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Alhassan, Mansur
 Department of Chemistry,
 Sokoto State University,
 Birnin Kebbi Road, Sokoto-
 Nigeria.

Garba, Abdulrashid Abubakar
 Department of Chemistry,
 Sokoto State University,
 Birnin Kebbi Road, Sokoto-
 Nigeria.

Suleiman, Mustapha
 Department of Chemistry,
 Sokoto State University,
 Birnin Kebbi Road, Sokoto-
 Nigeria.

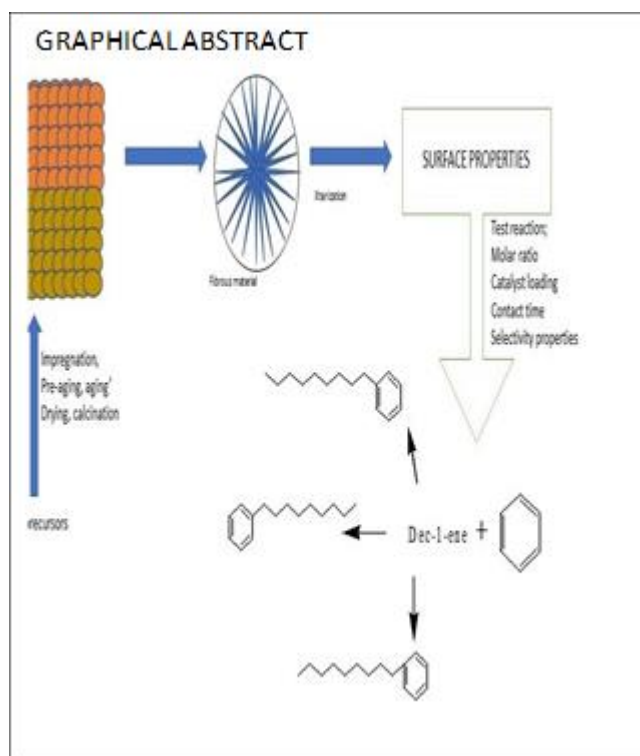
Correspondence:
Alhassan, Mansur
 Department of Chemistry,
 Sokoto State University,
 Birnin Kebbi Road, Sokoto-
 Nigeria.

Surface Properties of Acidic Heterogeneous Catalysts for Benzene Alkylation - A Comparative Study

Alhassan Mansur, Garba Abdulrashid Abubakar, Suleiman Mustapha

Abstract

Preparation of cheap, active, selective, and more eco-friendly heterogeneous catalysts for alkylation of benzene with alkene has been attempted. 3 set of catalysts; acidified and unacidified $\text{CuO-MoO}_3/\text{Al}_2\text{O}_3$ catalysts prepared by impregnation using suitable nitrate precursors as well as sulphuric acid-activated Shagari clay solid catalysts were calcined at 450°C for 2 h and activated (by soaking in 2M H_2SO_4 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. Presence of sulphate and alumina oxides was revealed by the FTIR analysis due to appearance of absorption bands around $1150\text{-}1170\text{cm}^{-1}$ and $850\text{-}600\text{cm}^{-1}$ respectively. The effects of reaction time and molar ratios on the selectivity, conversion and yield were determined in a fixed bed reactor using the catalysts. The alkylation results showed that the acidified catalysts were 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.



Keywords: Activated Clay, Acidified/Unacidified Heterogeneous Catalysts, Alkylation, Selectivity Properties.

Introduction

Use of Heterogeneous catalysts in the petrochemical industries is inevitable as there is minimization of wastes attributed to their homogeneous counterparts, ease in handling and product separation, catalyst re-use among others [1-2].

Production of styrene (the raw material for polystyrene), styrene-acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS), latexes as well as styrene-butadiene elastomers are produced via the alkylation reaction using benzene, alcohol and or alkene co-reactants [1,3-4].

Heterogeneous catalysts occur in the forms of molecular sieves, ceramics, fibres, wires, salts and mineral acids metals (skeletal metals), metal oxides, sulphides, heteropolyacids, nitrides, carbides, borides, alloys, etc. [5-7].

