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Catalytic Upgrading of Biomass-Derived Methyl Ketones to Liquid Transportation Fuel Precursors by an Organocatalytic Approach**

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Abstract: A highly efficient water-tolerant, solid-base catalyst for the self-condensation of biomass-derived methyl ketones to jet-diesel fuel precursors was developed by grafting site-isolated secondary amines on silica-alumina supports. It is shown that apart from the nature and density of amine groups and the spatial separation of the acidic and basic sites, the acidity of the support material plays a critical role in defining the catalytic activity. It is also found that a combination of weakly acidic silanol/aluminol with secondary amine groups can mimic proline catalysts and are more effective in catalyzing the selective dimerization reaction than the combination of amines with organic acids. In situ FTIR measurements demonstrate that acidic groups activate methyl ketones through their carbonyl groups leading to a favorable C–C bond formation step involving an enamine intermediate. DFT analysis of the reaction pathway confirms that C–C bond formation is the rate-limiting step.

As the world's accessible fossil reservoirs are gradually depleted, it is crucial to develop sustainable, long-term strategies based on the utilization of renewable feed stocks.^[1] Biomass-derived molecules are inherently oxygen-rich; consequently, the excess oxygen must be removed to raise the energy density of the products and make them suitable as transportation fuels.^[2] It has recently been reported that acetone/butanol/ethanol (ABE) mixtures produced by Clostridial fermentation of sugars can be catalytically converted to aliphatic ketones.^[3] In this process, the monoalkylation of acetone with ethanol or butanol produces pentan-2-one or heptan-2-one, respectively. Alternatively, C₅–C₆ methyl ketones (pentan-2-one, hexan-2-one) can be produced by ring opening hydrogenolysis of 2-methyl furan

and 2,6-dimethyl furan, respectively. Additionally, butan-2-one can be produced in high yields by an acid-catalyzed dehydration reaction of 2,3-butanediol (2,3-BDO) sugars or by decarboxylation of levulinic acids.^[4] However, due to their low carbon numbers and high O/C ratios, there is a strong thrust to develop catalytic methods for the self-condensation of methyl ketones that are fuel components in the gasoline, jet, and diesel range.

Aldol-type condensation provides an excellent pathway to increase the carbon number and decrease the O/C ratio of biomass-derived molecules. This approach requires the development of multicatalytic functions that cooperatively promote efficient one-pot reaction sequences.^[5,6] For example, in organisms, aldol condensations are catalyzed by aldolases that activate donor ketones using the amino groups of a constrained lysine to give enamines.^[7] With precisely positioned active sites, enzymes catalyze selective C–C bond-forming reactions by synergistic interactions. Site isolation is thus considered as one of the paradigms in heterogeneous catalysis, especially in the separation of mutually incompatible groups, such as acids and bases. Among the various heterogeneous catalysts screened for aldol-type condensation reactions, organic amines (basic sites) supported on silica surfaces (acidic sites) have shown outstanding catalytic performance.^[8–10] The use of such supported organocatalysts could eliminate the need for large quantities of caustic base, enabling condensation reactions to be carried out under solvent-less reaction conditions with little or no sensitivity towards water.^[11]

We report here the use of silica–alumina (Si–Al) supported organoamine catalysts for the selective dimerization of biomass-derived methyl ketones to produce liquid transportation fuel precursors. Since weakly acidic silanols (Si–OH) activate the electrophilic reactants through hydrogen bonding during carbon–carbon bond forming reactions, introducing stronger acidic groups (Si(OH)Al) onto the support surface was hypothesized to enhance the cooperative effect.^[12] Experiments were conducted to elucidate the nature of grafted amine groups, their density and the influence of spatial separation between the acid and base groups on the selective dimerization of methyl ketones. To the best of our knowledge, this is the first experimental and theoretical effort aimed at demonstrating the enhanced catalytic activity of supported amine catalysts for the selective dimerization of biomass-derived methyl ketones (C₄–C₁₅).

