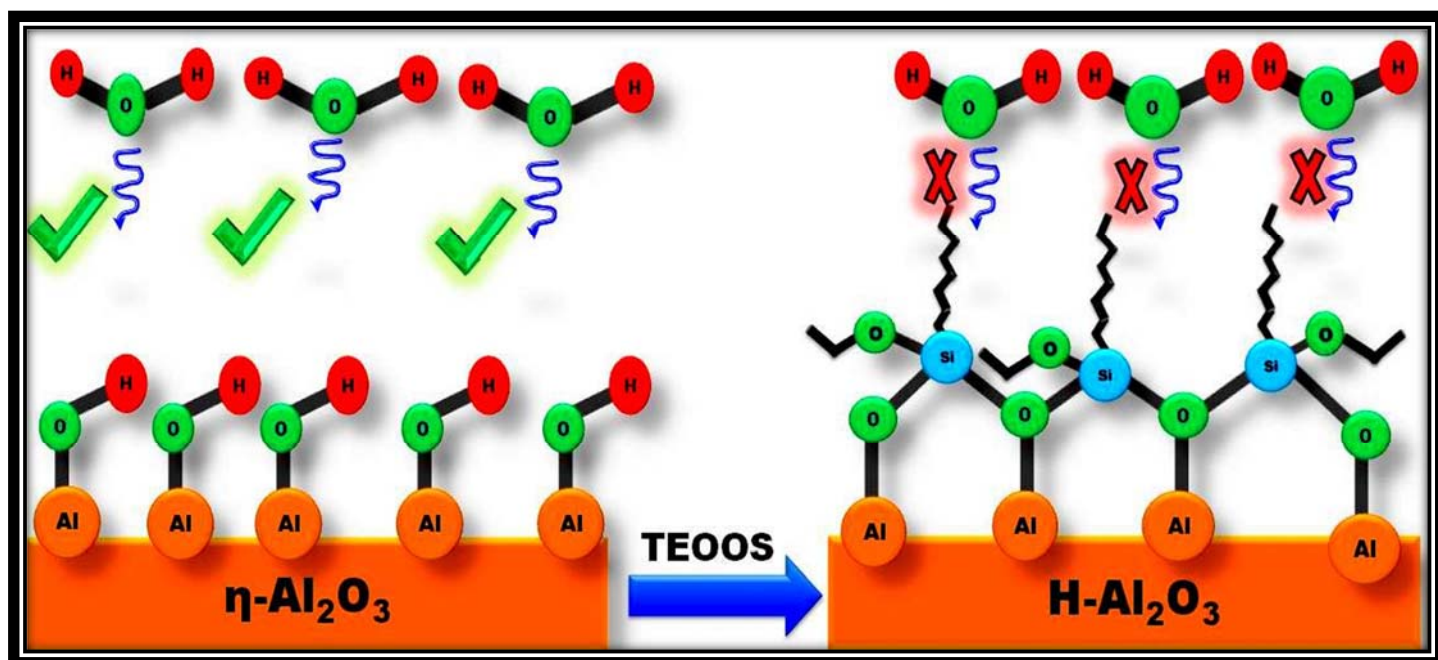


Figure 7: Comparison between hydrophobicity of catalyst surface of (a) pure η - Al_2O_3 , (b) 1% Ag/ η - Al_2O_3 , (c) 10% Ag/ η - Al_2O_3 , (d) 15% Ag/ η - Al_2O_3 and (e) H- Al_2O_3 .



Schematic 1: Schematic representation of the super-hydrophilicity of $\eta\text{-Al}_2\text{O}_3$ and converting it into super-hydrophobic alumina support using triethoxyoctyl silane reagent (TEOOS).

Figure 8 (a) and (b) show transmission electron micrographs of the structure in bright field TEM and HAADF-STEM respectively with a selected area electron diffraction pattern inset. Figure 8 (c) and (d) show the silver atoms dispersion over the surface of the $\eta\text{-Al}_2\text{O}_3$ catalyst structure as well as high-resolution TEM (HRTEM) of a single Ag particle. It is clear from the SAED and HRTEM that the Ag particles are crystalline in nature and the TEM data shows that the size of these crystallites generally of < 5 nm in size. These particles distribute with relative uniformity across the surface of the alumina and these results are in agreement with the SEM results.

