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Lanthanum-modified Boehmite-derivatives as Solid Acid-Base Catalyst for Highly Efficient Aldol Condensation

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To address the demands for sustainable development and a low-carbon economy, the catalytic conversion of biomass resources has been extensively investigated in recent decades. 3-Methyl-2-cyclopentenone (MCP), derived from biomass, has been recognized as a key intermediate in the synthesis of various natural products and gasoline additives. This study explores the selective synthesis of MCP from 2,5-hexanedione (HD) using La-modified boehmite catalysts by two different preparation methods of impregnation and co-precipitation with/without calcination.

In the case of La-supported boehmite catalysts prepared by an impregnation method (*imp*-La/AlOOH), it gave no activity without calcination. It was very attractive that the highest MCP yield of 60% at 84% conversion could be obtained when it was calcined at 500°C. On the other hand, La-Al mixed catalyst obtained by a co-precipitation method (*cp*-La-Al-(OH)) exhibited good performance without calcination; it served 55% yield of MCP and 65% conversion. While such nice performance was decreased after calcination as 40% yield of MCP at 50% conversion. XRD showed the main phases of both *cp*-La-Al-(OH) and *imp*-La/AlOOH without calcination were identified as boehmite (AlOOH) crystalline. While, after calcinations at 500 °C, γ-Al_2O_3 was retained as the dominant crystalline phase in both catalysts. The N_2 adsorption–desorption isotherms revealed the non-calcined *cp*-La-Al-(OH) catalyst displays less defined mesoporosity and more macroporous features whereas the non-calcined imp-La/AlOOH exhibited a clear Type

IV isotherm with distinct mesoporosity. These pore structures of both catalysts became were not significantly affected by the thermal treatment. Accordingly, it was very interesting that both *cp*-La-Al-(OH) and *imp*-La/AlOOH catalysts exhibited similar XRD crystalline structures with/without calcination, however their catalytic activities differed markedly.

Poisoning experiments confirmed that the reaction over the non-calcined *cp*-La-Al-(OH) catalyst proceeds via a base-catalyzed mechanism. The co-precipitation method generated unique basic surface sites without calcination, and then most of which disappeared or were weakened after calcination. In contrast, the reaction over the calcined *imp*-La/AlOOH catalyst proceeded through an acid–base cooperative mechanism, where calcination led to the formation of Lewis acid sites in addition to basic sites. These findings underscore the potential of non-calcined *cp*-La-Al-(OH) catalysts as effective solid base systems and highlight the importance of preserving surface basicity during catalyst design.

Keywords: Lanthanum-modified alumina; Co-precipitation; Impregnation; Aldol condensation; Acid–base catalysis