Details regarding the materials used, catalyst synthesis and characterization methods, and catalyst testing can be found in the Supporting Information (SI). A series of primary, secondary, and tertiary amine catalysts were prepared with

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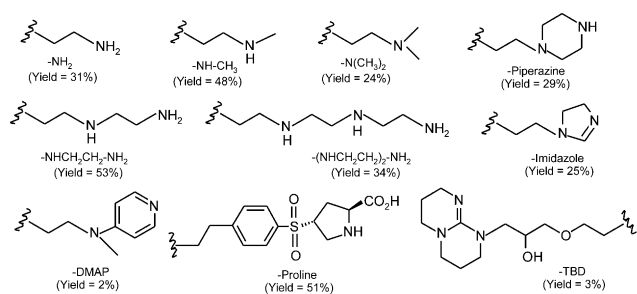
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Scheme 1. Amine catalysts screened for their activity in the dimerization reaction of methyl ketones. Reaction conditions: heptan-2-one (2 mmol, 0.228 g), catalyst (≈ 0.1 g), $t = 12$ h, $T = 443$ K.

similar amine loading so that a direct comparison is feasible with similar textural qualities (Scheme 1). Briefly, the silica–alumina support was first pretreated at 773 K and then contacted with an ethanol solution of the amine precursor under reflux for 16 h to functionalize the precursor onto the support. Solid-state ^{13}C magic-angle spinning (MAS) NMR spectroscopy confirmed the successful grafting of the respective organosilanes onto the Si–Al surfaces (SI). The observed chemical shifts of the organic groups agree well with those of the corresponding organosilane precursors measured in solution. ^{29}Si MAS NMR measurements further confirmed the presence of organic functional groups grafted on the Si–Al support. Peaks at $\delta = -110$, -100 , -90 , -65 , and -55 ppm were assigned to $\text{Q}^4(\text{Si}(\text{OSi})_4)$, $\text{Q}^3(\text{Si}(\text{OH})(\text{OSi})_3)$, $\text{Q}^2(\text{Si}(\text{OH})_2(\text{OSi})_2)$, $\text{T}^3(\text{SiR}(\text{OSi})_3)$, and $\text{T}^2(\text{Si}(\text{OH})\text{R}(\text{OSi})_2)$ sites, respectively.^[13] The presence of peaks at -65 and -55 ppm indicated the formation of T^n sites [$\text{RSi}(\text{OCH}_2\text{CH}_3)_n(\text{OSi})_{3-n}$] and a higher T^3/T^2 ratio from the ^{29}Si MAS NMR confirmed a strong covalent linkage between the organocatalysts and the Si–Al support (SI).

Screening of various amine catalysts under neat conditions for the dimerization of heptan-2-one showed that Si–Al-supported secondary amines are more active than primary amines, whereas tertiary amines are less active (Scheme 1). The only products observed under any of the conditions investigated were C_{14} dimers. Interestingly, under equal concentration of amine groups, Si–Al-supported secondary amines (Si–Al-NHR) produced similar conversion to that of supported proline. This result suggests that heterogenizing secondary amines on silica–alumina can mimic the constrained site isolation occurring in proline. Changing the R group in Si–Al-NHR from methyl to butyl did not change the yield of the dimerized product. The catalyst prepared with a diamine ($-\text{NHCH}_2\text{CH}_2\text{NH}_2$) afforded slightly better activity than the Si–Al-NHR catalyst, whereas heterogenizing a triamine ($-(\text{NHCH}_2\text{CH}_2)_2\text{NH}_2$) catalyst resulted in approximately two times lower activity than that found for the diamine catalyst. Supported tertiary amines, such as TBD and DMAP, showed no activity, whereas supported imidazole or piperazine exhibited moderate catalytic activity (Scheme 1). The low catalytic activity of the tertiary amine catalysts compared to the secondary amines suggests that enamines are the key intermediate, since tertiary amines have difficulty for forming enamines due to lack of hydrogen on the nitrogen atom.^[14,15]

Control reactions carried out with a homogeneous amine catalyst (*N*-methylbutylamine) did not furnish the desired products. A combination of Si–Al and a homogeneous base (*N*-methylbutylamine) demonstrated an intermediate level of conversion (27%), albeit significantly lower than that obtained from the acid–base bifunctional Si–Al-NHR catalyst. These results illustrate the necessity of having the immobilized acid and base groups in close proximity to realize cooperative catalytic enhancement. Further support for this conclusion was obtained by noting the absence of activity for Si–Al- C_1 -NHR, a catalyst in which the linker for the amine group contains only one carbon atom.^[16] Therefore, the amine groups must be flexible enough to work cooperatively with the acidic hydroxy groups but spaced far enough from these groups to avoid mutual neutralization of the acid and base groups. Blocking the silanol/aluminol groups by silylation using trimethoxysilane decreased the catalyst activity by five times.^[17] This observation confirms that acidic sites must work cooperatively with the supported amines to catalyze the selective dimerization of methyl ketones.

