




Article

# $\alpha$ -Alkylation of Aliphatic Ketones with Alcohols: Base Type as an Influential Descriptor

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**Abstract:** Current global challenges associated with energy security and climate emergency, caused by the combustion of fossil fuels (e.g., jet fuel and diesel), necessitate the accelerated development and deployment of sustainable fuels derived from renewable biomass-based chemical feedstocks. This study focuses on the production of long-chain (straight and branched) ketones by direct  $\alpha$ -alkylation of short chain ketones using both homogenous and solid base catalysts in water. Thus, produced long-chain ketones are fuel precursors and can subsequently be hydrogenated to long-chain alkanes suitable for blending in aviation and liquid transportation fuels. Herein, we report a thorough investigation of the catalytic activity of Pd in combination with, (i) homogenous and solid base additives; (ii) screening of different supports using NaOH as a base additive, and (iii) a comparative study of the Ni and Pd metals supported on layered double oxides (LDOs) in  $\alpha$ -alkylation of 2-butanone with 1-propanol as an exemplar process. Among these systems, 5%Pd/BaSO<sub>4</sub> with NaOH as a base showed the best results, giving 94% 2-butanone conversion and 84% selectivity to alkylated ketones. These results demonstrated that both metal and base sites are necessary for the selective conversion of 2-butanone to alkylated ketones. Additionally, amongst the solid base additives, Pd/C with 5% Ba/hydrotalcite showed the best result with 51% 2-butanone conversion and 36% selectivity to the alkylated ketones. Further, the screening of heterogenous acid-base catalysts 2.5%Ni/Ba<sub>1.2</sub>Mg<sub>3</sub>Al<sub>1</sub> exhibited an adequate catalytic activity (21%) and ketone selectivity (47%).

**Keywords:**  $\alpha$ -alkylation; aliphatic ketones; 2-butanone; alcohols; sustainable aviation fuels; liquid transportation fuels; Pd/BaSO<sub>4</sub>; LDO



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## 1. Introduction

The direct  $\alpha$ -alkylation of ketones with primary alcohols is the easiest and most versatile route for the C–C bond formation. This is also a prominent synthetic method for producing organic compounds such as pharmaceuticals, agrochemicals, functional materials, and long-chain ketones [1]. The long-chain ketones on hydrogenation give fuel range hydrocarbons (including jet fuels composed of molecules with ~7 to 18 carbons). Although the refining of crude oil is the prevalent synthesis pathway for jet fuel production, new processes to manufacture Sustainable Aviation Fuels (SAFs) utilizing alternative, renewable sources are currently under investigation worldwide, and some of them have found their slice of the market [2]. This is mainly because the US and the European Union have set the meticulous target of a greenhouse gas emission reduction of at least 55% by 2030 to deal with climate change issues.

Several processes have been reported to produce SAFs viz. pyrolysis, hydrothermal liquefaction, Fischer-Tropsch synthesis (FT), power-to-liquid FT, and alcohol-to-jet fuel [3–5].

However, most of these processes have their shortcomings as biobased routes require crops, which increase land use, resulting in land change impacts. Whereas electric fuels (e-fuels) require exceedingly large amounts of renewable electricity which could otherwise be used to reduce the emission intensity of the grid [6]. Recently, some researchers have demonstrated the synthesis of SAFs by using volatile fatty acids (VFAs) produced during the anaerobic digestion (AD) of wet waste [5]. This process is multistep and includes (i) captured methanogenesis of wet waste to obtain C3–C8 VFAs, (ii) Ketonization of VFAs to C8–C15 linear ketones, (iii) aldol condensation of linear ketones to branched and cyclic enones, and (iv) hydrodeoxygenation (HDO) of the fractions obtained in steps (ii) and (iii). Unfortunately, several challenges still exist in this process, including the key step of aldol condensation, which is underdeveloped for successful scale-up due to multiple process steps, lower product yields, and lower selectivity for long-chain hydrocarbons [7]. Under these circumstances, the  $\alpha$ -alkylation of ketones with alcohol provides a viable alternative to aldol condensation steps in SAF synthesis.

The most common method used for  $\alpha$ -alkylation reactions is using toxic alkyl halides as alkylating agents in the presence of strong bases [8]. Hence, several researchers found that the use of alcohol is a greener alkylating agent over alkyl halides in transition metal catalyzed  $\alpha$ -alkylation of ketones employing the borrowing hydrogen (BH) strategy as a promising alternative approach [9–11]. This BH strategy possesses a high atom economy, as water is the sole co-product. Inspired by a pioneering study of Grigg et al. on the use of alcohol as an alkylating agent for the N-alkylation of amines [12,13], several researchers have envisioned a variety of alkylation methods using iridium, ruthenium, rhodium, and other transition metal catalysts [1]. Despite their advantages, these systems still have obvious drawbacks, such as the use of expensive and toxic rare metal complexes or capricious ligands, large amounts of hydrogen acceptors or bases, and metal contamination in products [14].

On the contrary, recyclable heterogeneous catalysts offer a greener approach to the  $\alpha$ -alkylation of ketones with alcohols. Among the reported methods, heterogeneous palladium has been widely used for this transformation in the form of Pd/C [15], Pd/AlO(OH) [16], nano-palladium liganded to viologen polymers [17], palladium loaded titanate nanotube, bimetallic Au-Pd nanoparticles, Pd/MgO-Al<sub>2</sub>O<sub>3</sub> [18–20], and Pd on hydrotalcite [21]. This was despite these processes being majorly associated with the  $\alpha$ -alkylation of aromatic ketones with benzyl and long-chain secondary aliphatic alcohols with the requirements of hydrogen acceptors, large excess of base (up to 300 mol%), low product yield, use of organic solvents and high temperature [22]. According to a recent study, the 1%Pd single-atom supported on cubic CeO<sub>2</sub> was an efficient catalyst for the  $\alpha$ -alkylation of ketones, with primary alcohol even at low catalyst (~40 mg) and base (~0.25 mmol) concentration. However, the reactants employed were aromatic ketones, which react with primary aromatic and aliphatic alcohols in the presence of organic solvents like n-hexane [23]. There are only a few reports of the Pd-catalyzed  $\alpha$ -alkylation of aliphatic ketones with the aliphatic primary alcohol in aqueous medium being used. The very first study was by Anbarasan and co-workers, who proposed the Guerbet reaction route to convert acetone-1-butanol-ethanol (ABE) fermentation products into fuel using transition metal catalysts [24]. G. Xu and co-workers further performed the direct  $\alpha$ -alkylation of ketones with alcohols in a small autoclave, utilizing water as a solvent instead of toluene over various Pd/C catalysts by emulating the real aqueous ABE fermentation product [25]. Although considerable yields of desirable alkylated long-chain ketones (18–46%) and alcohol (11–50%) products were obtained, the equivalent quantity of various bases as ketones was also added. Sreekumar et al. demonstrated the benefits of a comprehensive approach to achieving synergy between chemical and biological processes by integrating Pd/HT and Cu/HT catalysts with isopropanol-butanol-ethanol fermentation [26]. Nonetheless, the product was high (>90%) under optimized conditions (240 °C, 24 h) in the presence of the excess amount of n-butanol (1 mL). Subsequently, another group demonstrated consecutive alkylation of acetone with ethanol and hydrodeoxygenation in a flow reactor containing two beds to

