



Preparation and Characterization of Mixed-Oxide Catalyst

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Abstract

Solid heterogeneous CuO-MoO₃/ZrO₂ catalyst was prepared by impregnation using suitable precursor materials supported over zirconia. Upon calcination at 450°C for 2 hours, available techniques were employed for the characterization. The available oxides and minerals in the catalyst were revealed by the XRF and XRD profiles respectively. The catalyst crystallite size (131.6nm) was obtained using the Bragg's equation from the latter. Thermal analysis showed three weight loss stages between (49.25-152.06°C), (152.06-559.47°C) and (559.47-752.0°C) while presence of sulphate and zirconia oxides was revealed by the FTIR analysis due to appearance of absorption bands around 1225-980cm⁻¹ and 700-600 cm⁻¹ respectively.

Introduction

Homogeneous and heterogeneous catalysis are the broad categories which catalysis is divided into, and benzene alkylation has been carried out by both methods. While homogeneous catalysis deals with study of catalysts and reactants in the same phase, heterogeneous catalysis deals with reactants and catalysts in different phases [1-2]. Homogeneous catalysts exist in the same (homogeneous phase) virtually almost always

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liquid phase. In heterogeneous catalysis, a solid catalyst is used for vapour or liquid phase reactions.

Depending on their uses, heterogeneous catalysts may be in the form of metals (skeletal metals), metal oxides, sulphides, heteropolyacids, nitrides, carbides, borides, alloys, molecular sieves, ceramics, fibres, wires, salts and mineral acids etc. [2-4].

The use of inorganic or mineral acid along with heterogeneous catalysts for liquid phase industrial reaction has become a focus. This is possible because there is ease in handling and product separation, catalyst re-use and minimization of wastes attributed to them. In addition, bimetallic supported catalysts are reported to be good catalysts for alkylation reactions [5-6].

Experimental

The CuO-MoO₃/ZrO₂ catalyst was prepared by the impregnation method as described by Haber et al. [5]. Aqueous saturated solution of ammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄.4H₂O] and copper nitrate [Cu(NO₃)₂] was prepared by adding 15.75g of each salt in a beaker containing 60cm³ of distilled water. Zirconia (38.5g) was slowly deposited into the solution and then mixed at 120rpm for 1 h. The mixture was dried overnight in an oven at 105°C.

The dried mass was calcined in a furnace at a temperature of 450°C for 2 hours.

Characterization

XRD analysis

The XRD analysis was carried out using 5g of the catalyst on a PAN analytical 2830ZT XRD analyser. Two-theta starting position was 4 degrees to 75 degrees with a two-theta step of 0.026261 at 8.67 seconds per step. The tube current was 40mA and the tension was 45VA. Values of theta, d-spacing, 2 theta and peaks corresponding to ejected electrons are obtained. The crystallite size (*t*) of the catalyst was established based on the XRD patterns using the relation:

$$t = \frac{K\lambda}{B \cos \phi}, \quad (1)$$

where t = crystallite size, K = constant with values from 0.92 to 1.0, λ = wave length of the incident X-ray (usually taken as 0.1542nm), B = full width at half maximum (FWHM) for the highest peak and must be converted to radians, using equation 2.2

$$B(\text{radians}) = \frac{2\pi \times B}{360}, \quad (2)$$

where $\pi = 3.142$, B = fullwidth at half maximum (FWHM) for the highest peak.

FTIR analysis

The IR spectra of the solid catalyst was obtained by grinding the catalyst into fine powder with a particle size about 1-2 microns. Seven milligram (7mg) of finely ground catalyst sample was placed on a KBr plate and a small drop of Nujol (mineral oil) was added. The sample was evenly distributed with the second KBr plate and placed in the sample holder which was scanned between 4000-400 cm^{-1} using an MB3000 IR analyzer and the spectra was generated using a high-tech Thermo Scientific Nicolet software.

XRF analysis

Two milligrams (2mg) of the ground samples of pulverized catalyst were placed into a sample cup. Elemental composition determination was carried out on a current of 14kv for major oxides and 20kv for the trace elements/rare earth metals. Selected filters were “kapton” for major oxides, Ag/Al-thin for the trace elements/rare earth metals. The spectra was developed using Horizon MB[®] XRF software. Each sample was measured for 100 seconds and the air medium was used throughout.