The acid–base pair effect was verified further by heterogenizing amines in combination with various alkyl-tethered organic acids like sulfonic acids ($\text{p}K_a = -2$), phosphoric acid ($\text{p}K_a = 3$), and carboxylic acid ($\text{p}K_a = 5$).^[18] The catalyst activity was found to decrease with decreasing $\text{p}K_a$ of the acid groups (Figure 1 a). This interesting result suggests that strong acids in close proximity to the basic sites can protonate the nitrogen to lower its nucleophilicity and slow down the formation of enamines. It was also observed that the cooperative interactions of amines with weakly acidic silanols/aluminols ($\text{p}K_a = 6-8$) are much more effective than organic acids unless the interaction between the amine and the acid groups is constrained as in proline (Scheme 1).^[19] Nevertheless, it should be emphasized that the Si–Al-supported amine showed a three-fold higher conversion than the corresponding silica-supported amine catalyst (SI). The improved catalytic activity for the amine-grafted Si–Al compared to that of amorphous silica suggests that the Brønsted acidity of the support plays an important role in enhancing the catalytic activity of the heterogenized amine

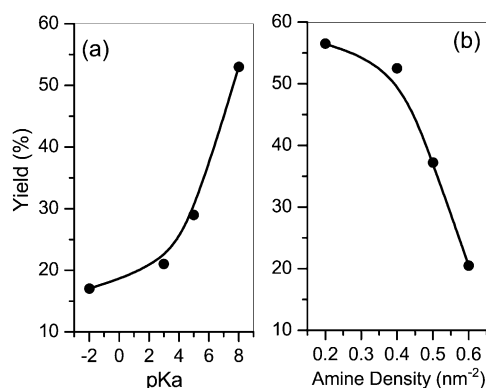


Figure 1. a) Effect of acid strength on the catalytic activity of the supported amine catalysts and b) effect of amine loading on the yield of dimer product. Reaction conditions: heptan-2-one (2 mmol, 0.228 g), Si–Al- $\text{NHCH}_2\text{CH}_2\text{NH}_2$ catalyst (0.1 g, 0.4 amines nm^{-2}), $t = 12$ h, $T = 443$ K.

samples. This result is corroborated by the strong upfield shift in the terminal carbon position by adsorbing homogenous triethylamine (NEt₃) on Si–Al than on silica.^[20] Remarkably, ¹³C CP MAS NMR spectroscopy of the amine-tethered Si–Al sample showed similar peak positions to that in the silica sample, indicating the absence of strong interactions between the Brønsted acid sites and the heterogenized amine groups (SI). These results suggest that amine–acid site isolation is maintained in Si–Al-supported amine catalyst because protonated amines are known to be less active for condensation reactions.^[16]

Having established supported diamine (–NHCH₂CH₂NH₂) as the most active catalyst for heptan-2-one dimerization, we examined the effect of varying the density of amines groups on the Si–Al surfaces. As shown in Figure 1 b, increasing the amine content on the Si–Al surface decreased the catalytic activity. Stated another way, at low amine loading, an increase in cooperativity between basic sites and silanols/aluminols was achieved by preventing amine aggregation on the Si–Al support surface.^[10]

We also note that the Si–Al-supported diamine catalyst is remarkably water tolerant and retains its catalytic activity even when the reaction is performed in a mixture containing 50 wt % water (Figure S10). By contrast, calcined hydrotalcite (MgAlO_x), completely loses its activity when less than 5 wt % of water is added to the reaction mixture. This observation clearly demonstrates the practical advantage of supported organocatalysts in biomass upgrading reactions over conventional inorganic solid-base catalysts, such as hydrotalcites.^[21]

The scope of the dimerization of methyl ketones catalyzed by Si–Al–NHCH₂CH₂NH₂ was examined for ketones containing 4–15 carbon atoms. All substrates exclusively produced dimers of the ketones with yields generally greater than 60 % (Figure 2). Only the C₁₅ substrate showed a low product yield, probably due to its long carbon chain and its difficulty in diffusing into the narrow pores of the support. The solid-supported organocatalysts were then used as catalysts for continuous flow process. Catalytic activity of the most active silica–alumina-supported amine catalyst (Si–Al–NCH₂CH₂NH₂) evaluated in the continuous, gas-phase self-condensation of butan-2-one showed excellent catalytic activity and did not exhibit significant deactivation over 30 h on stream (Figure S11).