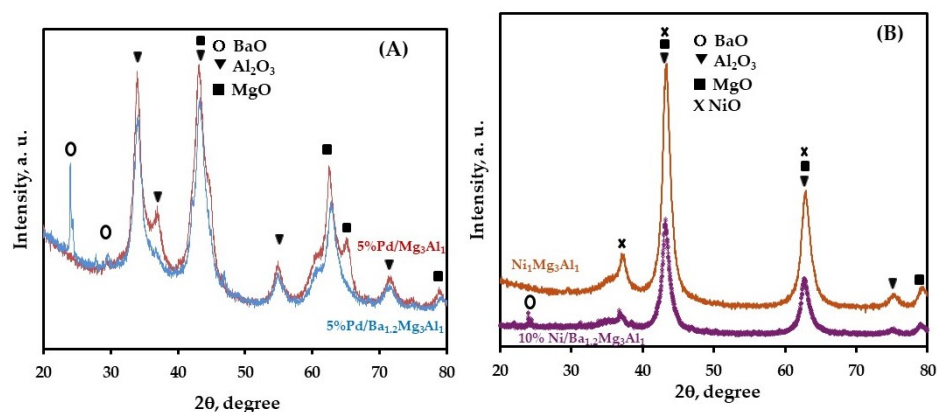
produce C5–C7 alkanes using 5%Pd/KOH/AC, Pd/HT and commercial catalysts in the vapor phase (250–300 °C) [21,27]. Lee and co-workers reported the solvent-free conversion of ABE using a mixture of Pd/C and CaO as heterogenous catalysts in a batch reactor at 180 °C. It produced a mixture of ketones and their corresponding alcohols with a 78% yield based on acetone [28].

These reports justify the feasibility of the Pd/C catalysts in alkylation and the need to enhance their activity under mild reaction conditions in water for upgrading biomass-derived chemical feedstocks. Our expertise in developing catalysts for renewable building block transformations [29–33] and the abatement of environmental pollutants [34–38] enable us to focus on the  $\alpha$ -alkylation of 2-butanone with 1-propanol to produce long-chain (straight and branched) alkylated ketones that can be used as fuel precursors. Initially, a comparative study for the activity and product selectivity of the homo- and heterogenous bases in combination with 5%Pd/C catalysts, ubiquitous in organic synthesis, for  $\alpha$ -alkylation of butanone with 1-propanol in aqueous medium was performed. It was found that the Pd/C+NaOH showed better activity with 91% 2-butanone conversion and 74.3% selectivity to expected alkylated ketones. Further screening of various supports for the Pd metal revealed that the 5%Pd/BaSO<sub>4</sub> catalysts exhibited efficient activity in the alkylation of butanone with 1-propanol using low catalyst loading (0.1 g) and base (0.5 mole eq.).

## 2. Results and Discussion

### 2.1. Catalysts Characterization

X-ray diffraction patterns of the calcined 5%Pd supported on Mg<sub>3</sub>Al<sub>1</sub>, Ba<sub>1.2</sub>Mg<sub>3</sub>Al<sub>1</sub> along with Ni-doped Mg<sub>3</sub>Al<sub>1</sub> and Ni-supported Ba<sub>1.2</sub>Mg<sub>3</sub>Al<sub>1</sub> are shown in Figure 1A and Figure 1B, respectively. The supporting LDOs were prepared by co-precipitation with a low supersaturation method followed by calcination. Pd or Ni-supported catalysts were prepared using the wet impregnation technique, whereas Ni-doped Ni<sub>1</sub>Mg<sub>3</sub>Al<sub>1</sub> was prepared by the co-precipitation method. In all four samples, XRD patterns showed two reflections at  $2\theta = 43.4^\circ$  and  $63^\circ$  (corresponding d-values = 2.11 and 1.49 Å, respectively) correlated to an MgO-like phase (periclase) or magnesia–alumina phase [39,40]. However, no reflections relating to the hydrotalcite phase coincide with the decomposition of the layered structure of Mg–Al-LDH into Mg–Al oxide phases, characteristic of calcined hydrotalcite-type materials. In Ba-doped LDOs, a well-defined diffraction peak at  $24^\circ$  implies crystalline BaO (JCPDS No. 47-1488) phase formation. A similar peak was also observed in the Ni-doped and supported LDO. In Pd-supported catalysts, the XRD pattern did not show diffraction peaks corresponding to crystalline PdO, which clarifies that the PdO particles were in a highly dispersed or amorphous state. However, the presence of PdO cannot be ruled out, which might be present as small crystallites beyond the XRD detection limit (Figure 1A).



**Figure 1.** X-ray diffraction patterns of: (A) 5%Pd supported LDO; (B) Ni doped and supported LDO.

In Pd-supported LDOs, the reflections at  $2\theta = 34.1^\circ$ ,  $55.0^\circ$ ,  $71.5^\circ$ , and  $37.0^\circ$  could suggest the formation of crystalline  $\theta$ - $\text{Al}_2\text{O}_3$  (JCPDS Card No. 96-120-0006) phases in these samples (Figure 1A). On the contrary, the diffraction peaks associated with the  $\text{Al}_2\text{O}_3$  ( $2\theta = 34.1^\circ$ ,  $55.0^\circ$ ,  $71.5^\circ$ , and  $37.0^\circ$ ) phase were tough to find in Ni-doped and supported catalysts, which indicates the dispersed or amorphous phase of  $\text{Al}_2\text{O}_3$  in the MgO structure and no segregation of the  $\text{Al}_2\text{O}_3$  phase (Figure 1B). Compared to Ni-supported LDOs, the diffraction peaks of NiMgAl are sharper, owing to the increased particle size and/or improved crystallinity in the sample. The peak at  $2\theta = 37.4^\circ$  may be identified as the (111) plane of the NiO phase; nevertheless, it was hard to distinguish the remaining NiO peaks from LDOs at  $2\theta = 43.2^\circ$ ,  $62.87^\circ$ ,  $75.2^\circ$ , and  $78.38^\circ$ .