TG analysis

Thermal analysis was carried out using a DTG-60AH thermogravimetric analyser with the heating rate set at 20°C/min and nitrogen flow rate 40 ml/min while the final heating temperature was 900°C. The spectra was developed using a versatile Proteus[®] software while maintaining a cooling time of approximately 12 minutes.

Results

The result obtained from catalyst characterization is presented in the following Tables 1-4 and Figures 1-2.

Table 1. Results of XRD analysis of the CuO-MoO₃/ZrO₂ catalyst.

Mineral	Chemical Formula	Composition (%)
Baddeleyite	Zr ₄ O ₈	42
Bonnatite	Cu ₄ S ₄ O ₂₈ H ₂₄	58

Table 2. Absorption peaks obtained from FTIR spectra of the CuO-MoO₃/ZrO₂.

Absorption range(cm ⁻¹)	Peak description	Functional group
3200-3600	Broad, intense	-OH
2700-2900	Medium	C-H stretch
1225-980	Medium	S-O
700-600	Medium	Zr-O

Table 3. TGA Results of the CuO-MoO₃/ZrO₂ catalyst.

Temperature range (°C)	Weight loss (mg)	Weight loss (%)
43-152	3.59	55
152-560	0.77	11.8
560-752	2.17	33.2

Table 4. The results of XRF analysis of the CuO-MoO₃/ZrO₂ catalyst.

Oxide Composition	% Abundance
P ₂ O ₅	9.90
SO ₃	11.00
TiO ₂	0.04
Fe ₂ O ₃	0.046
Co ₃ O ₄	0.007
CuO	12.93
As ₂ O ₃	0.034

ZrO ₂	50.91
BaO	0.14
CeO ₂	0.02
Tb ₄ O ₇	0.03
Er ₂ O ₃	0.03
PtO ₂	0.091
PbO	0.029
Bi ₂ O ₃	0.022
L.O.I	14.22

L.O.I = Loss on ignition.

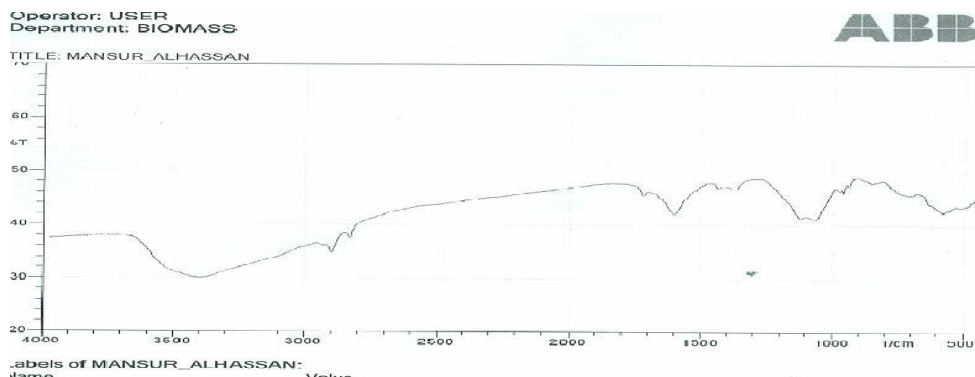


Figure 1. FTIR spectra of the CuO-MoO₃/ZrO₂ catalyst.