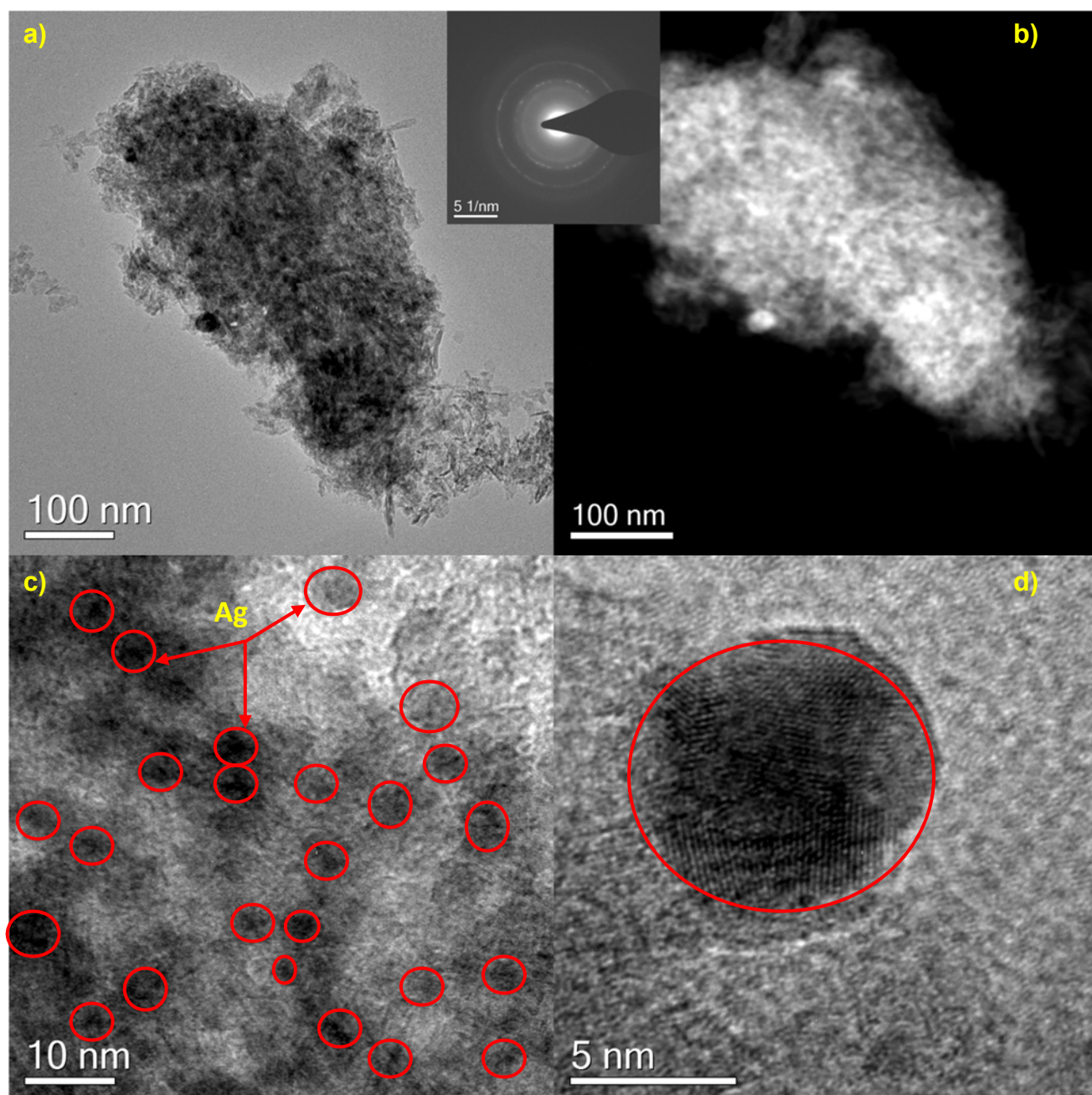


Figure 8: shows the TEM images (a) Bright field transmission electron micrograph of a 10% Ag/ η -Al₂O₃ structure. (b) HAADF-STEM image of the same region. (c) Bright field TEM image showing the Ag particle distribution across the surface of the alumina. (d) HRTEM image of a single grain of Ag. The inset image is the SAED (Selected Area Electron Diffraction) pattern of a single 10% Ag/ η -Al₂O₃ structure.

4.2. Mechanism study of Ag loaded on η -Al₂O₃ using DRIFTS

Figure 9 shows the DRIFT spectra of 10%Ag/Al₂O₃ sample obtained during the exposure to the reaction feed with a stepwise increase in the reaction temperature. The spectrum obtained for 10% Ag/ η -Al₂O₃