The surface areas and pore volumes of the 5%Pd- and Ni-supported LDO are shown in Table 1. For the 5%Pd-supported LDOs, as the support composition changed, the BET surface area changed as well, with the order 5%Pd/Mg<sub>3</sub>Al<sub>1</sub> > 5%Pd/Ba<sub>1.2</sub>Mg<sub>1.8</sub>Al<sub>1</sub> > 5%Ba<sub>1.2</sub>Mg<sub>3</sub>Al<sub>1</sub>. In the instance of Ni-supported LDOs, when Ni loading increased from 2.5% to 10%, the BET surface area decreased from 147 m<sup>2</sup>/g to 122 m<sup>2</sup>/g. The higher surface area at lower Ni loading could be attributed to the uniform dispersion of Ni on the LDO. As the loading increased, maximum surface coverage occurred, resulting in the aggregation of Ni particles, which concurrently affected the surface area. Overall, this demonstrates that the doping of Ba and/or impregnation with Pd/Ni may lead to a slight decrease in surface area.

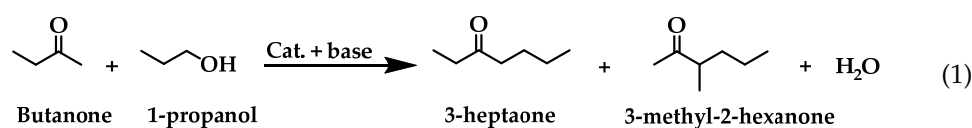
**Table 1.** Physical properties of the Pd- and Ni-supported LDOs.

Sr. No.	Catalyst	BET Surface Area, m <sup>2</sup> /g	Pore Volume, cm <sup>3</sup> /g
1	5%Pd/Mg <sub>3</sub> Al <sub>1</sub>	130	0.27
2	5%Pd/Ba <sub>1.2</sub> Mg <sub>1.8</sub> Al <sub>1</sub>	116	0.24
3	5%Pd/Ba <sub>1.2</sub> Mg <sub>3</sub> Al <sub>1</sub>	106	0.29
4	2.5%Ni/Ba <sub>1.2</sub> Mg <sub>3</sub> Al <sub>1</sub>	147	0.31
5	5%Ni/Ba <sub>1.2</sub> Mg <sub>3</sub> Al <sub>1</sub>	125	0.32
6	10%Ni/Ba <sub>1.2</sub> Mg <sub>3</sub> Al <sub>1</sub>	122	0.27

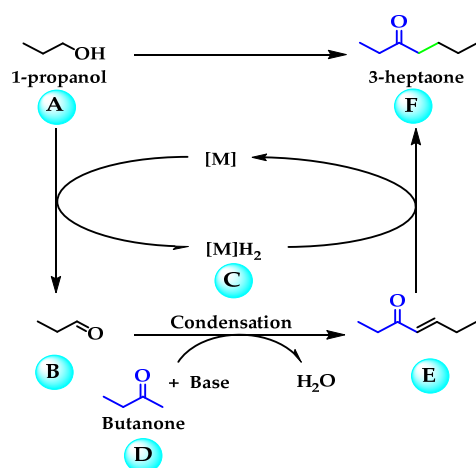
## 2.2. $\alpha$ -Alkylation of 2-Butanone with 1-Propanol

### 2.2.1. Product Distribution in $\alpha$ -Alkylation of Butanone

The  $\alpha$ -alkylation of butanone with 1-propanol by hydrogen auto transfer (or HB) strategy was chosen as a model reaction for supported Pd-base catalysts (Equation (1)).

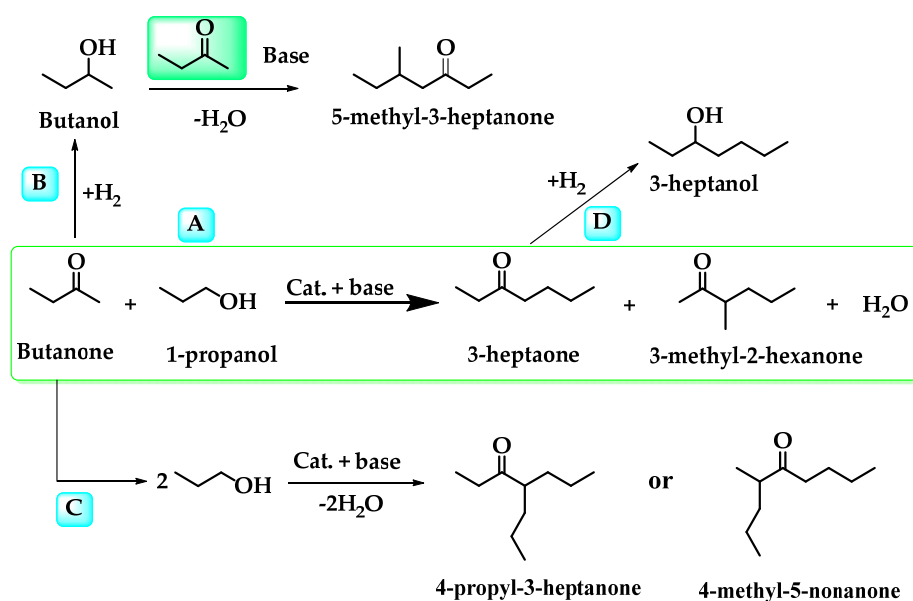


As shown in Scheme 1, the HB methodology consisted of the initial transition metal-catalyzed dehydrogenation of alcohols (A) to give corresponding aldehyde or ketones (B) and metal hydride species (C), followed by the base-mediated condensation reaction of in situ generated aldehydes or ketones with ketones (D) to form  $\alpha$ ,  $\beta$ -unsaturated ketones (E), which underwent hydrogenation using borrowed hydrogen atoms from the first step to give the desired  $\alpha$ -alkylated ketones (F) [1,41]. This represents the requirement of metal and base sites for synthesizing alkylated ketones from ketones and alcohols. This process does not require any external hydrogen acceptor or oxidant source. It liberates only water as the by-product, representing its atom-economic feasibility and environmental friendliness.



