



Mixed-Metal Oxide Catalyst for Liquid Phase Benzene Alkylation

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Abstract

Development of cheaper, active and more ecofriendly heterogeneous acid catalyst is a challenge mitigating the petrochemical industries. CuO-MoO₃/ZrO₂ solid catalyst was prepared by impregnation using suitable precursor materials supported over zirconia. Upon calcination at 450°C for 2 h and activation (by soaking in 2M H₂SO₄ for 30 minutes), 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 700-600cm⁻¹ respectively. The catalyst (1wt%) was tested for alkylation in a continuous stirred reactor at 80°C using variable (2:1, 4:1 and 10:1) benzene to 1-decene molar ratios. The effects of reaction time and molar ratios on the selectivity, conversion and yield were determined. The alkylation results showed that the catalyst is highly selective to 1-decylbenzene as low amount of side products was obtained. The product yield and conversion increased with reaction time and benzene /1-decene molar ratio while selectivity decreased with increase in benzene /1-decene molar ratio with time.

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Introduction

The dependence of petrochemical industries on active, selective and cheap heterogeneous catalysts cannot be overemphasized. A catalyst is a chemical substance which, even in a minute quantity, affects the rate of a chemical reaction either positively or negatively without being appreciably consumed in the reaction (Petrov et al. [16], Galadima and Muraza [10]).

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 (Mann and Saunders [15]). Homogeneous catalysts exist in the same (homogeneous phase) virtually almost always 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. (Smith and Notheisz [20], Galadima and Muraza [10], Gushchin et al. [11]).

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 (Wilson and Clark [22], Bolognini et al. [2]).

Alkylation is the reaction in which an alkyl (R-) group is added by means of substitution to an aromatic hydrocarbon. The unsaturated (or substituted) aryl or alkyl group usually added to the benzene ring (by substitution), could range from C₁-C₁₄. However, LABs (Linear Alkyl Benzenes) with alkyl or aryl groups within the range of C₁₀-C₁₄ are of rare use (Yuan et al. [23], Devassy et al. [6], Bordoloi et al. [3], Hernandez-Cortez et al. [13], Zhang et al. [24]).

Alkylation of benzene with olefins proceeds with a two-step mechanism via formation of a carbonium ion followed by attack on the benzene ring to form an alkyl benzene. The first step, involves the reaction of the olefin with the acid site to form an

alkyl carbenium ion (which can isomerize almost immediately) to other carbenium ions by hydrogen transfer (Hernandez-Cortez et al. [13]).

Experimental

Catalyst preparation

The CuO-MoO₃/ZrO₂ catalyst was prepared by the impregnation method as described by Haber et al. [12]. 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 h.

To provide the required Brønsted acid sites that can catalyse the reaction, the calcined solid catalyst was soaked in 60cm³ of 2M aqueous H₂SO₄ for 30 minutes. The catalyst was filtered and air dried for subsequent analysis.

Characterization

The XRD analysis was carried out using 5g of the catalyst on a PANalytical 2830 ZT 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* is crystallite size, *K* is constant with values from 0.92 to 1.0, λ is wave length of the incident x-ray (usually taken as 0.1542nm), *B* is 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* is full width at half maximum (FWHM) for the highest peak.

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 $4000-400\text{cm}^{-1}$ using an MB3000 IR analyzer and the spectra was generated using a high-tech Thermo Scientific Nicolet software.

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.

Thermal analysis was carried out using a DTG-60AH Thermogravimetric Analyser with the heating rate set at $20^{\circ}\text{C}/\text{min}$ and nitrogen flow rate $40\text{ ml}/\text{min}$ 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.

Catalyst evaluation

Alkylation of benzene is an important process in the petrochemical industry. One of the most useful alkyl benzenes, ethylbenzene (EB), is used as feedstock in the production of styrene, polystyrene etc. with higher olefins/substituted alkanes ($\text{C}_{10}\text{-C}_{14}$), linear alkyl benzenes (LABs), which are the primary raw materials for the synthesis of lab sulfonates and surfactant intermediates used in producing detergents, are produced (Devassy et al. [6], Hernandez-Cortez et al. [13], Zhang et al. [24]).