To obtain insights into the reaction mechanism, the Si–Al-supported amine catalyst was characterized by in situ FTIR spectroscopy using butan-2-one as a probe molecule (Figure 3). The spectrum recorded at 298 K over Si–Al–NHCH₂CH₂NH₂ catalyst showed a band at 1700 cm^{–1} followed by the formation of a strong band at 1660 cm^{–1} and a weak band at 1630 cm^{–1}. The 1700 cm^{–1} peak is related to the adsorption of methyl ketone on the Si(OH)Al groups which showed ca. 15 cm^{–1} downfield shift in carbonyl peaks from the gas phase whereas the sharp peak observed at 1660 cm^{–1} can be assigned to the formation of imine (–HC=N–) species.^[15,22] The ¹³C CP MAS NMR spectrum of the Si–Al–NHCH₂CH₂NH₂ sample after treatment with butan-2-one showed a peak at δ = 160 ppm (–N=CH–), and at δ = 63 ppm (N–CH₂), indicating the rapid formation of an imine intermediate by dehydration (SI).^[12,13] The shoulder at 1630 cm^{–1}

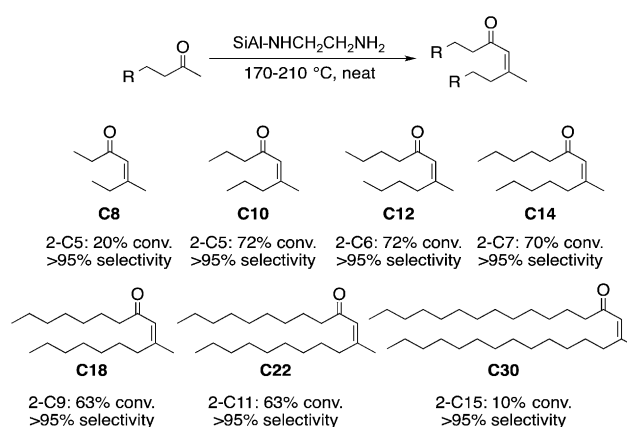


Figure 2. Substrate scope of the Si–Al–NHCH₂CH₂NH₂ catalyst in the selective dimerization reaction of C₄–C₁₅ methyl ketones. Reaction conditions: methyl ketone (2 mmol), Si–Al–NHCH₂CH₂NH₂ catalyst (0.1 g, 0.4 amines nm^{–2}).

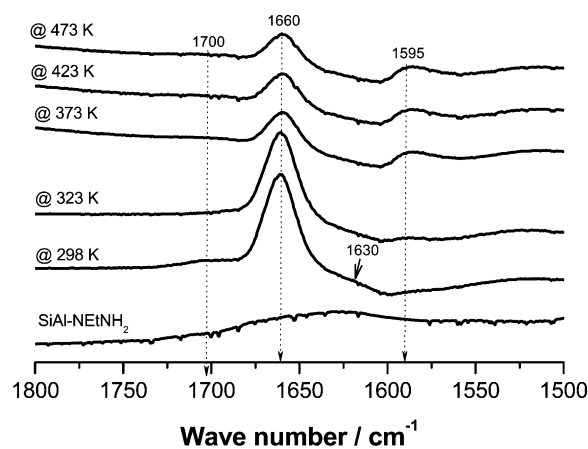


Figure 3. In situ FTIR spectra of the Si–Al–NHCH₂CH₂NH₂ catalyst using butan-2-one as a probe molecule at different reaction temperatures.