**Scheme 1.** Metal- and base-catalyzed  $\alpha$ -alkylation of butanone by 1-propanol with borrowed hydrogen methodology.

Possible reaction pathways and product distributions during the  $\alpha$ -alkylation of butanone are illustrated in Scheme 2. As the butanone had two nucleophilic  $\alpha$ -carbon centres with hydrogen atoms, this led to the formation of mono- (C7; 3-heptanone and 3-methyl-2-hexanone) and di-alkylated ketones (C10, 4-propyl-3-heptanone and 4-methyl-5-nonanone) (Scheme 2A,C) with 1-propanol as an alkylating agent. This was mainly dependent on the generation of enolate ions, such as if there was a formation of the methylene enolate ions which are thermodynamically more stable and generate 3-methyl-2-hexanone (C7) and 4-methyl-5-nonanone (C10), while enolate ions derived from the methyl group produce 3-heptanone (C7) and 4-propyl-3-heptanone (C10). However, generating methylene enolate ions requires higher activation energy and more stringent conditions than the generation of methyl enolate ions does [42]. Therefore, the products obtained from the methylene enolate ion are considered thermodynamic products, while those formed from the methyl enolate ion of 2-butanone are regarded as kinetic products [43]. Also, in the present study, the major product obtained was saturated ketones with a small amount of alcohol. This clarifies the fast hydrogenation of the double bonds by the hydrogen formed in situ in the presence of a Pd/C catalyst.



**Scheme 2.** Series and parallel reactions during  $\alpha$ -alkylation of butanone with 1-propanol.

### 2.2.2. Activity of Pd/C Catalysts with Added Homogenous Bases

Inspired by previous literature reports on a Pd/carbon catalyst for  $\alpha$ -alkylation of ketones with alcohol through the BH strategy [22,24], in the present study we initially screened several bases paired with 5%Pd/C under mild reaction conditions of 180 °C for 22 h, using water as a solvent. The amounts of Pd and base were set to 0.23 mol% and 0.5 mole eq., respectively, for butanone. Beginning by unraveling the role of metal and base in the alkylation reaction, the control experiments with only the Pd/C and NaOH were performed (Table 2, entries 1 and 2). It was observed that the Pd/C showed lower (25.0%) butanone conversion compared with the NaOH (39.0%), and the major product obtained was 2-butanol, the transfer hydrogenation product of butanone (Scheme 2B), along with 12.0% selectivity to branched alkylated ketone (B) (Scheme 2C) without formation of  $\alpha$ -alkylated ketones [straight (S), Scheme 2A]. On the contrary, the use of NaOH facilitates the formation of S-alkylated ketones (24%), along with branched alkylated ketones (42%) and 2-butanol (33.3%). The Meerwein–Ponndorf–Verley–Oppenauer (MPV-O) redox reaction facilitated the formation of ketones and butanol without any transition metal catalysts, consistent with the previous report by Xu et al. [14]. This demonstrates the crucial role of the base in the formation of  $\alpha$ -alkylated ketones (S, B), whereas metal catalysts are efficient for hydrogenation rather than the dehydrogenation required for the  $\alpha$ -alkylation reaction. However, three-times-enhanced butanone conversion (91%) with the highest selectivity to desirable ketones (82%), 7% to long-chain alcohol (Scheme 2D), and 11% to undesirable 2-butanol were obtained when Pd/C was used in combination with NaOH. This clarifies the co-operative role of base and Pd/C catalysts in improving the activity and selectivity of desired products in the  $\alpha$ -alkylation of butanone with primary aliphatic alcohol. Other bases such as KF and Hunig's base were checked, and the activity decreased in the order of NaOH > Hunig's > KF, indicating that the strong base showed better performance. KF showed the least activity (entry 4, 1.0%) with major selectivity to branched alkylated ketones (72%), while Hunig's Base (entry 5) gave 2-butanol (88%) as a major product along with 11.9% of branched alkylated ketones.

**Table 2.** Influence of different bases on  $\alpha$ -alkylation activity of 5%Pd/C catalysts in aqueous medium.

Entry	Base	Conversion, %	Product Selectivity, %			
			S-Alkylated Ketones	B-Alkylated Ketones	Long Chain Alcohol	2-Butanol
1	-	25.0	0.0	12.0	0	88.0
2	NaOH <sup>a</sup>	39.0	24.0	42.0	1.0	33.0
3	NaOH	91	40.0	42.0	7.0	11.0
4	KF	1.0	22.0	72.0	0	7.0
5	Hunig's base <sup>b</sup>	10.0	0.0	12.0	0	88.0
6	NaOH <sup>c</sup>	73	41.0	50.0	5	5.0

Reaction conditions: 2-butanone, 0.02 mol; 1-propanol, 0.04 mol, 5%Pd/C, 0.1 g; deionized water, 60 mL; NaOH, 0.4 g; time, 22 h; temperature, 180 °C. <sup>a</sup> Without 5%Pd/C; <sup>b</sup> N,N-Diisopropylethylamine; <sup>c</sup> reaction with 0.5 g of phase transfer catalyst, tetrabutylammonium bromide [TBAB].

Considering the two-phase reaction, the surfactant tetrabutylammonium bromide (TBAB) was used as a phase transfer agent to promote organic transformation in an aqueous medium along with the Pd/C + NaOH catalyst (entry 6). The butanone conversion and the yield of alkylated ketone obtained with the TBAB agent were 73% and 66%, respectively, which is lower than that from the reaction without a phase transfer agent (74% yield of alkylated ketones). Hence, there was no need for a phase transfer agent to improve activity and product selectivity in the  $\alpha$ -alkylation of butanone in the presence of Pd/C + NaOH catalysts. Another observation is that in none of the reactions there was no detection of  $\alpha,\beta$ -unsaturated ketones convening in situ-hydrogenation of the unsaturated ketones being predominant, and the formation of Pd-H intermediate was robust. In addition, the production of ketone was higher than that of the corresponding alcohols, demonstrating

that Pd is more active in the hydrogenation of C=C bonds than in the hydrogenation of C=O bonds. This aligns with previous findings for Pd in the upgrading of acetone [44].

### 2.2.3. Activity of Pd/C Catalysts with Added Heterogenous Bases

Considering the large energy consumption requirement for separating homogeneous bases and waste treatment, heterogeneous bases are preferred over water-soluble homogeneous bases. Hence, in the present study, in combination with Pd/C, we screened several conventional metal oxide bases, viz., CeZrO<sub>2</sub>, MgO, HT, etc., and the results are reported below in Table 3. The alkylation activity and ketone product selectivity obtained with heterogeneous bases were inferior compared to homogeneous bases. This is deducible due to the strong basicity of homogeneous bases and the homogeneous active phase [28].