Liquid phase alkylation reaction is of great industrial use. Although benzene alkylation could be carried out within temperature range of $70\text{-}180^{\circ}\text{C}$ and far above as reported, Yuan et al. [23] established that at 80°C , there is an improved selectivity (>26.0) and conversion (98.4%) of 1-dodecene. The reaction was reported to have been achieved through variable reaction conditions. The main catalysts used to achieve this reaction are the Lewis acids, like AlCl_3 , FeBr_3 etc. at about 900°C and 1 atm. However, a temperature of 300°C has been reported elsewhere in the alkylation of m-cresol (Bolognini et al. [2], Khlebnikova et al. [14]).

Three sets of alkylation reactions were carried out; using 2:1, 4:1 and 10:1 benzene-dec-1-ene molar ratios. 2:1 molar ratio consisted of pure benzene (18cm^3), 0.03g (1wt%) of the prepared catalyst and 19cm^3 of 1-decene. 4:1 molar ratio contained 36cm^3 of benzene, 19cm^3 of 1-decene and 0.045g (1wt%) of the solid catalyst while 10:1 consisted of 90cm^3 of benzene, 19cm^3 of 1-decene and 0.092g (1wt%) of the catalyst. The set up was maintained and refluxed for 2 h reaction time, taking a fraction of the products every 40 minutes.

Product analyses and selectivity properties determination

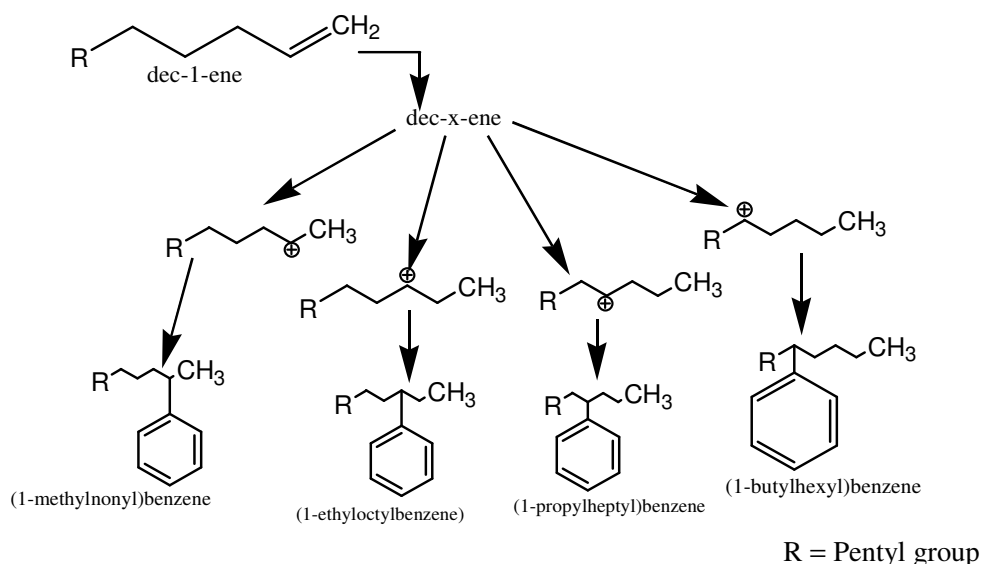


Figure 1. Possible obtainable alkylation products from benzene alkylation with 1-decene. Source: Hernandez-Cortez et al. [13].

Agilent 7890A GC coupled with 5977MS was used for the analysis of the alkylation products in the variable fractions. $1\mu\text{l}$ of the sample was punctured through the inlet using an automatic sampling device. As the sample pass through the column (located in a temperature-controlled oven), equipped with an HP-5 capillary column ($30\text{m}\times 0.25\text{mm}$ i.d) with a coating of $0.25\mu\text{m}$ thick to the detector, the GC was temperature-programmed from 50°C to 300°C at $5^\circ\text{C}/\text{min}$ held at final temperature for 20 minutes with hydrogen as the carrier gas with a flow rate of $1\text{ml}/\text{min}$, pressure of 50 kPa. Representative peaks matching the available compounds were generated by Agilent ChemStation software.