seems to be similar, to some extent, to that of pure alumina with some differences. The spectrum obtained at 50°C is characterised by negative bands of surface hydroxyl groups (i.e. 3738, 3688 cm^{-1}) and bands corresponding to surface methoxy groups (2941, 2888, 2822, 2595 cm^{-1})^{9, 29-31}. In addition, the spectrum shows bands at 3260, 1800 and 1451 cm^{-1} corresponding to hydrogen-bonded hydroxyl groups, adsorbed CO and carbonate-carboxylate species, respectively²⁹. By increasing the temperature, a progressive decrease in the intensity of the bands at 3260, 2595, 1800 and 1451 cm^{-1} is observed. In addition, bands at 3639, 1592, 1390 and 1374 cm^{-1} started to appear starting from temperature 150 °C and then, their intensities increased with increasing temperature. The band at 3639 can be attributed to isolated hydroxyl groups which may be formed due to formate decomposition²⁹, which implies that decomposition of formate species produced OH groups. The bands at 1592, 1390 and 1374 cm^{-1} are attributed to surface formate species. There are some differences between the spectra in the case of pure $\eta\text{-Al}_2\text{O}_3$ catalyst and that in the case of 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ catalyst. The removal of methoxy species over 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ seems to be faster and started at lower temperatures compared to that in the case of pure $\eta\text{-Al}_2\text{O}_3$. In addition, the removal of carbonate-carboxylate species was also faster over 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ surface and the band at 1451 cm^{-1} was completely disappeared at 200°C. Furthermore, the bands corresponding to formate species appeared at a lower temperature in the case of 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ catalyst. Regarding the reaction mechanism, it is clear that the two DRIFTS spectra of pure ($\eta\text{-Al}_2\text{O}_3$) and silver modified alumina (10% Ag/ $\eta\text{-Al}_2\text{O}_3$) are qualitatively similar which indicates that the reaction mechanism over the two catalysts is the same. From the DRIFTS results, the reaction seems to be faster over 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ catalyst compared to a pure $\eta\text{-Al}_2\text{O}_3$ sample which is one of the important factors responsible for the higher activity of 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ catalyst compared to pure $\eta\text{-Al}_2\text{O}_3$ sample. This enhancement in the reaction rate is probably due to the increase in surface hydrophobicity upon loading Ag on $\eta\text{-Al}_2\text{O}_3$. The increased hydrophobicity is expected to fasten the removal of the produced water from the catalyst surface which will eventually enhance the rate of reaction. This is in agreement with the FTIR-Pyridine results where both the two catalysts showed only Lewis acidic sites with 10% Ag/ $\eta\text{-Al}_2\text{O}_3$ showed higher acidity

(Figure 5), implying that it is indeed more active than the pure alumina in MTD reaction as it is an acid catalysed reaction.