According to Alhassan et al. [2] the use of mineral acid along with heterogeneous catalysts for liquid phase industrial reaction has become a focus. This is possible because [8-9] reported successful commercialization of USY [10-11], Beta [12] and MCM-22 [13] catalysts for liquid-phase alkylation of benzene operated at low temperatures and high pressure with longer catalyst life time.

Thermal stability, reactivity as well as porosity are key reasons why clay/ clay materials are facing attention and widely utilized as catalysts and catalyst supports (Thomas and Thomas [14]; Faghihian and Mohammadi [15]).

Although, solid catalysts such as zeolites [15-18], clays [19-21] as well as supported and surface-modified metals and metal oxides, carbides, borides, wires etc [2,10,17-19] have been studied as alkylation catalysts. However, some chemical and thermal activation steps are needed.

A significant role is also played by supported catalysts in the industrial processes. Supports stabilize the dispersion of the active components e.g (metals, supported on oxides, provides high surface area for availability of the active components to the reaction medium. Supports are although often considered to be inert; they may interfere actively with the catalytic processes [20-22].

Alkylation of aromatics is currently carried out using Friedel-Craft's catalysts such as $AlCl_3$, $FeCl_3$, HF or strong Brønsted acids. Serious problem attributed to these materials as heterogeneous catalysts is their low surface area, recyclability, corrosion, pollution, handling, safety and separation among others [1-2, 6-9,20-22].

The substituted or unsaturated alkyl/aryl group usually added to the benzene ring (by substitution), could range from C_1 - C_{14} . Alkylation is the reaction in which an alkyl (R-) group is added by means of substitution to an aromatic hydrocarbon via a carbocation.

However, [17,23-25], reported that LABs (Linear Alkyl Benzenes) with alkyl or aryl groups within the range of C_{10} - C_{14} are of rare use and that is why this study will use a long chain alkene.

Experimental

Procurement of Materials

Anhydrous Copper (II)nitrate, $Cu(NO_3)_2$; ammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$; Aluminium (III) oxide Al_2O_3 ; Benzene C_6H_6 ; 1-dodecene, $CH_2=CH(CH_2)_7CH_3$ and Sulfuric acid H_2SO_4 were purchased from Sigma Aldrich and used with no further treatments. Clay Sample used in the work was obtained

from Shagari Earth Dam, Shagari town of Sokoto State, Nigeria.

Physical Treatment of Raw Clay

Clay paste was prepared, cellulose waste materials in the slurry were removed, the clay paste was oven-dried, grinded to fine powder and stored until use.

Preparation of Catalysts

Three sets of catalysts were prepared prepared by the impregnation method as reported by [22] and [25] viz: Two sets (acidified and unacidified) $CuO-MoO_3/Al_2O_3$. Aqueous saturated solution of ammonium heptamolybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ and copper nitrate $[Cu(NO_3)_2]$ were prepared by adding 15.75g of each salt in a beaker containing 60 cm^3 of distilled water. Alumina (38.5g) was slowly deposited into the solution mixed at 120 rpm for 2h until thick slurry is formed.

Acid Activation

Sieved (dry) clay sample (70g); one portion of $CuO-MoO_3/Al_2O_3$ precursors) were each soaked in 60 cm^3 of 2M aqueous H_2SO_4 for 30 minutes in order to provide the required Brønsted acid sites that can catalyse the reaction. The catalyst residue was filtered and air dried for subsequent analysis.

Heat Treatment

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.

Characterization

The XRD analysis was carried out using 5g each 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 FTIR spectra of the solid catalysts was obtained by grinding each of the catalysts into fine powder with a particle size about 1-2 microns. Seven milligram (7mg) each of finely ground catalyst sample was placed on a KBr plate and a small drop of Nujol (mineral oil) was added. The samples were 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 analyser and the spectra was generated using a high-tech Thermo Scientific Nicolet software.