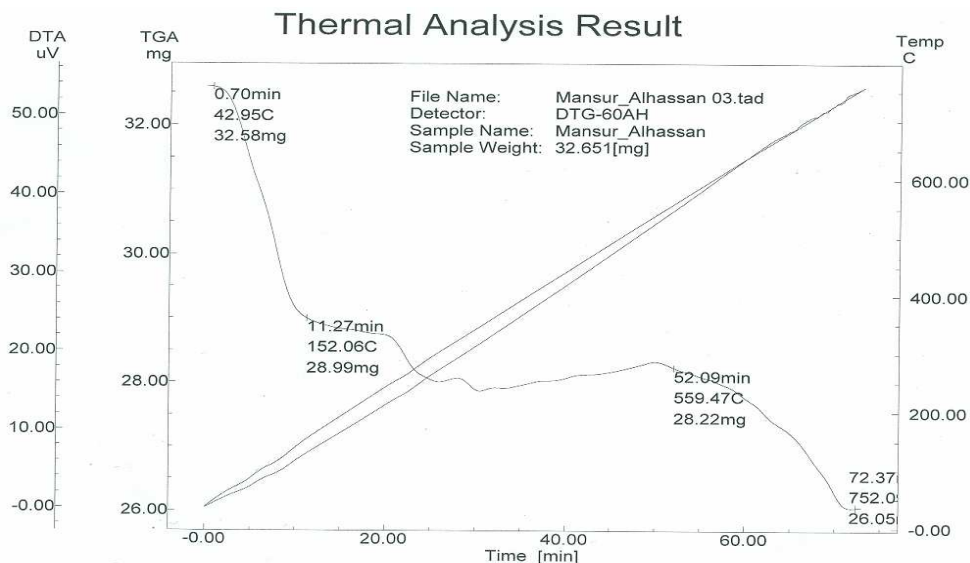


Figure 2. TGA spectra of the CuO-MoO₃/ZrO₂ catalyst.

Discussion

The result of XRD analysis of the prepared catalyst presented in Table 1 indicated the presence of two principal minerals; Baddeleyite (42%) and Bonattite (58%). Baddeleyite (Zr₄O₈) is equivalent to ZrO₂, the catalyst support material while Bonattite (Cu₄S₄O₂₈H₂₄) is equivalent to CuSO₄.12H₂O. The principal mineral components in the catalyst precursor are ZrO₂ (as shown by Tables 1 and 4) and hydrated copper sulphate (CuSO₄.3H₂O); constituting up to 42% of the solid catalyst; which agrees with Zhang et al. [8], that up to 40wt % of the support can be employed.

Although after calcination at 450°C, moisture due to physisorbed water is removed from the catalyst, the XRD analysis showed up to 12 moles of water. The calcined catalyst might absorb some moisture after cooling prior to the XRD analysis and possibly some remnant of water of crystallization. According to Haber et al. [5], surfaces of solid heterogeneous catalysts could be blocked by physisorbed water. Zhang et al. [8] and Yuan et al. [9] reported that fraction of water of crystallization could be noticed even after calcination. The presence of copper sulphate mineral (bonattite) is attributed to the precursor salt, copper nitrate Cu(NO₃)₂ while sulphate species comes from the sulphuric acid acidification process in the catalyst activation step.

There were no traces of molybdenum reported in the XRD results of the prepared CuO-MoO₃/ZrO₂ catalyst. It could be that the molybdenum phase is either washed away during preparation process along with excess water or decomposed during calcination or heat treatment processes.

The crystallite size (*t*) of the catalyst was determined to be 131.6 nm which was much greater than size of < 2 nm (diameter) reported by Devassy et al. [10] for zirconia-supported 12-tungstophosphoric acid utilized as solid catalyst for the synthesis of linear alkyl benzenes. However, Wilson and Clark [6] alongside Zhang et al. [15], reported that upon calcination, diffractions shifts to higher angles with reduced intensities leading to an increased crystallinity. The large crystallite size could possibly be due to the absence of molybdenum.

Table 2 (and Figure 4) presents result of FTIR analysis of the CuO-MoO₃/ZrO₂ catalyst. Showing the peaks corresponding to the available oxides in the catalyst. The mild absorption peak that appeared around (700-600 cm⁻¹) was due to Zr-O bond confirming the presence of ZrO₂ which agrees with the XRD spectra that showed an abundance of 42%.