can be related to the formation of iminium species, the formation of which have been reported frequently for homogenous secondary amine catalysts.^[14] The formation of iminium/enamine groups observed over secondary amines is in good accordance with previous reports that these catalysts operate through an enamine mechanism. Increasing the temperature from 298 K to 473 K produced a progressive decrease in the peak at 1700 cm^{–1} and the appearance of a new peak for carbon–carbon vibrations at 1595 cm^{–1}. These observations show that enamines interact with the adsorbed methyl ketones to produce the ketone dimer. To validate this finding, in situ IR spectra of Si–Al–NHCH₂CH₂NH₂ were acquired by first saturating the sample with pyridine prior to exposure of the catalyst to butan-2-one. Saturation of the sample with the pyridine prior to the addition of butan-2-one resulted in the absence of a peak at 1700 cm^{–1}. This observation shows that pyridine passivates the sites at which the ketone adsorbs and subsequently reacts to form C–C bond. The IR results also support the need for a combination of basic amine groups and acidic Si(OH)Al groups and

explain why supported amines are more active than the homogenous amine catalysts.

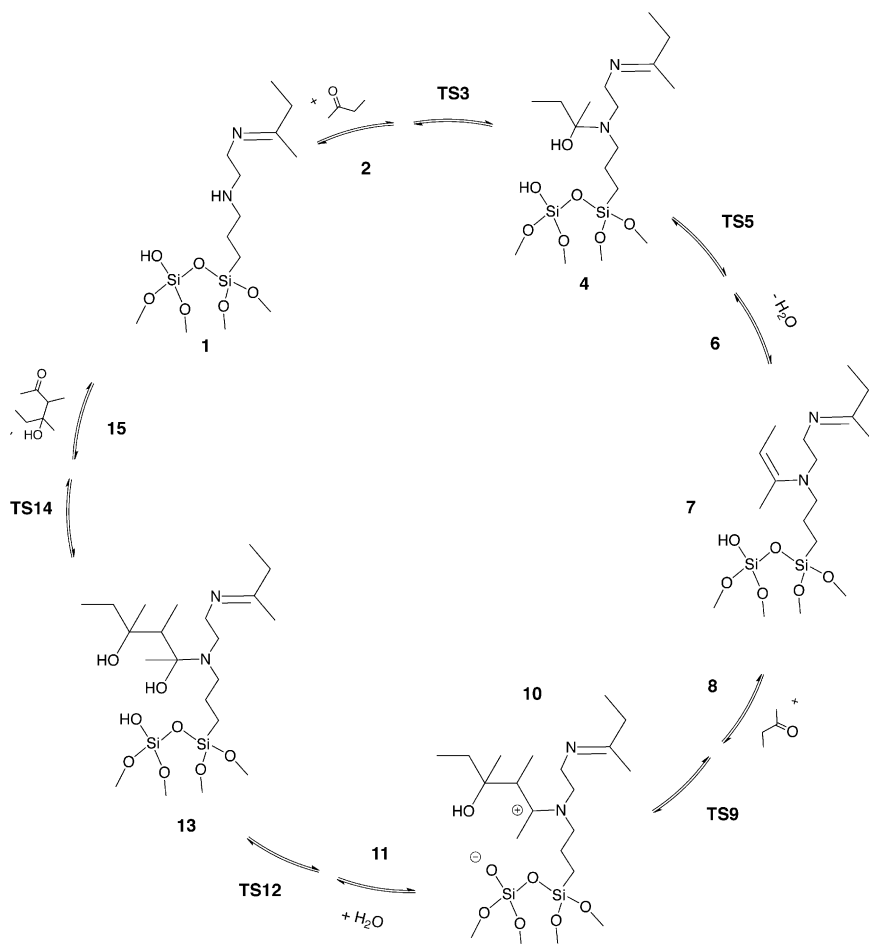
A theoretical analysis of the aldol condensation reaction pathway was carried out to verify the proposed reaction mechanism, determine the rate-limiting step, and explain the high selectivity to dimers shown by the Si-NHCH₂CH₂NH₂ catalyst.^[22] The changes in enthalpy (at the reaction temperature, 343.15 K) along the reaction pathway of butan-2-one condensation calculated at the ωB97X-D/6-311++G-(3df,3pd) level of theory and the corresponding free-energy (343.15 K) changes are shown in the SI.