**Table 3.** Influence of different solid bases on  $\alpha$ -alkylation activity of 5%Pd/C catalysts in aqueous medium.

Entry	Base	Conversion, %	Product Selectivity, %			
			S-Alkylated Ketones	B-Alkylated Ketones	Long Chain Alcohol	2-Butanol
1	CeZrO <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
2	MgO	27.0	1.5	2.0	0.0	96.5
3	HT	18.0	4.5	4.0	0.0	91.5
4	CHT <sup>a</sup>	30.0	3	3.0	0.0	94.0
5	5%Ba/HT	51.0	19.5	16.5	1.0	63.0
6	30%KF/Al <sub>2</sub> O <sub>3</sub>	28.0	0.0	0.3	0.0	99.7
7	5%Pd/CeZrO <sub>2</sub> <sup>b</sup>	55.0	1.0	3.3	0.0	96.0

Reaction conditions: 2-butanone, 0.02 mol; 1-propanol, 0.04 mol; 5%Pd/C, 0.1 g; deionized water, 60 mL; solid bases, 1.0 g; time, 22 h; temperature, 180 °C. <sup>a</sup> Hydrotalcite was calcined at 450 °C for 6 h before use; <sup>b</sup> 5%Pd directly supported on commercial CeZrO<sub>2</sub> without adding 5% Pd/C separately.

Compared with other heterogeneous basic catalysts, 5%Ba/HT showed butanone conversion of 51%, with relatively less undesirable product butanol selectivity of 63% and remaining selectivity to straight (19.5%) and branched (16.5%) alkylated ketones, and 1% long-chain alcohols (Table 3, entry 5). The activity trend obtained from other added bases along with Pd/C, was CHT > 30%KF/Al<sub>2</sub>O<sub>3</sub> > MgO > HT and this exhibited >90% selectivity to 2-butanone, which was undesirable. One important observation was that the calcined (CHT) led to ~12.0% higher butanone conversion than non-calcined HT (Entries 3 and 4). This was obvious because, after calcination, the obtained CHT or layered double oxide (LDO) acquired unique properties, viz., increased basicity, high surface area, formation of homogeneous mixtures of oxides with tiny crystal size, and stability to thermal treatments, etc. [45]. Surprisingly, Pd/C, in combination with commercial CeZrO<sub>2</sub> as a base, gave nil activity, whereas direct 5%Pd supported on CeZrO<sub>2</sub> exhibited 55% butanone conversion (Table 3, entry 7). Conversely, the major product obtained was undesirable butanol (96%) with the least 1% and 3% selectivity to S and B chain alkylated ketones, respectively. This may be due to the Pd impregnated on CeZrO<sub>2</sub> interacting directly with CeZrO<sub>2</sub> support to generate active sites required for the reaction sequence to proceed well. These results are closely commensurate with the finding of heterogeneous Co, MgO, and TiO<sub>2</sub> mixture used for  $\alpha$ -alkylation of acetophenone and benzyl alcohol [46]. This finding led us to compare the activity of several solid bases as Pd support with Pd/C catalysts in the presence of homogeneous NaOH as a base additive.

### 2.2.4. Influence of Different Supports on $\alpha$ -Alkylation Activity of Pd

The support effect was examined using conventional metal oxide, which includes BaSO<sub>4</sub>, HT, CeZrO<sub>2</sub>, CaCO<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>, and prepared 5%Ba/TiO<sub>2</sub> (Table 4, entry 8). The activity results revealed that the 5%Pd/BaSO<sub>4</sub> showed the best catalytic performance with 94% butanone conversion and 84% selectivity to desired alkylated ketones, 4% to long-chain alcohol, and only 12% to undesirable butanol selectivity. The 5%Pd/C cata-

lyst exhibited comparable activity, giving 91% butanone conversion with almost similar selectivity to straight chain (40%) and branched chain (42%) alkylated ketones, whereas Pd/BaSO<sub>4</sub> showed relatively higher selectivity to branched-chain ketones (52%). Gratifyingly, there was considerable butanone conversion and a significant amount of  $\alpha$ -alkylated ketones (S and B) with all supports except the Pt/Al<sub>2</sub>O<sub>3</sub> and 5%Pd-5%Ba/TiO<sub>2</sub> catalysts. The butanone conversion trend observed was 5%Pd/BaSO<sub>4</sub> > 5%Pd/C > 5%Pd/HT > 5%Pd/CeZrO<sub>2</sub> > 5%Pd/CaCO<sub>3</sub> > 5%Pd/Al<sub>2</sub>O<sub>3</sub> > 5%Pt/Al<sub>2</sub>O<sub>3</sub> > 5%Pd-5%Ba/TiO<sub>2</sub>. Indeed with 5%Pd-5%Ba/TiO<sub>2</sub> and 5%Pt/Al<sub>2</sub>O<sub>3</sub>, the major product obtained was 2-butanol (89 and 43%, respectively), and the least selectivity to desirable alkylated ketones representing transfer hydrogenation was dominated by enolate ion formation (Table 4, entries 7 and 8). Collectively, the 5% Pd/BaSO<sub>4</sub> and 5% Pd/C were identified as promising candidates for the  $\alpha$ -alkylation of aliphatic ketones and alcohols using water as a solvent under mild reaction conditions. The activity achieved with both Pd/BaSO<sub>4</sub> and Pd/C catalysts resulted in higher conversion and yield of the alkylated ketone compared to the results previously reported by Xu et al., who used Pd/C + K<sub>3</sub>PO<sub>4</sub> and KOH catalysts under both microwave and conventional reaction conditions [25]. Also, the base used by Xu et al. ranged from 2 to 6 eq. for ketone, whereas in the present study, it was 0.5 eq. Furthermore, based on a recent literature review, this is the first report of  $\alpha$ -alkylation of aliphatic butanone with 1-propanol using the BaSO<sub>4</sub> support for Pd, which has not previously been utilized as a catalyst for this reaction.

**Table 4.** Influence of different supports on the  $\alpha$ -alkylation activity of supported 5%Pd metal and NaOH as a base in an aqueous medium.