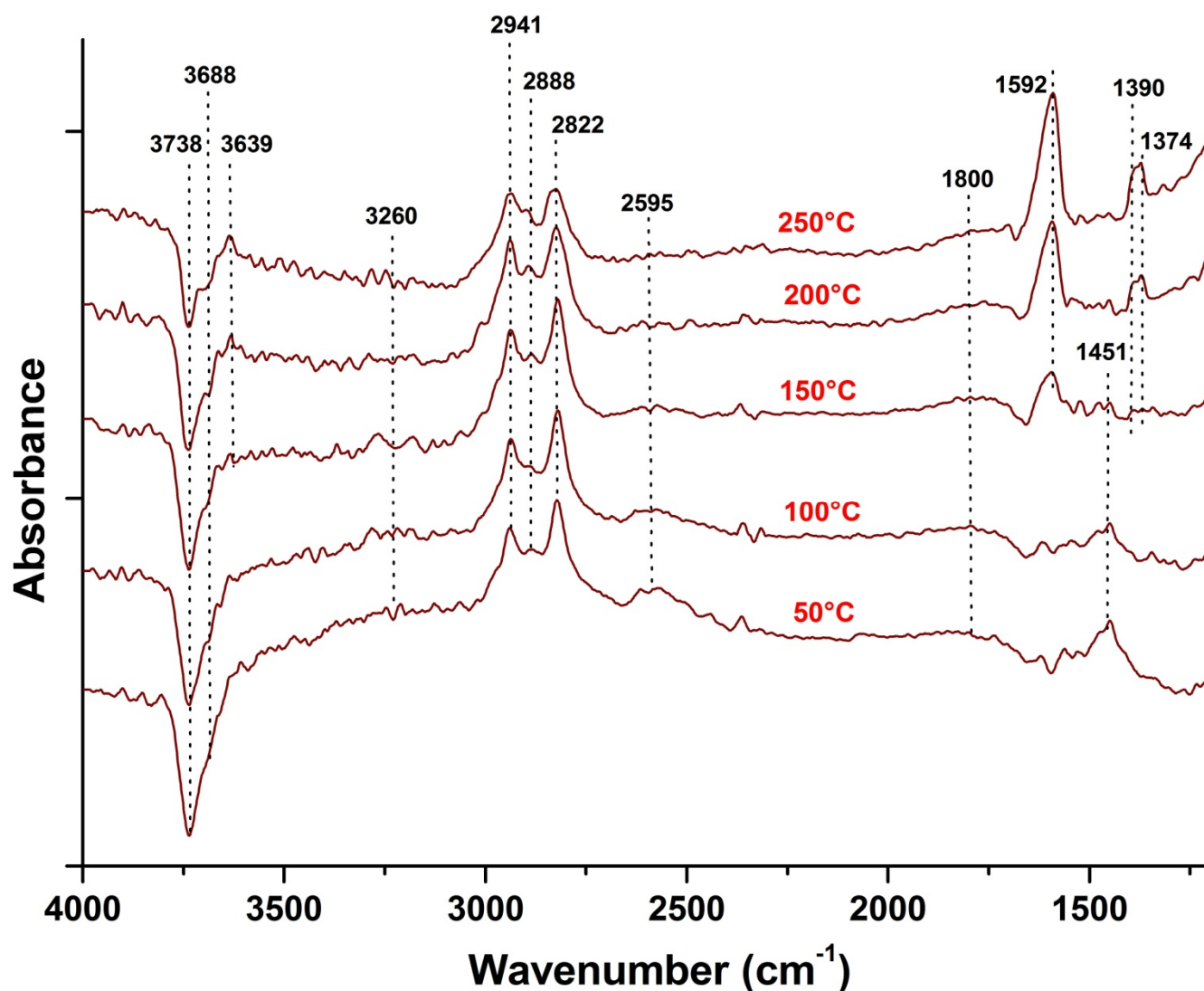


Figure 9: In-situ DRIFT spectra obtained over the 10% Ag/ η -Al₂O₃ catalyst during the interaction under reaction feed (20% MeOH+ He gas as an inert in the feed) at 50°C for 20 min followed by a stepwise heating to the indicated temperatures under the same reaction feed.

The TPR profiles of 1% Ag/η-Al₂O₃, 10% Ag/η-Al₂O₃ and 15% Ag/η-Al₂O₃ catalysts are shown in Figure 10. At low silver loading i.e. 1% wt. Ag, the catalyst showed three reduction peaks at 130, 193 and 565 °C, while at high Ag loadings (10 and 15 wt. %) these peaks were merged and appeared at approximately 120

and 200 °C. Interestingly, the pure η -Al₂O₃ catalyst showed no reduction peaks in the temperature range of -20 °C to 700 °C, so all the reduction peaks are characterised of the silver oxide species. The presence of three reduction peaks at 1% Ag/ η -Al₂O₃ gives an indication of the presence of hardly reduced silver oxide species, especially the reduction peak at 565 °C. This is in line with the XPS results that showed Ag $3d_{5/2}$ and $O1s$ peaks shift to lower binding energy with increasing silver loading i.e. the Ag loading facile the oxidation cycle ³⁹. Catalyst 10% Ag/ η -Al₂O₃ showed the lowest reduction peak at 119 °C indicating a facile reduction at 10 wt. % Ag, while at the highest Ag loading, this peak was shifted to a higher temperature (130 °C). By increasing the Ag₂O species with the loading of Ag as confirmed from the XRD and XPS results, consequently, the reduction peaks (hydrogen consumption) increase with the silver loading as seen in Figure 10.