Two milligrams (2mg) each of the ground samples of pulverized catalyst were placed into a sample cup. XRF 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.

Test Reaction/ Catalyst Evaluation

Reaction was carried out using a fixed bed glass reactor placed over a heating mantle equipped with a magnetic stirrer. 3 sets of alkylation reactions were carried out for 2h each, using variable (2;1, 4:1 and 10:1) benzene to 1-dodecene molar ratios. Fractions of the reaction container were taken at regular interval of 40 minutes each to study the selectivity, product yield and reactants conversion.

Results

Table 1: Result of XRF Analyses of the Acidified/un acidified CuO-MoO₃/ZrO₂ Catalysts.

Acidified CuO-MoO ₃ / Al ₂ O ₃	Un acidified CuO-MoO ₃ / Al ₂ O ₃	Oxide Composition (%)
9.50	9.90	P ₂ O ₅
13.45	3.42	SO ₃
0.78	0.05	TiO ₂
-	0.058	Fe ₂ O ₃
0.014	0.009	Co ₃ O ₄
14.02	13.05	CuO
0.009	0.034	As ₂ O ₃
52.98	50.91	Al ₂ O ₃
0.07	0.014	BaO
0.20	0.02	CeO ₂
0.05	0.03	Tb ₄ O ₇
0.09	0.03	Er ₂ O ₃
0.100	0.091	PtO ₂
0.046	0.029	PbO
0.028	0.022	Bi ₂ O ₃
8.663	22.207	LOI

LOI=Loss on ignition

Table 2: Result of XRF Analysis of Activated Shagari Clay.

Oxide/ Parameter	Shagari Clay	Other Clay samples			
		Rousel, Magnia[26]	Montm. Cf [27]	Magnia RM [26]	Bentonite Cf [27]
Al ₂ O ₃	18.47	18.04-19.02	17.15-20.27	24.3	9.682
CaO	0.32	1.05-2.95	0.23-4.90	0.98	17.042
Fe ₂ O ₃	0.48	1.98-2.94	0.50-5.65	2	18.809
MgO	0.56	0.11-2.65	0.23-0.72	3.58	3.971
MnO	1.78	2.49	-----	-----	-----
Na ₂ O	1.01	0.86-2.42	Tr-1.32	0.70	0.139
K ₂ O	1.04	1.14-1.21	0.28-1.27	1.06	1.768
SO ₃	0.98	0.1	-----	0.10	0.065
P ₂ O ₅	0.04	<0.05	-----	0.02	-----
SiO ₂	56.52	54.10-54.98	50.04-57.49	55	48.523
TiO ₂	0.39	0.14-0.16	0.12-0.48	0.10	-----
*LOI	18.41				

Montm. Cf= Montmorillonite family, Bentonite Cf=Bentonite clay family, LOI= Loss on Ignition

Table 3: Prominent bands in the FTIR spectra of the Catalysts.

Catalyst	Bands (cm ⁻¹)	Peak Assignment [ref]
Unacidified CuO-MoO ₃ / Al ₂ O ₃	700	Al-O stretching [38]
	790	Al-O stretching [38]
	900	Al-Fe-OH bending vibration [38]
Acidified CuO-MoO ₃ / Al ₂ O ₃	670	Al-O stretch vibration [35]
	800	Si-OH stretch [38]
	850	Al-Fe-OH bending vibration [38]
	930	Symmetric stretching of SO ₄ ²⁻ tetrahedral [38]
	1030	In plane (Si-O) stretching [38]
	1150	SO ₄ ²⁻ stretch [33,34]
Activated Shagari Clay	1200	SO ₄ ²⁻ stretching [33-34]
	650	O-H deformation [38]
	790	Al-O stretching [38]
	820	Al-Mg-OH deformation [38]
	930	Al-OH [35]
	1000	Kaolinite [35]
	1050	Muscovite[35]
1170	SO ₄ ²⁻ stretching [35,33] Out of plain Si-O stretch for montmorillonite [38]	

Table 4: Product Yield obtained for the various molar ratios with the Catalysts.