The moles of limiting reactant and that of the target product of the reaction were used to determine the yield, as presented in equation (3) (Yuan et al. [23]).

$$\% \text{ yield} = \frac{\text{Moles of target product}}{\text{Moles of limiting Reactant}} \times 100. \quad (3)$$

The percentage conversion was obtained by using the equation (4) (Yuan et al. [23]).

conversion

$$= \frac{\text{Initial moles of limiting reactant} - \text{Moles of limiting reactant consumed}}{\text{Initial moles of limiting reactant}} \times 100. \quad (4)$$

The selectivity is the ability of the catalyst to cause, direct or favor the formation of one product in a process where several others are possible. It was obtained using the equation (5) (Yuan et al. [23]).

$$\text{selectivity} = \frac{\text{Moles of target product}}{\text{Moles of total products}} \times 100. \quad (5)$$

Results

The results obtained from catalyst characterization and testing are presented in the following Tables 1-6 and Figures 1-5.

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

Mineral	Chemical Formula	Composition (%)
Baddeletite	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.

Table 5. Alkylation products obtained using 2:1, 4:1 and 10:1 molar ratios.

Reaction time (min)	Decyl benzene (%)			Other products (%)		
	2:1	4:1	10:1	2:1	4:1	10:1
40	13.19	18.77	32.91	*11.93	*14.75	*32.23
80	31.03	37.91	58.41	*20.25	*12.57	*11.09
120	51.22	39.81	68.54	*10.23	*21.85	*20.83

*Other products (that appeared) in all molar ratios with time are:

10:1- Hexadecane, Toluene, 1-octene, Nonadecane, Eicosane, Heneicosane and Undecylbenzene.

4:1- Hexadecane, 2-octene, Eicosane, Octadecane, Heneicosane, Heptacosane, 4-decene and 5-undecene.

2:1- Hexadecane, 1-octene, 4-undecene, 2-undecene, 4-decene, 2-octene, 1-decene.

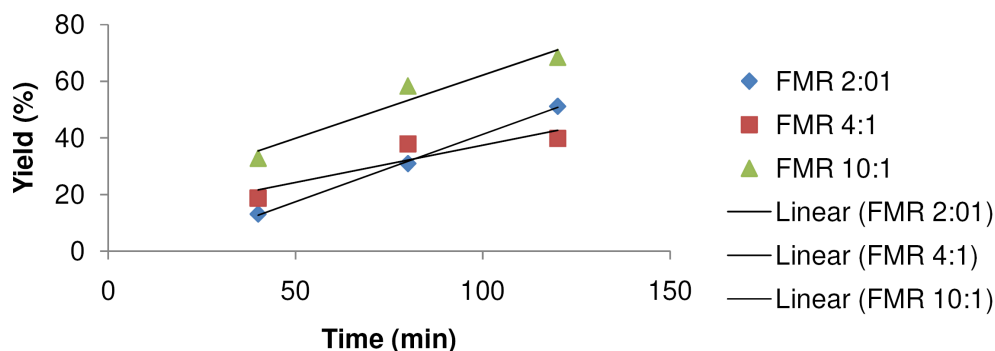


Figure 2. Graph showing variation in % decyl benzene and change in substrate molar ratio with time.