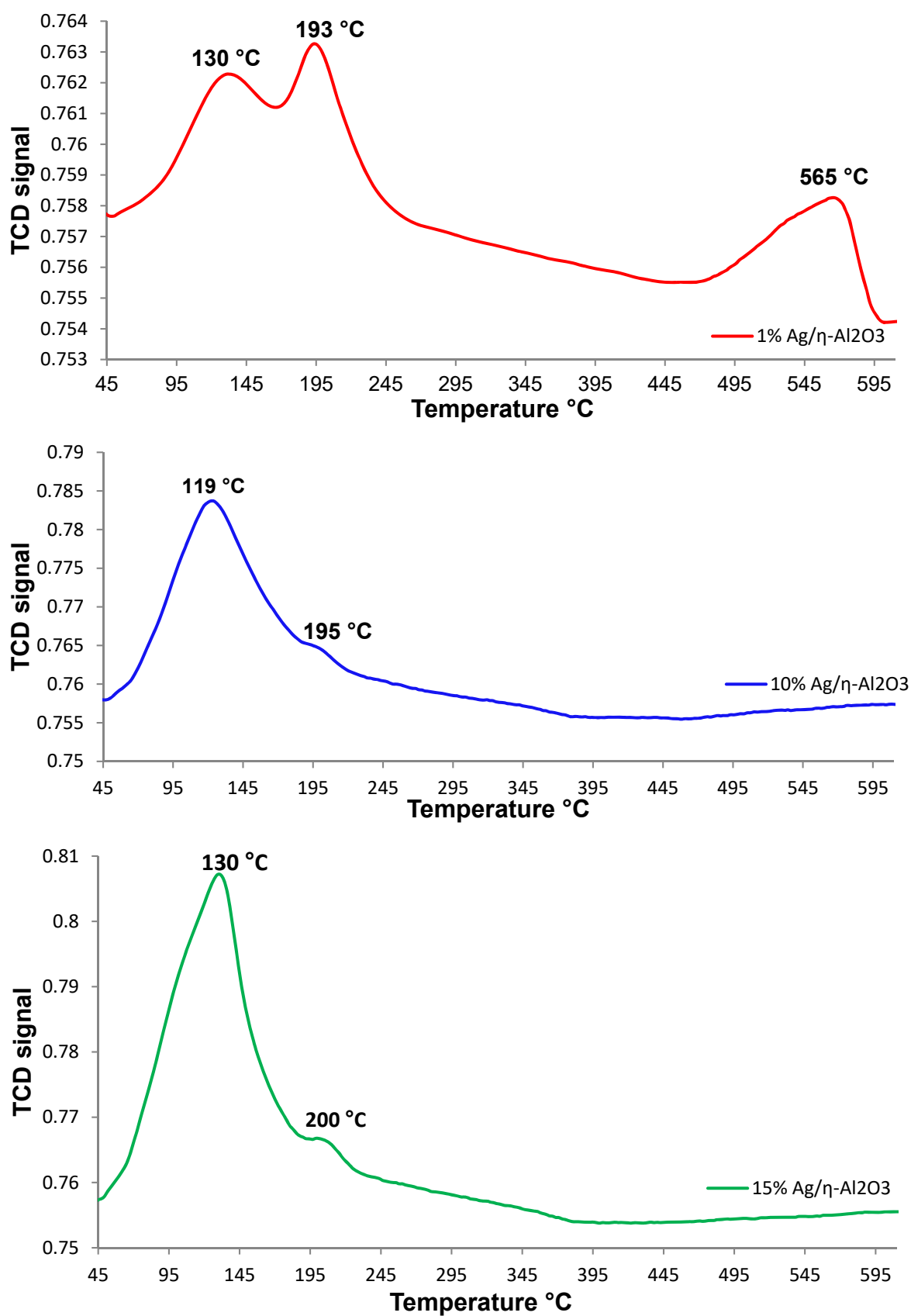


Figure 10: TPR profiles of 1% Ag/η-Al₂O₃, 10% Ag/η-Al₂O₃ and 15% Ag/η-Al₂O₃ catalysts.

4.3 Catalyst activity of Ag modified alumina catalyst

The effects of Ag loading on the η -Al₂O₃ catalyst for the MTD reaction carried out over the temperature range 180-300 °C along with the commercial γ -Al₂O₃ are shown in Figure (11). The catalytic activity was clearly increased with the increase in the Ag loading until it attained the maximum at an Ag loading of 10 wt. %, after which it slightly declined with further increase in the Ag loading (15 wt. %). For instance, at a high reaction temperature of 300 °C, the conversion of methanol over η -Al₂O₃ was 76.4 % which only increased by 8% i.e. to 84.5% upon adding 10 wt. % Ag and then decreased to 81.6 % over 15% Ag loading. Although there was a little enhancement in the catalytic activity at high temperature compared with the pure η -Al₂O₃, the conversion approached the equilibrium curve (dashed curve in Figure 11). Clearly, there was a significant increment in the catalytic performance at a low reaction temperature of 250 °C, where the conversion of methanol over η -Al₂O₃ was 18 % which increased more than twice to 39.5 % over 10%Ag/ η -Al₂O₃ and then again slightly declined to 34% over 15% Ag loading. The same result can be observed from the DME reaction rate (not shown). Such differences are ascribed to differences in the surface acid strength as well as hydrophobicity properties. As discussed above for the 10% Ag loading, the hydrophobicity of the surface improved from superhydrophilic to hydrophilic (see Figure (7)) and stronger Lewis acidic sites were observed in the FTIR-Pyridine (Figure (5)). To test the hypothesis that hydrophobicity is the only factor that affects the MTD reaction, a superhydrophobic alumina catalyst (H-Al₂O₃) was prepared and showed a CA of 170.6° implying a superhydrophobic surface, however, during the transformation of the superhydrophilic alumina into H-Al₂O₃, most of the acidic sites were removed and consequently the catalytic activity decreased as shown in Figure 11. To sum up, a balance between acidity and hydrophobicity is needed to achieve an optimum activity during the MTD reaction.

Heterogeneous catalyst deactivation can take place as a result of poisoning, vapour compound formation, fouling and vapour/solid or solid/solid reactions. The most common factors causing catalyst deactivation are poisoning, fouling or sintering. From the previous work, η -Al₂O₃ showed a high degree of stability

and had double the activity of the commercial γ -Al₂O₃ or 87% of the activity of commercial ZSM-5 (80) at 250 °C at WHSV of 12.1 h⁻¹. Raoof et al.¹⁴ reported that water had the highest inhibition effect and dramatically deactivate the alumina catalyst by adding water in the reaction feed.