Molar ratio	Time (min)	Yield (%)		
		Unacidified CuO-MoO ₃ / Al ₂ O ₃	Acidified CuO-MoO ₃ / Al ₂ O ₃	Activated Shagari Clay
2:1	40	1.04	13.19	10.66
	80	1.86	31.03	12.78
	120	2.43	51.22	18.99

4:1	40	2.26	18.77	11.06
	80	1.98	37.91	17.54
	120	4.02	39.81	19.92
10:1	40	3.03	32.91	13.78
	80	3.66	58.41	19.22
	120	3.97	68.54	23.56

Table 5: Percentage Selectivities in the Alkylation Products with Time.

Molar ratio	Time (min)	Selectivity (%)		
		Unacidified CuO-MoO ₃ / Al ₂ O ₃	Acidified CuO-MoO ₃ / Al ₂ O ₃	Activated Shagari Clay
2:1	40	12.05	52.50	26.67
	80	10.42	60.50	28.74
	120	10.76	83.35	30.22
4:1	40	7.23	55.99	31.45
	80	6.88	75.09	33.62
	120	9.62	64.56	40.46
10:1	40	13.58	60.09	32.69
	80	14.02	84.04	39.98
	120	14.66	76.69	43.80

Table 6: Percentage Conversion in the alkylation products with time.

Molar ratio	Time (min)	Conversion (%)		
		Unacidified CuO-MoO ₃ / Al ₂ O ₃	Acidified CuO-MoO ₃ / Al ₂ O ₃	Activated Shagari Clay
2:1	40	8.63	25.12	39.97
	80	17.85	51.29	44.46
	120	22.50	61.45	62.83
4:1	40	31.25	33.52	35.16
	80	28.77	50.48	52.17
	120	41.78	61.66	49.23
10:1	40	22.30	54.76	42.15
	80	26.10	69.50	48.07
	120	27.08	89.37	53.78

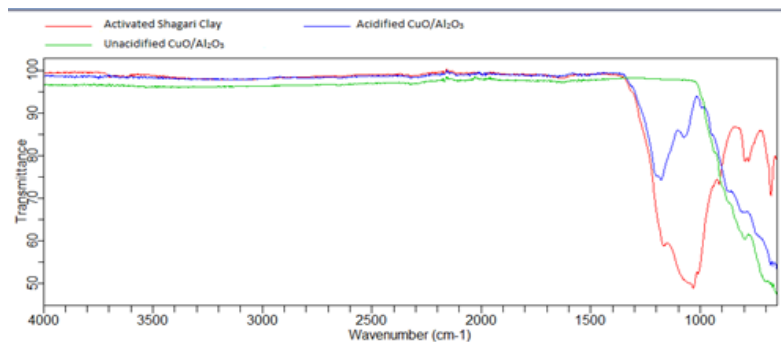


Fig 1: FTIR Spectra of unacidified and Acidified CuO/Al₂O₃ and Activate Shagari Clay.

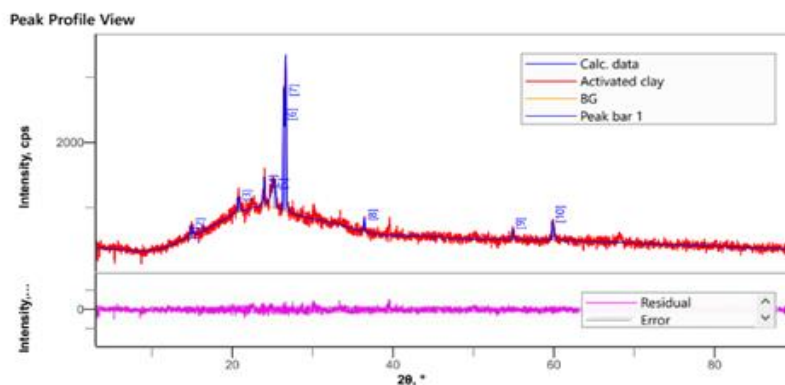


Fig 2: x-ray diffraction pattern of sulphuric acid-activated Shagari clay.