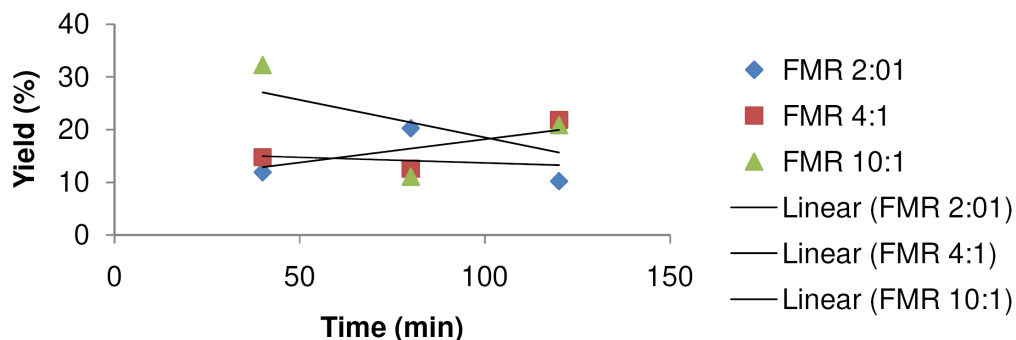


Figure 3. Graph showing variation in % other products and change in substrate molar ratio with time.

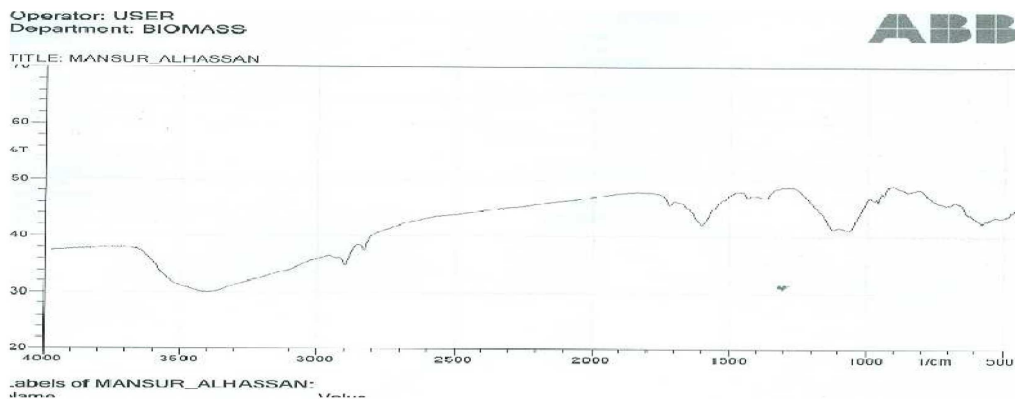


Figure 4. FTIR spectra of the CuO-MoO₃/ZrO₂ catalyst.

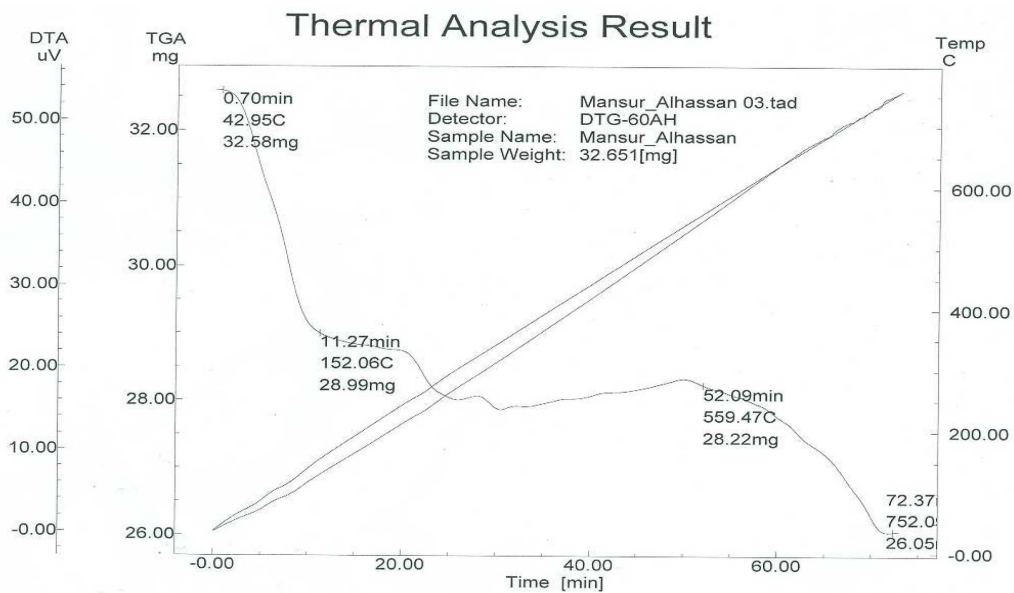


Figure 5. TGA spectra of the CuO-MoO₃/ZrO₂ catalyst.