Figure 11 (b) shows the stability tests over a period of 60 h for the pure η -Al₂O₃ and the optimum modified silver catalyst (10% Ag/ η -Al₂O₃). Stability is one of the main requirements for such catalysts, while both catalysts were reasonably stable, the optimum catalyst in terms of both activity and stability appeared to be 10% Ag/ η -Al₂O₃ catalyst. In addition, the conversion of η -Al₂O₃ at 250 °C was clearly around 18 % while for 10% Ag/ η -Al₂O₃ catalyst, the conversion was approximately twice that with a value of 39 %.

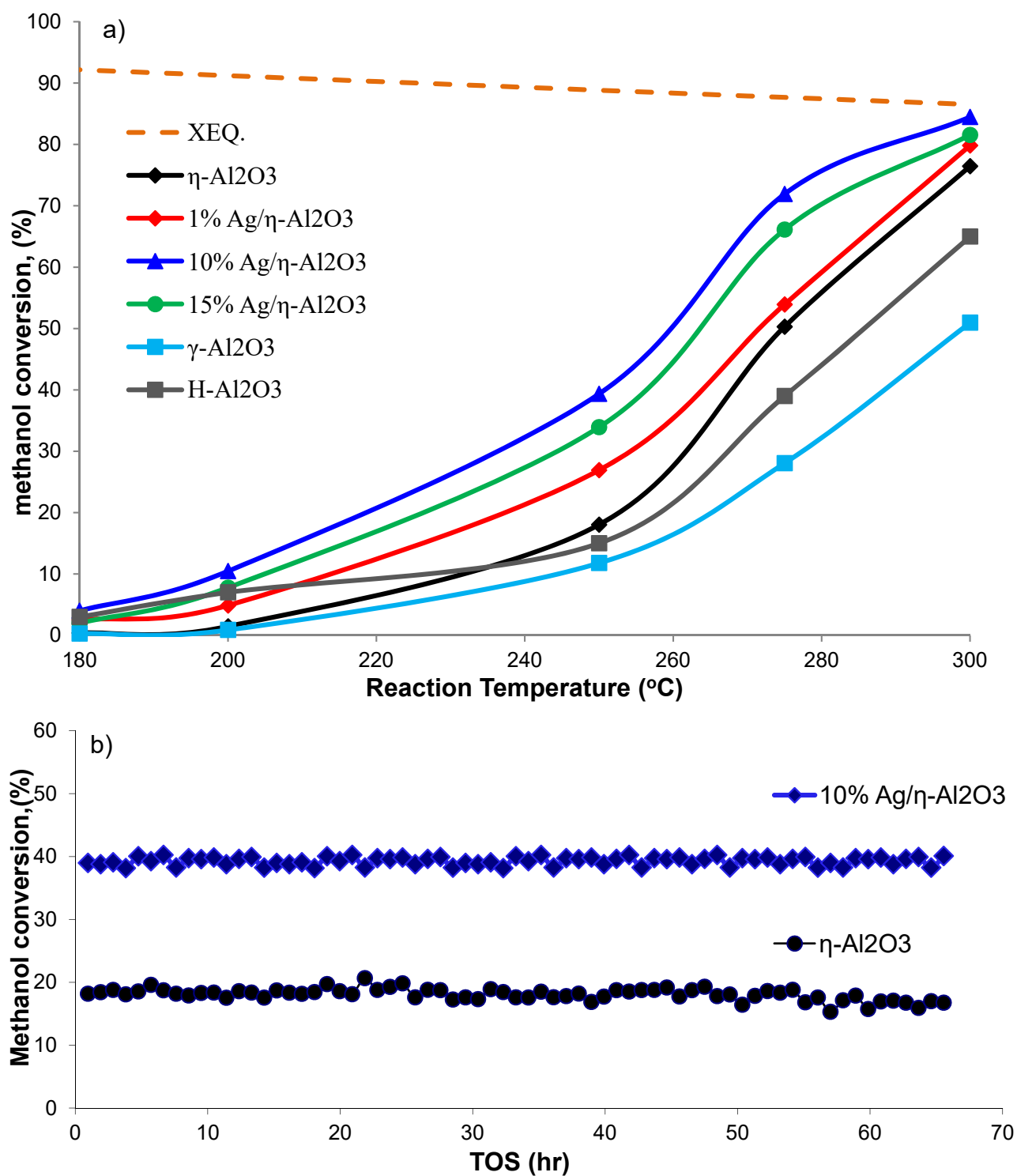


Figure 11: Catalytic activity profiles a) effect of reaction temperature on methanol dehydration to DME with different Ag loading along with the super-hydrophobic alumina (H-Al₂O₃), reaction condition; T= 180-300 °C; catalyst weight= 50 mg; He flow rate = 80 ml/min; WHSV: 48.4 h⁻¹. b) The time on stream test at 250 °C for the 10% Ag/ η -Al₂O₃ and pure η -Al₂O₃ catalysts.