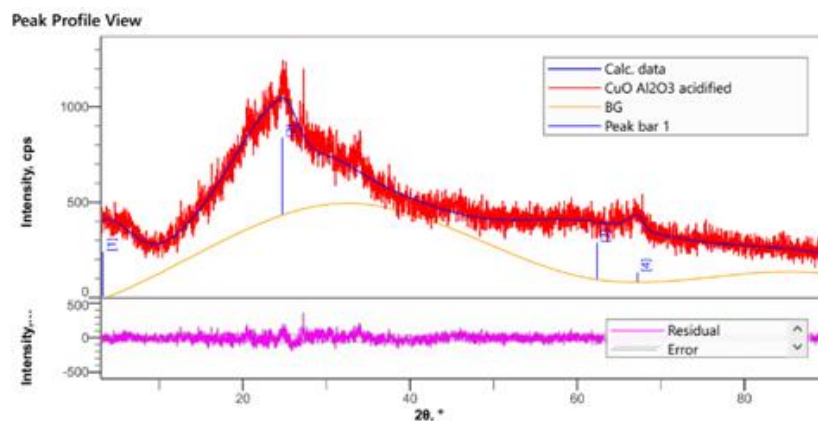


Fig 3: XRD Profile of Acidified CuO-MoO₃/Al₂O₃ catalyst.

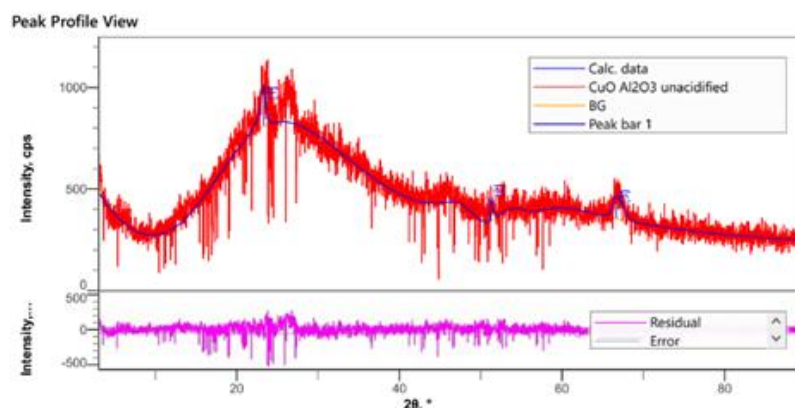


Fig 4: XRD Profile of the Unacidified CuO-MoO₃/Al₂O₃ catalyst.

Discussion

X-ray fluorescence spectroscopy result of acidified/unacidified CuO-MoO₃/Al₂O₃ catalysts presented in Table 1 shows the oxide composition in each of the two catalysts. Predominantly, containing Al₂O₃, CuO, P₂O₅ and SO₃ with percentage abundance of 50.91, 13.05, 9.90 and 3.42 for unacidified catalyst while 52.98, 14.02, 9.50 and 13.45 respectively in the acidified catalyst. The wide variation in the SO₃ composition between the acidified and unacidified (10.03) catalyst could be attributed to the mineral acid activation used for the acidified catalyst. Traces of As₂O₃, TiO₂, CeO₂, BaO, PbO, PtO₂, Tb₄O₇ appeared in almost all the two catalysts with the exception of Fe₂O₃ which do not appear in the acidified catalyst. Similar reports by Alhassan et al. [2] showed presence of impurities in trace amounts in the prepared catalysts.

However, Al₂O₃ in the acidified catalyst (52.98%) outweighed 50.91 in the unacidified catalyst due possibly to the sulphuric acid activation which According to [12,16-19] makes the sulphated alumina even more acidic.