Table 6. Percentage selectivity, yield and conversion in the different alkylation products with time.

Molar ratio	Catalyst Testing	Reaction time (minutes)		
		40	80	120
2:1	Selectivity (%)	52.50	60.50	83.35
	Yield (%)	13.19	31.03	51.22
	Conversion (%)	25.12	51.29	61.45
4:1	Selectivity (%)	55.99	75.09	64.56
	Yield (%)	18.77	37.91	39.81
	Conversion (%)	33.52	50.48	61.66
10:1	Selectivity (%)	60.09	84.04	76.69
	Yield (%)	32.91	58.41	68.54
	Conversion (%)	54.76	69.50	89.37

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 (Zr_4O_8) is equivalent to ZrO_2 , the catalyst support material while Bonattite ($Cu_4S_4O_{28}H_{24}$) is equivalent to $CuSO_4 \cdot 12H_2O$. The principal mineral components in the catalyst precursor are ZrO_2 (as shown in Tables 1 and 4) and hydrated copper sulphate ($CuSO_4 \cdot 3H_2O$); constituting up to 42% of the solid catalyst; which agrees with Zhang et al. [24] 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. [12], surfaces of solid heterogeneous catalysts could be blocked by physisorbed water. Zhang and co-workers [24] and Yuan et al. [23] reported that fraction of water of crystallization could be noticed even after calcination. The presence of copper sulphate mineral (bonatite) is attributed to the precursor salt, copper nitrate $Cu(NO_3)_2$ 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 and co-workers [6] for zirconia-supported 12-tungstophosphoric acid utilized as solid catalyst for the synthesis of linear alkyl benzenes. However, Zhang et al. [24] 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 (700-600cm⁻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 (3000-2800cm⁻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 and co-workers [6] 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 (Baran [1]). The FTIR spectra corroborated the absence of Mo-O absorption band which should have appeared around 998cm⁻¹. Hardcastle and Wachs [9] assigned stretching frequencies and bond distances in tetrahedrally coordinated molybdenum oxide reference compounds between 998-280cm⁻¹.

The thermogravimetric analysis (thermal evolution) result of the CuO-MoO₃/ZrO₂ catalyst (presented in Table 3 and Figure 5) 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 NH₃ and NO₂ have decomposed during the calcination process which was carried out at 450°C for 2 h. 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 CuSO₄.12H₂O (bonattite) was approximately 57.5% and the TGA spectra (Figure 5) indicated a significant weight loss between room temperature to 100 or 125°C within which all absorbed water would evaporate. Hernandez-Cortez and co-workers [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 Davis [21] 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 CuO-MoO₃/ZrO₂ catalyst. The principal oxide (ZrO₂), with the support constituting 50.91% of the total oxides in the catalyst. This is in agreement with the suggestion of Zhang et al. [24] that support materials could be up to > 40wt% of a solid heterogeneous catalyst. CuO, SO₃ and P₂O₅ are the next dominant oxides with 12.93%, 11.00% and 9.90% abundance respectively. Trace amount of As₂O₃, PtO₂, Bi₂O₃, PbO, Er₂O₃, Tb₄O₇, Co₃O₄, TiO₂ and CeO₂ were also discovered. Compounds lost on ignition (L.O.I) amounted to 14.22% (second most dominant, next to ZrO₂). Most components of the LOI may range from physisorbed water, water of crystallization or water originating from acidic protons as reported by Devassy et al. [6]. 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. [12] 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. The absence therefore justifies that molybdenum oxide has been lost from the preparation process, which was only noticed at the point of characterization. Therefore it can be concluded that the prepared catalyst was CuO/ZrO₂.

Traces of metal oxides like As₂O₃, PtO₂, Bi₂O₃, PbO, Er₂O₃, Tb₄O₇, Co₃O₄, TiO₂ and CeO₂ that appeared in the XRF result could be attributed to impurities in the zirconia.