Entry	Supports	Conversion, %	Product Selectivity, %			
			S-Alkylated Ketones	B-Alkylated Ketones	Long Chain Alcohol	2-Butanol
1	BaSO <sub>4</sub>	94.0	32.0	52.0	4.0	12.0
2	C	91.0	40.0	42.0	7.0	11.0
3	HT	87.0	26.0	39.0	4.5	30.0
4	CeZrO <sub>2</sub>	85.0	29.0	51.0	4.0	16.0
5	CaCO <sub>3</sub>	84.0	36.0	33.0	4.0	27.0
6	Al <sub>2</sub> O <sub>3</sub>	82.5	24.0	43.0	5.0	28.0
7	Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	68.0	17.0	36.0	4.0	43.0
8	5%Ba/TiO <sub>2</sub>	61.0	2.0	8.0	1.0	89.0

Reaction conditions: 2-butanone, 0.02 mol; 1-propanol, 0.04 mol, 5%Pd/C, 0.1 g; deionized water, 60 mL; NaOH, 0.4 g; time, 22 h; temperature, 180 °C. <sup>a</sup> instead of Pd, 5%Pt supported on Al<sub>2</sub>O<sub>3</sub>.

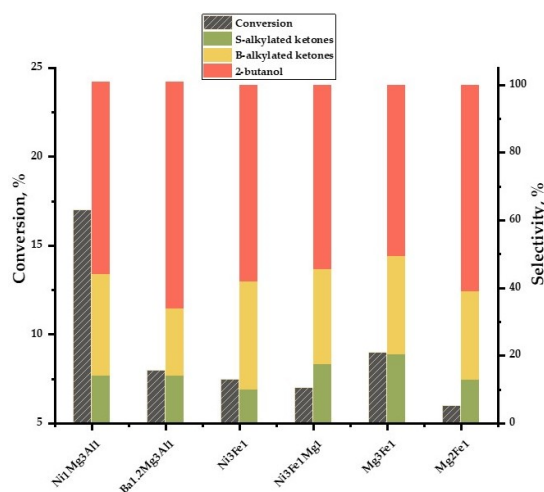
### 2.2.5. Product Distribution and Activity of Heterogeneous Catalysts in $\alpha$ -Alkylation Reaction without Added Base

Although the 5% Pd/BaSO<sub>4</sub> + NaOH showed efficient activity and product selectivity in alkylation reactions, the use of heterogeneous catalysts containing inexpensive transition metal is desirable due to their recyclability and economic benefits. Based on the results discussed above, the alkali (Ba) and inexpensive transition metal (Ni, Fe) modified calcined LDHs were further used for  $\alpha$ -alkylation of butanone with 1-propanol.

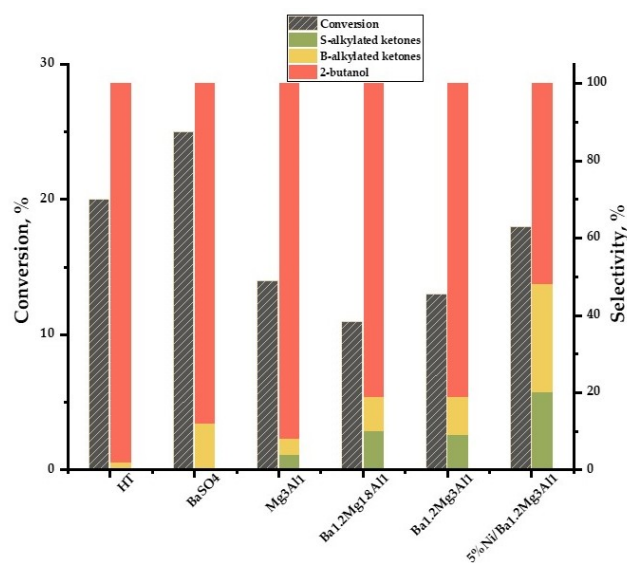
First, we selected several types of hydrotalcite to check their efficiency for alkylation reactions. As shown in Figure 2, among the screened hydrotalcite, Ni<sub>1</sub>Mg<sub>3</sub>Al<sub>1</sub>O<sub>x</sub> gave a relatively higher butanone conversion of 16.6%, with 44% selectivity to total alkylated ketone (S and B chain) and 56% selectivity to undesirable 2-butanol. However, other LDOs exhibited inferior activity compared to Ni<sub>1</sub>Mg<sub>3</sub>Al<sub>1</sub>O<sub>x</sub> LDO, giving a butanone conversion in the range of 6–9% with ~40% selectivity to alkylated ketones, and remaining to the butanone hydrogenation product butanol, which is not a desirable product at all. Here, the selectivity obtained for alkylated ketones was improved compared to using HT in combination with Pd/C, as discussed in Section 2.2.3. However, the butanone conversion was still low. Therefore, to enhance butanone conversion, we impregnated active metals like Pd and Ni onto LDHs, and their performance was compared to the 5%Pd/BaSO<sub>4</sub> catalyst



(showing better activity with NaOH base additive) in terms of butanone conversion and selectivity to alkylated ketones (Figure 3).



**Figure 2.**  $\alpha$ -alkylation of 2-butanone with 1-propanol over different LDOs catalysts. Reaction conditions: 2-butanone, 0.02 mol; 1-propanol, 0.04 mol, catalyst, 0.4 g; deionized water, 60 mL; time, 22 h; temperature, 180 °C.

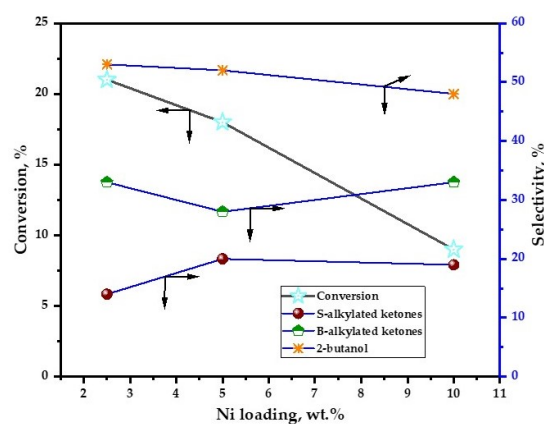


**Figure 3.**  $\alpha$ -alkylation of 2-butanone with 1-propanol over 5%Pd and 5%Ni-supported LDOs without an added base. Reaction conditions: 2-butanone, 0.02 mol; 1-propanol, 0.04 mol; catalyst, 0.4 g; deionized water, 60 mL; time, 22 h; temperature, 180 °C.