Table 2 captured the oxide compositions in the activated Shagari clay in comparison to the works of Djebbar and Coworkers [26]. The principal oxides in the Shagari clay as in others, are Al₂O₃ (18.47%), SiO₂ (56.52%) and traces of K₂O, Na₂O, MnO, Fe₂O₃, CaO, SO₃, P₂O₅ and TiO₂. The values fall within the montmorillonite clay family ranges shown in the Table with the exception of MnO, SO₃ and P₂O₅, whose values were not available. A close look at the values of oxides reported by [26] and [27] displayed in Table 2 confirms that Shagari clay compares favourably in oxide compositions with most of its counterparts.

The IR values of the prepared catalysts shown in Table 3 were recorded over a spectral range of 400-4000cm⁻¹.

Many clays minerals /solid catalysts have been identified using IR techniques [2, 22,26] absorption bands appearing at 1100.78cm⁻¹ is probably due to Si-O stretching while the bands at 521.24cm⁻¹, 456.84 as well as 830.38 cm⁻¹ are attributed to Si-O-Mg, si-O-Fe and Si-O-Al vibrations respectively. This testifies that the clay mineral used in this study is of kaolinite and montmorillonite origin as supported by the XRF results.

Table 4 presents Alkylation results (yield) obtained using 2:2, 4:1 and 10:1 benzene to 1-decene molar ratios at 40, 80 and 120 minutes. The percentage decylbenzene in the unacidified CuO-MoO₃/Al₂O₃ catalyst increased at 40 minutes from 1.04 in 2:1, to 2.26 and 3.03 in 4:1 and 10:1 molar ratios respectively.

Similar trend is noticed in the yield of decyl benzene obtained in 2:1, 4:1 as well as 10:1 at 40, 80 and 120 minutes. The highest value observed using the unacidified CuO-MoO₃/Al₂O₃ catalyst is 4.025 at 120 minutes in 4:1 molar ratio. This, according to [28] is true because at the beginning of a reaction, reactants continue to disappear with time while products keep appearing with time. On the contrary, there is decrease in yield at 120 minutes (10:1) for unacidified catalyst.

Accordingly, Activated Shagari clay showed percentage above that of the unacidified catalyst in all molar ratios with time. One feature observable in all the results is that, even though the activated clay showed less product yield than acidified CuO-MoO₃/Al₂O₃, it appeared to overshadow the percentage products in all molar ratios at all contact times for the unacidified catalyst. At 40 minutes in 2:1 reaction for example, 1.04% in the unacidified catalyst corresponded to 10.66% in the Activated clay. Similarly, in 4:1 molar ratio at 40 minutes, 2.26% in the

unacidified catalyst corresponded to 11.06 in the activated clay. However, the differences between yield of unacidified and activated clay catalysts becomes less as the contact time increases in all molar ratios, similar to reports of [29]. The fact that the values in the Activated clay multiplies those in the unacidified catalyst with time in the early stage of the reaction (40 minutes), suggests that the Activated clay is more active in the beginning of the reaction contrary to the unacidified catalyst, and less active as the reaction proceeds to completion. [25] as well as [30] are of the view that certain alkylation catalysts lose activity almost immediately after beginning of the reaction as is the case with Shagari clay. On the other hand, the Acidified CuO-MoO₃/ Al₂O₃ catalyst showed excellent percentage yield of decyl benzene in all molar ratios with time, compared to its other two counterparts. Therefore, the observable increase in the percentage decylbenzene with time in all (2:1,4:1 and 10:1) molar ratios shows that the (acidified CuO-MoO₃/ Al₂O₃) catalyst is active, and do not seize activity with time.

On the contrary, the unacidified CuO-MoO₃/Al₂O₃ catalyst showed poor product yield especially, in the beginning of the reaction; and unlike the shagari clay, which lost activity (almost instantly) with time. As a result, the observed trend in the beginning of the reaction for the two catalysts (Activated clay and unacidified) catalysts has changed with time throughout the reaction.