XPS was carried out to investigate the probability of reduction of Ag^{+1} under the reaction conditions and determine silver oxidation state in the spent Ag modified catalysts. Ag $3d_{5/2}$ binding energies are very close for metallic silver and its oxides and generally, it is difficult to assign the oxidation state from Ag $3d$ alone. However, the auger peak Ag MNN allows reliable distinguishing of Ag(0) and Ag(+1) ⁴¹. In the subsequent study, Ag $3d$ and Ag MNN Auger structure region were acquired on the fresh and spent 10% Ag/ η - Al_2O_3 and 15% Ag/ η - Al_2O_3 catalysts keeping acquisition times short and consistent to minimise beam effects. Ag $3d_{5/2}$ binding energies for the fresh and spent catalysts show only 0.1 - 0.2 eV shift (Figure S6). However, the auger Ag MNN peaks in Figure 12 show significant differences for the fresh and spent catalysts. The 10% Ag/ η - Al_2O_3 fresh catalyst shows two peaks at kinetic energies(KE) approx. 348.5 eV and 354.9 eV. The modified Auger parameter ⁴² calculated at 716.7 and 723.1 eV is consistent with Ag^{+1} species ⁴¹. However, Ag MNN structure of the 10% Ag/ η - Al_2O_3 spent catalyst shows three peaks. The peaks at 352 and 357.8 eV gives auger parameters at 720.1 eV and 725.9 eV and are consistent with metallic Ag ⁴¹. However, the third peak at 348.5 eV remains in the spent catalyst indicative of the presence of silver oxide and thus clearly suggesting that not all Ag^{+1} is reduced to silver, and that both Ag and Ag^{+1} coexist. The 15% Ag/ η - Al_2O_3 spent catalyst also show the same peak structure (Figure 12 (d)). It is likely that Ag^{+1} at only some sites are more prone to reduction, or those on the surface may reduce easily in the feed reducing environment. As the 10% Ag/ η - Al_2O_3 catalyst was stable in the time on stream test over a period of 60 h, this suggests that presence of Ag enhance the surface hydrophobicity of alumina regardless of its oxidation state whether it was (0) or (+1). Moreover, it was reported that Ag (0) can promote the surface hydrophobicity ¹⁸.

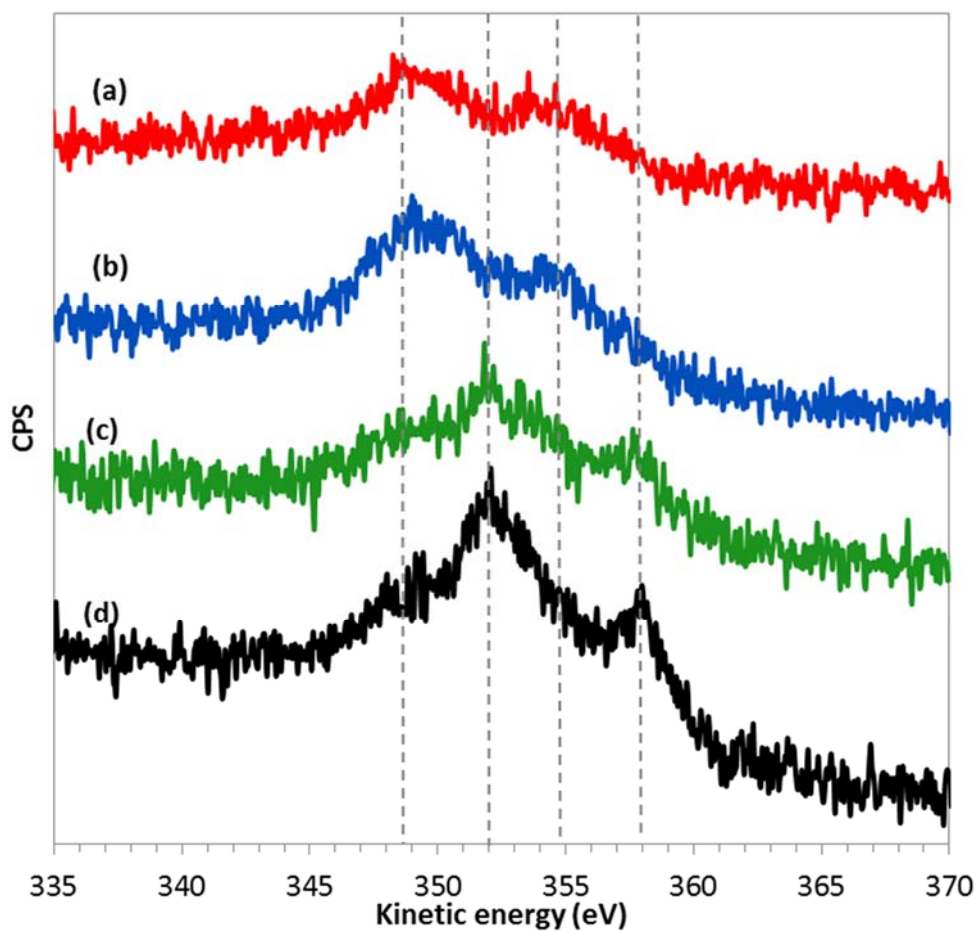


Figure 12: Ag MNN Auger structure region for (a) fresh 10% Ag/ η -Al₂O₃ (b) fresh 15% Ag/ η -Al₂O₃ (c) spent 10% Ag/ η -Al₂O₃ and (d) spent 15% Ag/ η -Al₂O₃ respectively.

