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Selectivity properties and concentration effects in the alkylation pathway of activated clay and CuO-MoO₃/Al₂O₃ catalysts

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Abstract

Selectivity properties of reaction (alkylation) products using three different catalytic substances viz: Acidified Shagari clay, Acidified as well as unacidified CuO/MoO₃/Al₂O₃ catalysts was determined using benzene and 1-decene as co-reactant. The reaction was carried out in a glass reactor at

80°C for 2h. Variable molar ratios (2:1, 4:1 and 10:1) benzene to 1-decene concentration were used. Reaction parameters and selectivity properties (reaction yield, selectivity for decyl benzene and conversion) were studied for the variable molar ratios.

Keywords: Alkylation, Reactants molar ratio, Activated clay, Selectivity properties

Introduction

Long-chain Linear alkylbenzenes (LAB) with long-chains (mostly 10–16 carbon) are often used as precursors in the industrial manufacture of detergents. The typical alkylations of aromatic hydro carbons are manufactured commercially using the well-known Friedel–Crafts method. Acidic catalysts such as AlCl₃, HF, H₂SO₄ which are extremely corrosive, hard to separate from the reaction stream with maximum selectivity to 2-phenyl isomers only about 20% [1-2].

In most cases the electrophile (carbocation) that is generated when the halide (leaving group) complex with aluminium chloride is to make the halogen a better leaving group.

Although the most common method for generating the electrophile for the alkylation reaction employs an alkyl halide and aluminium trichloride, it can be generated in other ways also. For example, reaction of an alcohol and an acid to produce the carbocation which acts as an electrophile and reacts with a pair of pi electrons of the aromatic ring [3].

Thus the leaving group, i.e AlCl₄⁻, which is a weaker base and a better leaving group than chloride anion. Alternatively, the carbocation can be generated by protonation of an alkene. This reaction resembles the additions to alkenes as the one carried out in this work.

Several limitations to the Friedel-Crafts alkylation are; first, the alkyl group(-R-Cl) that is added to the ring acts as an activating group, thus the alkylated product becomes more reactive (by a factor of about 2) than the starting aromatic compound [4].

A significant amount of product(s) where two or more alkyl groups have been added is commonly formed. The best solution to this problem is to use a large excess of the aromatic compound that is to be alkylated. This can easily be accomplished for compounds that are readily available, such as benzene or toluene, by using them as the solvent for the reaction [5-7].

Zeolite catalysts are widely studied to replace the anhydrous solid acid HF or AlCl₃ catalysts [8-11].

According to [3], in the actual alkylation of the phenolic compound it is desirable that the alkene hydrocarbon may be either in excess of or deficient to that of the phenolic compound. The mixture is then heated at a temperature of 70-150° C and that informed the choice of the temperature at which the reaction was carried out.

Experimental

Procurement of Precursors/ Starting Materials

Ammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄.4H₂O]; Anhydrous Copper(II)nitrate, Cu(NO₃)₂; Zirconium (IV) oxide, ZrO₂; Aluminium (III) oxide Al₂O₃; Benzene C₆H₆; 1-dodecene, CH₂=CH(CH₂)₇CH₃ and Sulfuric acid H₂SO₄ were purchased from Sigma Aldrich and used with no further treatments. Clay was obtained from Shagari Earth Dam in Shagari Town, Shagari Local Council of Sokoto State, Nigeria.

Preparation/ Calcination of Catalysts

The methods reported by [5, 6] was adopted for the catalyst preparation. Aqueous saturated solutions of ammonium heptamolybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ and copper nitrate $[\text{Cu}(\text{NO}_3)_2]$ were prepared by adding 15.75g of each salt in a beaker containing 60cm³ of distilled water in separate beakers. Alumina (38.5g) was gradually added into each solution followed by stirring at 120rpm for 2h. The mixtures were dried overnight in an oven at 105°C.

One portion of the dried mass was activated by soaking in 60cm³ of 2M aqueous H_2SO_4 for 30 minutes, while the other was not acidified. Both were calcined in a furnace at a temperature of 450°C for 2 h.

Clay Activation/Calcination

Sieved clay sample (70g) was soaked in 60cm³ 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

Characterization

The supposed-catalysts are not characterized as there is no confirmation that they would be active in the alkylation process. However, since they show some activity and the work is on-going, they would be characterized in the subsequent works.

Alkylation Reactions

The catalysts were tested on the alkylation of benzene with linear C₁₀-C₁₃ olefins (1-decene) in a fixed-bed laboratory reactor. The reaction was carried out in liquid phase at temperatures of 80-90 °C with molar ratio benzene/alkenes from 1 to 10. The main parameters considered were the catalytic activity, the selectivity of the catalysts for decyl benzene, the product yield and percentage conversion.

Results

Table 1: Product Yield

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 2: Percentage Selectivity for Decylbenzene

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 3: Percentage Conversion

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

Discussion

Table 1 presents Alkylation results (yield) obtained using 2:1, 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 decylbenzene revealed by the results 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 Alhassan *et al.* [5], 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.

Amarilli *et al.* [3] studied catalytic activity, linearity of the LAB products and catalyst life of solid acids for benzene alkylation with long chain linear alkenes and reported poor life time for Al-PILC and ERB-1 zeolite of 16 and <40 respectively. 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.

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), shows 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. Yuan *et al.* [12], Alhassan *et al.* [5]; Zhang *et al.* [13]

As well as Ortego *et al.* [14] 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 decylbenzene 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 proved that the (acidified CuO-MoO₃/Al₂O₃) catalyst is active, and do not sieze activity with time.

On the contrary, the unacidified catalyst showed poor product yield especially, in the beginning of the reaction (40 to 80 minutes); 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.

Generally, there appeared to be observable increase in percentage decylbenzene with increase in the reactants molar ratios [5, 12-15]. Reported that there is always increase in desired alkylation products with increase in reactants molar ratios. Percentage selectivity for decylbenzene in the variable alkylation products with time in all the molar ratios for the three catalysts is presented in Table 2. It is clear that

unacidified CuO-MoO₃/Al₂O₃ had the least selectivity in all the molar ratios with time. Similar to the table 1, 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 decylbenzene 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 reactants ratio.

Supported by the works of [3, 5, 7-9, 12-15] selectivity for desired 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; justifying the reports of [4, 12, 16] that alkylation catalysts are selective to desired product only when they bear Brønsted acidic sites.

Table 3 presents the product conversion (%) computed for the three alkylation reaction with time. The product conversion in unacidified CuO-MoO₃/Al₂O₃ gave the best result in 4:1 molar ratio at 120 minutes (41.78%). It is observed that conversion in all the reactions at 2:1, 4:1 and 10:1 molar ratios increase with time using all the catalysts except for unacidified CuO-MoO₃/Al₂O₃ 4:1 (80 minutes) where it is observed to have decreased from 31.25 to 28.77 but shot up to 41.78 at 120 minutes and activated shagari clay (4:1, 80 minutes) where the conversion (52.17) also decreased to 49.23 at 120 minutes.

The best conversion (89.37) is obtained using acidified CuO-MoO₃/Al₂O₃ 10:1 reactants molar ratio at 120 minutes. The reports of [5, 12-18] confirmed similar effects of change in conversion with time.

Further Work

To analyse the surface properties of the prepared materials using XRD, FTIR, TGA and XRD techniques.

Conclusion

The unacidified CuO-MoO₃/Al₂O₃ catalyst showed least activity among all the catalysts. Although, all the catalysts seized activity with decrease in product yield and time, they also appear to some extent, active. Shagari clay is good potential for similar use.

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