Presence of sulphate species was confirmed by the appearance of S-O absorption around (1225-980cm⁻¹). This further testified the sulphuric acid acidification in the catalyst activation process. The broad peak that appeared between 3200-3600cm⁻¹ and (3000-2800 cm⁻¹) could be attributed to hydrogen bonded hydroxyl groups and physisorbed or crystallization water molecules. This was responsible for the presence of water molecules in the catalyst as indicated by the XRD profile. Devassy et al. [10] reported similar results for zirconia supported 12-tungstophosphoric acid as a solid catalyst for the synthesis of linear alkyl benzenes. Cu-O bond is IR inactive hence, no peak could be attributed to its presence. The stretching related to the Cu-O bonds are located at frequencies below 400cm⁻¹ [9-11]. The FTIR spectra corroborated the absence of Mo-O absorption band which should have appeared around 998cm⁻¹. Hardcastle and Wachs [12] assigned stretching frequencies and bond distances in tetrahedrally coordinated molybdenum oxide reference compounds between 998-280 cm⁻¹.

The thermogravimetric analysis (thermal evolution) result of the CuO-MoO₃/ZrO₂ catalyst (presented in Table 3 and Figure 2) showed that the first weight loss stage

occurred within temperature range of 42.95°C to 152.06°C and accounted for 55% weight loss. The second occurred between 152.06°C to 559.47°C while the third occurred between 559.47°C to 752.0°C and accounted for 11.8% and 33.2% respectively. The volatile components in the solid catalyst like NH_3 and NO_2 have decomposed during the calcination process which was carried out at 450°C for 2 hours. Carbonate and acetate ions that did not completely decompose during calcination perhaps contributed to the weight loss recorded in the TGA analysis. The first and second weight loss stages were due to evaporation of 66.8% physisorbed water, other carbonates and acetates while the third weight loss stage accounted for 33.7% water of crystallization.

The percentage moisture in $\text{CuSO}_4 \cdot 12\text{H}_2\text{O}$ (bonattite) was approximately 57.5% and the TGA spectra (Figure 2) indicated a significant weight loss between room temperature to 100 or 125°C within which all absorbed water would evaporate. Hernandez-Cortez et al. [13] outlined that in solid samples; the first weight loss stage occurring from room temperature to about 152°C was due to physisorbed water and accounted for 55 weight loss (%). The mass loss between 152°C to 752°C was attributed to loss of water molecules due to crystallization and accounted for 11.8%. Wan and Mark [14] reported 1.9wt% water loss for a heterogeneous catalyst used for naproxen asymmetric synthesis.

Table 4 presented the results for XRF analysis of the solid $\text{CuO-MoO}_3/\text{ZrO}_2$ catalyst. The principal oxide (ZrO_2), with the support constituting 50.91% of the total oxides in the catalyst. This is in agreement with the suggestion of Zhang et al. [8] that support materials could be up to > 40wt% of a solid heterogeneous catalyst. CuO , SO_3 and P_2O_5 are the next dominant oxides with 12.93%, 11.00% and 9.90% abundance respectively. Trace amount of As_2O_3 , PtO_2 , Bi_2O_3 , PbO , Er_2O_3 , Tb_4O_7 , Co_3O_4 , TiO_2 and CeO_2 were also discovered. Compounds lost on ignition (L.O.I) amounted to 14.22% (second most dominant, next to ZrO_2). Most components of the LOI may range from physisorbed water, water of crystallization or water originating from acidic protons as reported by [8-10]. The disappearance of molybdenum or any of its oxides in the XRF results of the catalyst just like in the XRD, further justifies the absence of molybdenum in the prepared solid catalyst. Haber et al. [5] reported in the manual of methods and procedure for catalyst preparation and characterization that, during processes of catalyst preparation, important active components may be lost due to washing, drying or calcination of

impregnated precursor. Traces of metal oxides like As_2O_3 , PtO_2 , Bi_2O_3 , PbO , Er_2O_3 , Tb_4O_7 , Co_3O_4 , TiO_2 and CeO_2 that appeared in the XRF result could be attributed to impurities in the zirconia.

Conclusion

The result of the research has shown that the prepared catalyst did not contain molybdenum oxide justifying that molybdenum oxide has been lost likely, from the preparation process. It can be concluded that the prepared catalyst was CuO/ZrO_2 . Further work will focus on establishing reasons for its disappearance, testing its usability in catalyzing alkylation reactions and reusability.

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