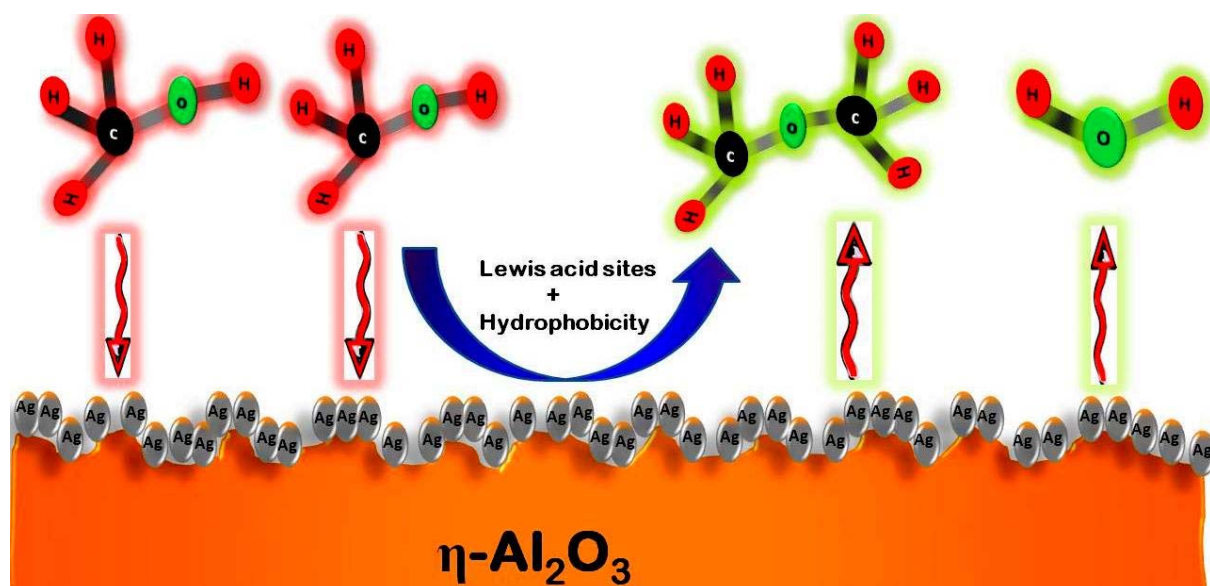
5. Conclusions

In-situ DRIFTS were studied to investigate the reaction mechanism of methanol dehydration over the pure η -Al₂O₃ catalyst. Moreover, the effect of silver loading on the catalytic performance of η -Al₂O₃ was examined in a fixed bed reactor under the reaction conditions where the temperature ranged from 180-300 °C with a WHSV= 48.4 h⁻¹. The addition of silver to the support improved the catalytic activity and herein, the optimum catalyst was 10% Ag/ η -Al₂O₃. The Ag loadings clearly resulted in an improvement in the Lewis acidity and in the secondary improvement of the bulk surface properties by changing the surface from superhydrophilic to hydrophilic at 10% Ag loading with an increase in the CA from 1.6 to 50.7 ° for pure η -Al₂O₃ and 10% Ag/ η -Al₂O₃, respectively. Furthermore, 10% Ag/ η -Al₂O₃ catalyst exhibited a high degree of stability under steady-state conditions and this is attributed to the enhancement in both surface Lewis acidity and hydrophobicity. To test the hypothesis that hydrophobicity is the only factor that affects the MTD reaction, a superhydrophobic alumina catalyst (H-Al₂O₃) was prepared and showed a CA of 170.6°, however, during the transformation of the superhydrophilic alumina into H-Al₂O₃, most of the acidic sites were removed and consequently the catalytic activity decreased compared with the pure η -Al₂O₃. To summarise, a balance between acidity and hydrophobicity is needed to achieve an optimum activity during the MTD reaction which was achieved herein in the 10%Ag/ η -Al₂O₃ catalyst.

Supporting Information: Nitrogen adsorption-desorption isotherms, SEM images, EDX data, FT-IR and In-situ DRIFT, XPS

Competing financial interests: The authors declare no competing financial interests.

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TOC Graphic

6. References

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