The adsorption of butan-2-one to the catalyst surface is exothermic ($\Delta H = -45 \text{ kJ mol}^{-1}$) and is characterized by a hydrogen bonding interaction between butan-2-one and the grafted amine (**2**, butanone adsorption, Scheme 2). The formation of a carbinolamine species proceeds through a concerted C–N bond formation and proton transfer reaction (**4**, carbinolamine). The enamine state is produced by intramolecular water elimination. The desorption of water upon enamine formation exhibits a favorable free energy change due to the additional gain in entropy (**7**, enamine). The -30 kJ mol^{-1} change in free energy upon desorption of water suggests that the enamine intermediate, which is the resting state of the catalyst, is not significantly poisoned by water.

The adsorption of butan-2-one in the presence of the enamine resting state is exothermic ($\Delta H = -32 \text{ kJ mol}^{-1}$) and is promoted by hydrogen bonding between the silanol group and the carbonyl group of butan-2-one (**8**, butanone adsorption). The formation of the C–C bond (**TS9**) proceeds through protonation of the butan-2-one carbonyl group by the silanol group and C–C bond formation between the enamine and the alpha-carbon of butan-2-one in a concerted fashion to produce an iminium species (**10**, iminium). The C–C bond formation rate-determining step occurs much more readily in the case of Si–Al than SiO₂ due to the increased Brønsted acidity of Si(OH)Al relative to Si–OH groups. The hydrolysis (**TS11**) proceeds from the iminium by the attack of water on the complex (**12**, carbinolamine II). This process leads to a concerted proton transfer from the water molecule to the deprotonated silanol group, leaving the final product, 3,4-dimethyl-4-ol-hexan-2-one, in the chemisorbed state. The final step of the reaction pathway is the desorption of 3,4-dimethyl-4-ol-hexan-2-one, which produces the C₈ dimer and leaves the catalyst active site in its original form.

C–C bond formation (**TS9**) is determined to be the rate-determining step of the dimerization reaction. The calculated apparent activation energy, calculated as the change in enthalpy between intermediate **7** and **TS9**, is 90 kJ mol^{-1} , in good agreement with the experimentally determined activation energy of 95 kJ mol^{-1} for butan-2-one condensation over the Si-NHCH₂CH₂NH₂ catalyst.

Theoretical analysis of the trimerization pathway was performed to understand the high selectivity to the dimer product relative to the trimer (SI). Trimerization of butan-2-one occurs when carbinolamine II (**13**) undergoes dehydration (**TS16**) rather than desorption (**TS14**) to form a C₈ enamine (**21**). The dehydration and release of water to form (**21**) is endothermic but exergonic due to the gain in entropy upon releasing two molecules of water. C–C bond formation (**TS23**) is found to be the rate-determining step of the trimerization reaction. The difference in selectivity can be rationalized by examining the difference in the Gibbs free energy of activation ($\Delta\Delta G^\ddagger$) between the dimerization (**TS9**) and trimerization (**TS23**) C–C bond formation transition states. At the reaction temperature of 343.15 K, $\Delta\Delta G^\ddagger = 58 \text{ kJ mol}^{-1}$, which suggests that the catalyst will selectively dimerize butan-2-one except at high temperature. The difference in the entropy of activation between (**TS23**) and (**TS9**), $\Delta\Delta S^\ddagger = 6 \text{ J mol}^{-1} \text{ K}^{-1}$, is small and positive; therefore an increase in the reaction temperature will result in a less positive value of $\Delta\Delta G^\ddagger$ between



Scheme 2. Proposed reaction mechanism of butan-2-one condensation reaction over Si–Al–NHCH₂CH₂NH₂ catalyst.

dimerization and trimerization transition states, and thus an increase in the selectivity to the trimer product.

Taken together, we have shown that silica–alumina-supported secondary amines can perform the selective dimerization of biomass-derived methyl ketones. Secondary amines in combination with Si(OH)Al groups provide the best acid–base pair and the spacing between acid–base groups must be controlled to maximize their cooperative action and minimize acid–base neutralization. Results further demonstrate that secondary amines supported on silica–alumina are water-tolerant and are more active than primary or tertiary amines. In situ IR spectroscopy shows that Brønsted acidic groups assist in the adsorption and polarization of ketones so that a favorable attack of the nucleophilic enamine species can occur that leads to the formation of the C–C bonds. DFT analysis of the reaction pathway confirms that C–C bond formation is the rate-limiting step, in agreement with the experimental findings.

Keywords: aldol condensation · methyl ketones · organocatalysts · secondary amines · silica–alumina

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