As depicted in Figure 3, Pd supported on BaSO<sub>4</sub> and HT exhibited higher butanone conversion of 25% and 18% respectively, however, the major product obtained with Pd/HTC was 2-butanol (98%) while 5%Pd/BaSO<sub>4</sub> showed only 12% selectivity to branched alkylated ketones without formation of S-alkylated ketones. On the contrary, LDO and Ba-doped LDO showed comparable butanone conversion in the range of 11–13% while with Ba-doped Mg<sub>x</sub>Al<sub>x</sub>O<sub>x</sub> LDO the formation of branched and straight-alkylated ketones with almost equal selectivities to each (~9.5%) and remaining to butanol (81%) was demonstrated. The undoped Mg<sub>3</sub>Al<sub>1</sub>O<sub>x</sub> gave 92% selectivity to undesirable 2-butanol with only 8% selectivity to collectively desirable S- and B-chain alkylated ketones, which justifies that the doping of Ba facilitates the formation of S- and B-chain ketones. This may be associated with its basic nature.

In light of the few reports about the better water resistance (up to 3 wt% only) of Ni-based catalysts for the highly selective conversion of either solventless ABE mixture or in the presence of hexane to C5-C15 at relatively higher temperatures (200–240 °C) [47,48]. Herein, we prepared 5%Ni supported  $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1\text{O}_x$  LDHs and checked the activity for the alkylation of butanone with 1-propanol. The catalysts exhibited slight enhancement in butanone conversion (18%) with almost twice the selectivity to expected S- and B-chain alkylated ketones, 20 and 28% respectively, compared to Pd-supported LDOs. The remaining product obtained was 2-butanone with 52% selectivity. If we compare the surface areas and pore volume of the 5%Pd-supported LDO and 5%Ni/LDO the trend obtained was 5%Pd/ $\text{Mg}_3\text{Al}_1$  > 5%Ni/ $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1$  > 5%Pd/ $\text{Ba}_{1.2}\text{Mg}_{1.8}\text{Al}_1$  >  $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1$  (Table 1). However, this trend was not commensurate with the activity results of the catalysts.

As the 5%Ni/ $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1$  showed better performance compared to Pd supported catalyst, the influence of Ni loading in the range of 2.5 to 10% on butanone conversion and alkylated ketones was studied (Figure 4). It was demonstrated that as the Ni loading increased from 2.5% to 10% the butanone conversion was dropped from 21.0% to 9.3% with almost comparable selectivity to alkylated ketones and 2-butanone. A similar trend was observed with the BET surface area, 2.5%Ni/ $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1\text{O}_x$  (147  $\text{m}^2/\text{g}$ ) > 5%Ni/ $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1$  (125  $\text{m}^2/\text{g}$ ) > 10%Ni/ $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1$  (122  $\text{m}^2/\text{g}$ ) (Table 1). The higher surface area at lower Ni loading may be one of the reasons for the better performance of the 2.5%Ni/ $\text{Ba}_{1.2}\text{Mg}_3\text{Al}_1\text{O}_x$  catalyst.



**Figure 4.** Influence of Ni loading on 2-butanone conversion and product selectivity in  $\alpha$ -alkylation of 2-butanone and 1-propanol. Reaction conditions: 2-butanone, 0.02 mol; 1-propanol, 0.04 mol, catalyst, 0.4 g; deionized water, 60 mL; time, 22 h; temperature, 180 °C.

The butanone conversion and alkylated product selectivity obtained with Ni- and Pd-supported solid acid-base LDOs were still low compared to the Pd/ $\text{BaSO}_4$  + NaOH catalysts. This may be associated with LDH's serious water-resistance problem caused by an inherent memory effect of HT materials [49]. Therefore, from the perspective of sustainable and green chemistry, it is more important to enhance the activity of Ni/LDOs in water for the alkylation of butanone with 1-propanol. Consequently, a detailed understanding of active sites is necessary through the characterization of acid and base sites, particle size, and process optimisation studies, *viz.*, ketone-to-alcohol ratio and temperature, which are currently in progress.

### 3. Materials and Methods

#### 3.1. Chemical Reagents

Commercial 5%Pd/C, 5%Pd/ $\text{BaSO}_4$  was purchased from Sigma Aldrich, Scotland, UK, and 5%Pt/ $\text{Al}_2\text{O}_3$  (4.85%) was obtained from Johnson Matthey, Enfield, UK, while 5%Pd/ $\text{CaCO}_3$  was procured from Alfa Aesar, Lancashire, UK. Platinum (IV) nitrate (15.98%) was obtained from Johnson Matthey, Enfield, UK. Aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\geq 98\%$ ), cerium(III) nitrate hexahydrate ( $\geq 99\%$ ), zirconium(IV) oxyni-

trate hydrate ( $\geq 99\%$ ), magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ), hydrotalcite synthetic, and 2-butanone (GC grade,  $\geq 99.8\%$ ) were purchased from Sigma Aldrich, Scotland, UK. 1-propanol (99.5%) was obtained from Fisher Scientific, Waltham, MA, USA. All the precursors used were reagent grade and without further purification.

### 3.2. Catalysts Preparation

The commercial catalysts used were 5%Pd/C, 5%Pd/CeZrO<sub>2</sub>, 5%Pd/BaSO<sub>4</sub>, 5%Pd/CaCO<sub>3</sub>, KF, and hydrotalcite (HT). The supports used here were prepared by the deposition precipitation method, while supported catalysts were prepared by the impregnation method. The detailed catalyst preparation procedures are as follows.

#### 3.2.1. Preparation of Layered Double Hydroxides (LDHs)

Layered double hydroxide catalysts were prepared by co-precipitation with a low supersaturation method [45]. Briefly, Solution A was prepared by dissolving the metal nitrates in water with the desired molar ratios. Solution B was prepared by dissolving 15 g of sodium hydroxide in 100 mL of deionized water and verifying the pH of the suspension to around 10. Solution A was added dropwise to Solution B under stirring at 70 °C. The obtained precipitate was flowed with nitrogen for 20 min. and then the stirring was turned off and the glass bottle sealed. Then, the suspension was kept overnight at 70 °C in an oil bath. The precipitate was filtered and washed thoroughly with deionized water until the pH reached roughly 6 or 7. The resulting product was gel-like and was dried overnight in an oven at 120 °C then calcined in a furnace at 500 °C for 4 h. This material was used as a support for Pd and Ni metals. The list of prepared LDOs, along with notations, is given below (Table 5).