Table 5 depicts the variation with time, of percentage decyl benzene and other side products realized from the 2:1, 4:1 and 10:1 benzene to 1-decene molar ratio. There is an observable increase in the quantity of decyl benzene realized with time. The % yield for decyl benzene increased from 13.19% to 51.22% at 40 and 120 minutes respectively. There is an observable increase as well, in the available side products from 40 minutes to 80 minutes. This clearly indicated the effect of residence time as reported by Yuan et al. [23] that at reaction time, an increase in yield and selectivity is generally observed. However, the final conversion decreases with increase in temperature. Saxena et al. [18] reported the highest conversion of 86.6% on alkylating benzene with zeolite-based catalyst and concluded that increase in reaction temperature could not enhance product conversion.

The percentage decyl benzene obtained at 40 minutes (18.77%) increased to 37.91% at 80 minutes which increased slightly to 39.81% at 120 minutes. As compared to the percentage products realized using 2:1 (Table 5), percentage decyl benzene increased from 13.19% (2:1, 40 minutes) to 18.77% (4:1, 80 minutes). Also, 31.03% (2:1, 80 minutes) shot up to 37.91% (4:1, 80 minutes) while 51.22% (2:1) decreased to 39.81% (4:1) at 120 minutes. This shows that the reaction gives better yield at lower molar ratio and longer reaction time. A contrary report by Yuan et al. [23] showed that conversion for 1-decene increases with increase in benzene content in the reactant mixture. However, the decrease in percentage decyl benzene (39.81%) observed in 4:1 at 120 minutes compared to 51.22% in 2:1, 120 minutes could be attributed to the higher catalytic activity at the beginning of reactions which decreases gradually with time. The

same reason has been reported by Yuan et al. [23], Faghihian and Mohammadi [8], Zhang et al. [24] and Khlebnikova et al. [14]. It could similarly be observed that, there was an increase in the product (decylbenzene) yield with time. Gushchin et al. [11] reported a yield of 88.11% at 30 minutes, which decreased to 60.06% at 5 h reaction time in the alkylation of benzene using dimethyldichlorosilane.

Product yield at 80 minutes (31.03%) in 2:1 increased to 37.91% in 4:1, 80 minutes; but 51.22% observed at 120 minutes in 2:1 decreased to 39.81% in 4:1, 120 minutes.

Table 5 (and Figure 2) presents the alkylation results obtained for 10:1 benzene to alkene molar ratios at 40, 80 and 120 minutes reaction time. The percentage decyl benzene realized at 40 minutes (32.91%) shot up to 58.41% at 80 minutes and further to 68.54% at 120 minutes. As compared to alkylation products obtained using 2:1 and 4:1 benzene to 1-decene molar ratios, the percentage decyl benzene obtained using 10:1 molar ratio at 40, 80 and 120 are higher. Decyl benzene (product) yield at 40 minutes increased from 13.19% (2:1) to 18.77% (4:1) and further to 32.91% (10:1). The product yield (32.91%) observed in 10:1 (40 minutes) nearly doubles 18.77% obtained for 4:1 (40 minutes) showing a multiple increase in yield with increase in reactants molar ratio. This is further observed in product yield at 80 minutes from 31.03% (2:1) to 37.91% (4:1) and further to 58.41% (10:1). It has been reported by Yuan et al. [23], Ebrahimi et al. [7], Zhang et al. [24], Faghihian and Mohammadi [8] and Devassy et al. [6], that, higher benzene to alkene molar ratios favours product yield. Faghihian and Mohammadi [8] reported this as the reason why industries use high (8.75:1) benzene to alkene molar ratios for alkyl benzene productions. Similarly, the percentage side products (Table 5 and Figure 3) obtained in the reactions at 40 minutes increased from 11.93% (2:1) to 14.75% (4:1) and further to 32.23% (10:1) followed this trend. In addition, the decrease in the percentage side products at 80 minutes from 20.25% (2:1) to 12.57% (4:1) to 11.09% (10:1) indicates a decrease in side products with increase in benzene molar ratio in alkylation reactions. Zhang et al. [24], Faghihian and Mohammadi [8], Devassy et al. [6] and Guschin et al. [11] reported that excess molar of benzene over olefin could be used to reduce the amount of dialkylated products.