Generally, there appeared to be observable increase in percentage decyl benzene with increase in the reactant's molar ratios. [1-2] as well as [6-8] reported that there is always increase in desired alkylation products with increase in reactants molar ratios.

Percentage selectivity for decyl benzene in the variable alkylation products with time in all the molar ratios for the three catalysts is presented in Table 5. It is clear that unacidified CuO-MoO₃/ Al₂O₃ had the least selectivity in all the molar ratios with time. Similar to the table 4, selectivity values observed in the activated clay doubles those recorded in the unacidified catalyst. 12.05%, 7.23 and 13.58% recorded at 40 minutes in 2:1, 4:1 and 10:1 all shot up to 26.67,31.45 and 32.69% for activated clay respectively.

Selectivity for decyl benzene generally increased with contact time in all the reactants molar ratios except for the unacidified CuO-MoO₃/ Al₂O₃ catalyst where it reduced from 7.23% at 40 to 6.88% at 80 in 4:1 reactant ratio.

Supported by the works of [31], [32] and [33]; selectivity for desire products in alkylation catalysts requires that the catalyst be acidic. This is evident from the fact that almost all the selectivity values observed in the acidified CuO-MoO₃/ Al₂O₃ and activated clay exceed those in the unacidified catalyst by far. [33] reported that alkylation catalysts are selective to desired product only when they bear Brønsted acidic sites.

Effect of Catalyst Acidification

Benzene Alkylation using alkene (1-decene) takes place via carbonium mechanism at the catalyst acid-site. However, stabilities of the ions determine which product dominates [17]. Catalyst's acidity affects the stability, selectivity and activity of the catalyst. Acid strength, density and acid type for instance Brønsted and Lewis acidity sites need to be strong for the reaction to occur [9,16]. Deactivation (quickly) occurs when catalyst pores are clogged, weak and

medium acid sites domination, decrease in calcination temperature etc.

The two acidified catalysts showed excellent product yield (Table 4) compared to unacidified catalyst possibly due to the stated reasons. Table 5 showed the selectivity values obtained for acidified catalysts as well as the unacidified catalyst. Polymers produced via polymerization on small acid site pores are blocked which leads to catalyst deactivation. Accordingly, open mesoporosity coupled with acid sites determines the reaction optimum performance [6,15,18,28]

Effect of Benzene to 1-decene Molar ratio

Results presented for the alkylation reactions in Tables 4-6 showed variable values for 2:1, 4:1 and 10:1 benzene to alkene molar ratios. It is clear that product yield (Table 4), showed gradual increase from 2.43 to 4.02 to 3.97 at 120 minutes in 2:1, 4:1 and 10:1 molar ratios respectively.

Similar trend is observed in the selectivity and product conversion with the molar ratios. Alhassan et al [2], [6-9] and [17-19] reported that reactants molar ratio usually affects product yield, selectivity and conversion.

Accordingly, when benzene to 1-decene molar ratio drops to a low value, there is more chance for polymerization and less susceptibility for the target product [12]. For this reason, benzene to alkene molar ratio is increased in alkylation reactions in order to increase the yield, conversion and selectivity [24-25].

Effect of Reactants Contact Time

Basically, reactants disappear while products appear with time for any feasible chemical reaction. Accordingly, the product yield, selectivity and conversion in all the three catalysts increase with time.

The trend in the values presented in Tables 4-6 showed that at 2:1, there is gradual increase (from 40 to 120 minutes) in product yield, selectivity and conversion with time.

Similarly, at 4:1 and 10:1, there is observable shoot-up in the yield, selectivity and conversion with time. Reports from the works of [9], [20] and [23-27] are of the view that reactants' contact time has a direct impact on the yield of the product. The longer the contact time, the higher the yield. Results presented in tables 4-6 are in total conformity to these findings.

Conclusion

Effect of acidification on the activity of CuO-MoO₃/Al₂O₃ has been established. Shagari Clay show promising selectivity especially at high reactant molar ratios. Acidity, Contact time as well as molar ratio variation are key parameters that control alkylation reactions using alkenes.

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