**Table 5.** List of prepared LDOs.

Sr. No.	LDHs Composition	Notations
1	MgOH-Al(OH) <sub>3</sub> (3:1)	Mg <sub>3</sub> Al <sub>1</sub>
2	BaOH-MgOH-Al(OH) <sub>3</sub> (1.2:1.8:1)	Ba <sub>1.2</sub> Mg <sub>1.8</sub> Al <sub>1</sub>
3	BaOH-MgOH-Al(OH) <sub>3</sub> (1.2:3:1)	Ba <sub>1.2</sub> Mg <sub>3</sub> Al <sub>1</sub>
4	NiOH-MgOH-Al(OH) <sub>3</sub> (1:3:1)	Ni <sub>1</sub> Mg <sub>3</sub> Al <sub>1</sub>
5	NiOH-MgOH-Fe(OH) <sub>3</sub> (3:1:1)	Ni <sub>3</sub> Mg <sub>1</sub> Fe <sub>1</sub>
6	NiOH-Fe(OH) <sub>3</sub> (3:1)	Ni <sub>3</sub> Fe <sub>1</sub>
7	MgOH-Fe(OH) <sub>3</sub> (3:1)	Mg <sub>3</sub> Fe <sub>1</sub>
8	MgOH-Fe(OH) <sub>3</sub> (2:1)	Mg <sub>2</sub> Fe <sub>1</sub>

#### 3.2.2. Preparation of Supported Catalysts

The impregnation method was used to prepare 5%Pd, 5%Ba, and 30%KF supported on different supports [50,51]. Firstly, the calculated amount of metal nitrate precursor was dissolved into an adequate quantity of methanol and 0.3 mL of water. The catalyst support was then added to the clear nitrate precursor solution and the suspension was stirred overnight. The methanol was removed using a vacuum rotary dryer and the resultant solid was oven-dried at 120 °C for 4 h. Finally, it was calcined at 500 °C for 4 h.

### 3.3. Catalyst Characterization

A Micromeritics ASAP 2010 instrument was used to determine the specific surface area and pore volume of the catalysts using a nitrogen (N<sub>2</sub>) adsorption–desorption technique. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation and pore volume calculated by the BJH method.

The crystal structure of the catalyst was determined by powder X-ray diffraction (XRD) with X'PERT Pro, equipped with an x'Celerator solid state detector and with a Cu K $\alpha$  radiation ( $\lambda = 1.504 \text{ \AA}$ ), operating at 40 kV voltage and 40 mA current. The XRD patterns were measured over the  $2\theta$  range of 20–80°.

### 3.4. Alkylation Reaction Procedure

The alkylation of 2-butanone with 1-propanol was performed in a 100 mL stainless steel autoclave (supplied by Autoclave Engineers, Whitburn, UK) equipped with a magnetic stirrer, thermocouple, and overhead stirrer. Initially, 0.4 g of NaOH dissolved in 60 mL of deionized (DI) water, and then 0.02 moles of 2-butanone with 0.1 g of catalyst were transferred into the autoclave reactor and the mixture was stirred for about 20 min. Then, 0.04 moles of 1-propanol were added to the reactor. Once the set temperature of 180 °C was reached, the agitation started at the speed of 1500 rpm and the progress of the reaction was started recording. The reaction was performed under autogenous pressure for 22 h. After the completion of the reaction, the autoclave was cooled to room temperature. The obtained reaction mixture was analyzed by gas chromatography (Agilent technologies, Santa Clara, CA, USA, 6890N) equipped with a Phenomen 7HM-G007-17 ZB-WAX capillary column (30.0 m) connected with to a flame ionization detector (FID). A similar process was followed for the activity testing with solid bases but with 1g of a solid base. The 2-butanone conversion, as well as product selectivity and yield, were calculated by considering 3-heptanone as an example, via Equations (2), (3), and (4), respectively.

$$\%C_{2\text{-butanone}} = \frac{A_{\text{products}}}{A_{\text{products}} + A_{2\text{-butanone}}} \times 100 \quad (2)$$

where,

$\%C_{2\text{-butanone}}$ —the amount of 2-butanone converted,

$A_{\text{products}}$ —the GC peak area of all the products

$A_{2\text{-butanone}}$ —the GC peak area of 2-butanone

$$\%S_{3\text{-heptanone}} = \frac{A_{3\text{-heptanone}}}{A_{\text{products}}} \times 100 \quad (3)$$

where,

$\%S_{3\text{-heptanone}}$ —selectivity of 3-heptanone

$A_{3\text{-heptanone}}$ —GC peak area of 3-heptanone

$A_{\text{products}}$ —GC peak area of all the products

$$\%Y_{3\text{-heptanone}} = \frac{\%S_{3\text{-heptanone}} \times \%C_{2\text{-butanone}}}{100} \quad (4)$$

where,

$\%Y_{3\text{-heptanone}}$ —yield of 3-heptanone

$\%S_{3\text{-heptanone}}$ —selectivity of 3-heptanone

$\%C_{2\text{-butanone}}$ —amount of 2-butanone converted

## 4. Conclusions

In summary, we have reported an improved process for  $\alpha$ -alkylation of butanone with 1-propanol in pure water through the borrowing hydrogen (BH) strategy using Pd/C and Pd/BaSO<sub>4</sub> catalysts. The activity obtained with Pd/BaSO<sub>4</sub> and Pd/C catalysts in the presence of added homogenous NaOH was found to be higher compared with the literature-reported Pd/C catalysts and under mild reaction conditions of 180 °C for 22 h. The supported Pd catalysts were 0.23 mol% and base 0.5 mole eq. for butanone, while the literature benchmark was in the range of 2–6 mol eq. of base. Notably, Pd/BaSO<sub>4</sub> + NaOH showed better efficiency with 94% butanone conversion, maximum 84% selectivity to desirable straight and branched alkylated ketones (C7–C11), 4% to long-chain alcohols, and only 12% to undesirable 2-butanol. This is the first report using Pd/BaSO<sub>4</sub> as a catalyst for the  $\alpha$ -alkylation of aliphatic ketones with primary alcohols. Hence, the results have significant potential to provide a new, efficient catalytic option for the desirable long-chain

fuel component production from different biomass feedstocks having two-, three-, and four-carbon precursors.

Subsequent preliminary results from applying LDOs as heterogeneous basic supports revealed that Ni supported on Ba<sub>1.2</sub>Mg<sub>3</sub>Al<sub>1</sub> hydrotalcite was more active (21%) and had higher alkylated ketone selectivity (44%) than Pd metal. Nevertheless, further investigations are needed to enhance the catalytic activity of Ni- and Pd-supported LDOs, and to improve their stability in an aqueous medium.

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