The increase in yield with increase in benzene to 1-decene molar ratios; the increase in product yield with residence time and the decrease in catalyst activity with time are outlined from the above statements.

The calculated percentage selectivity, yield and conversion obtained for the various

benzene to 1-decene molar ratios at 40, 80 and 120 minutes is presented in Table 6. The selectivity for 1-decene using 2:1 (benzene to 1-decene) molar ratios increased from 52.5% (40 minutes) to 60.5% (80 minutes) which further shot up to 83.35% (120 minutes). This clearly indicated that selectivity is favoured by increase in residence time as reported by Faghihian and Mohammadi [8], Saxena et al. [18] that increase in selectivity is noticed with increase in reaction time.

At 4:1 benzene/1-decene molar ratios, the selectivity shifted from 55.99% (40 minutes) to 75.09% (80 minutes). However, at 120 minutes, it decreased to 64.56%. The increased selectivity from 55.99% to 75.09% at 40 and 80 minutes respectively, could be attributed to the difference in the residence time. On the other hand, the selectivity in 4:1 benzene /1-decene molar ratio decreased from 75.09% (80 minutes) to 64.56% (120 minutes) shows a decrease in selectivity at high molar ratios with time. Yuan and co-workers [23] reported a decrease in selectivity (26.0% - 22.6%) at high molar ratios.

At 10:1 benzene/1-decene molar ratios, the selectivity increased from 60.09% (40 minutes) to 84.04% (80 minutes) but decreased to 76.69% (120 minutes). This further confirms the decrease in selectivity with time at high reactant ratios.

The product selectivity at 40 minutes increased from 52.5% (2:1) to 55.99% (4:1) and further to 60.09% (10:1). This shows the effect of increased selectivity with increase in benzene/1-decene molar ratios. The selectivity for decyl benzene in all molar ratios increased with increase in benzene / 1-decene molar ratios but decreased with time at higher molar ratios. The selectivity for decylbenzene in all the molar ratios increased with increase in benzene-alkene molar ratios except in 4:1, 80 minutes (75.09%) which decreased to (64.56%) at 120 minutes and 10:1, further at 80 minutes (84.04%) which also decreased to (76.69%) at 120 minutes. An effect of benzene-alkene molar ratio plays a significant role in alkylation reaction. The highest selectivity observed for 10:1 (80 minutes) is 84.04% which is much higher than 26.0% (selectivity) reported for USY zeolite for alkylation of benzene with 1-Dodecene by Yuan et al. [23]. The difference in residence time and reactant molar ratios could account for this, as reported by Yuan et al. [23], Faghihian and Mohammadi [8] and Gushchin et al. [11].

The product selectivity at 120 minutes for 2:1 (83.35%) was higher than 64.56% (4:1, 120 minutes) and 76.69% (10:1, 120 minutes) showing a decrease in selectivity at higher molar ratios. Yuan and co-workers [23] reported a decrease in selectivity for USY zeolite catalyst (26.0%-22.6%) at higher molar ratios. According to Galadima and

Muraza [10], Gushchin et al. [11], increase in benzene to alkene molar ratio promotes catalyst selectivity to both mono- and dialkylated benzenes when the temperature and space velocity are kept constant.

Conclusion

The prepared solid catalyst (CuO/ZrO_2) was found active, selective and gave desired products along with some by-products. In addition, benzene to alkene molar ratios has positive effects on product yield, conversion and selectivity for alkyl benzene. Highest conversion of 89.37%, selectivity of 84.04% and yield of 68.54% were obtained.

Furthermore, reaction residence time increases the product yield, conversion and selectivity of alkylation reaction. Reaction is still on going to explore new parameters such as catalyst lifetime, optimal performance and deactivation properties for process upgrade.

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