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Full Length Article

# TUD-1 type aluminosilicate acid catalysts for 1-butene oligomerisation

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## ABSTRACT

TUD-1 type mesoporous aluminosilicates were explored for the acid-catalysed oligomerisation of 1-butene, under high pressure, continuous flow operation, which is an attractive route to produce sulphur-free synthetic fuels with reduced aromatics content. The solid acid catalysts were synthesised via one-pot synthesis (HT) or stepwise approach (PG), without using surfactants as templates, which is an eco-friendly characteristic of the TUD-1 family. While the HT approach may be advantageous in terms of process intensification in relation to the PG one, the latter may lead to relatively low molar ratios Si/Al. The catalysts possessed Si/Al ratios in the range 3–5 and 17–35 for the PG and HT approaches, respectively, pore sizes in the range 10–14 nm, and essentially Lewis acidity. To the best of our knowledge, this is the first report of siliceous oxide TUD-1 furnished with acidity via post-synthesis grafting (PG) of Al-species. For comparative studies, an ordered mesoporous aluminosilicate was synthesised via the PG approach using surfactant mixtures. All materials prepared promoted the reaction of 1-butene to higher molar mass products. The best-performing catalyst in terms of space-time yields of the 170–390 °C cut (boiling point range) products (of the type middle distillates) was Al-TUD-1(25)-HT synthesised via the HT method. The products were analysed by comprehensive two-dimensional gas chromatography (GC × GC) combined with time-of-flight mass spectrometry (ToFMS). The influence of material properties and process parameters on the catalytic reaction, and catalyst stability were studied. The catalytic performances were benchmarked with ZSM-5 (zeolite used in commercial oligomerisation processes).

## 1. Introduction

The concerns about global warming, and the awareness of the increasingly stringent environmental legislation/policies regarding emissions have been driving research efforts towards developing efficient, sustainable production routes to chemicals and quality fuels with reduced environmental impact. The oligomerisation of light olefins is an attractive route, since it may lead to sulphur-free synthetic fuels with reduced aromatics content. For example, synthetic fuels such as those of the type middle distillates have large applications; land/sea/air transportation, domestic/commercial heating, power generation, construction/agricultural machinery, or for producing intermediates for lubricants, surfactants, etc. The European demand for diesel/gasoil (middle distillates) in the transportation sector continues growing [1–3]. Light olefins may be obtained from treatment/conversion processes of non-renewable and renewable sources of organic carbon: from fossil sources, e.g. olefins present in light cracked naphtha (LCN) [4–6], methanol-to-olefins (MTO) plants [7], Fischer-Tropsch (FT) plants [8–10]; and from renewable sources, e.g. butenes from carbohydrate biomass, and ethene/butene from biobased ethanol/butanol [11–17].

Olefin oligomerisation requires an acid catalyst, involves exothermic reactions and the overall process leads to complex reaction mixtures since several side reactions may occur (exemplified for 1-butene in Scheme 1). Commercial oligomerisation processes use heterogeneous catalysts, operating in a continuous mode. In particular, zeolites (microporous crystalline aluminosilicates) with MFI topology are used as solid acid catalysts in the commercial olefin oligomerisation processes, Mobil Olefins to Gasoline and Distillate (MOGD) [7,18] and Conversion of Olefins to Distillate (COD) [19,20]. In processes such as these, involving relatively bulky intermediates/products, microporous catalysts may present drawbacks associated with internal diffusion limitations and/or catalyst deactivation due to pore blockage by the long chain olefins and bulky byproducts, impacting negatively on the catalyst stability and productivity. In this sense, mesostructured solid

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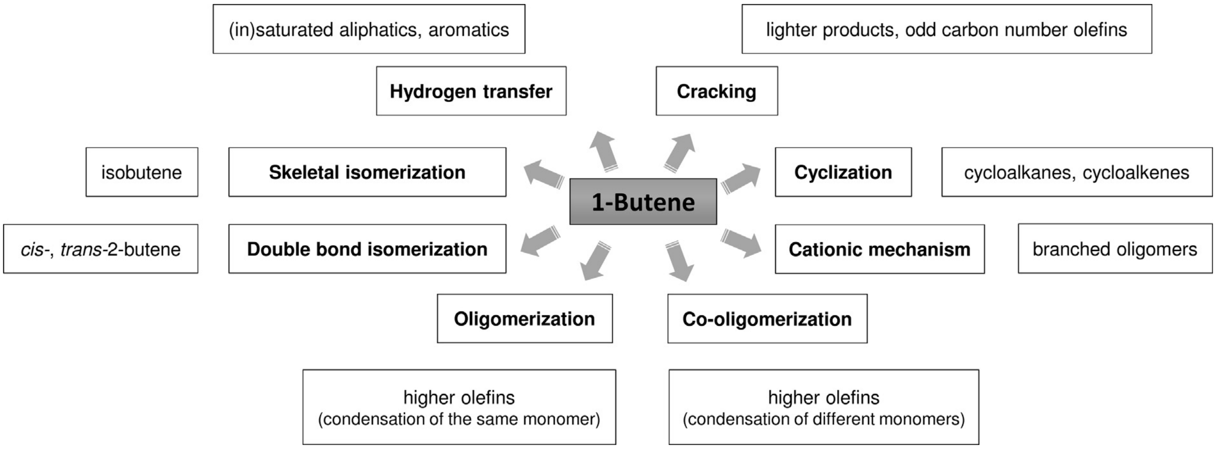

**Scheme 1.** Olefin oligomerisation exemplified for 1-butene, and possible pathways involved in the complex reaction process.

acid catalysts possessing high specific surface area and enhanced active site accessibility seem attractive. Ordered mesoporous silicates (OMPS) of the type MCM-41 possessing aluminium sites exhibited fairly good stability (steady activity under continuous operation) for the conversion of $C_4$ and $C_5$ olefins [21–23], in relation to disordered porous materials such as amorphous silica-alumina [22], or ordered microporous materials such as BEA [22,23] and MFI [22] type zeolites. The MCM-41 family of materials are synthesised using surfactants as templates, which have negative environmental impact. Thus, OMPS were developed focusing on surfactant-free routes, such as SBA-15. It was reported that Al-containing SBA-15 promoted the oligomerisation of ethene [24] and hexene [25,26]. Nevertheless, SBA-15 type materials are synthesised using copolymers as templates which are rather expensive. A nice compromise in terms of cost and eco-friendliness of OMPS synthesis methodologies was achieved with the development of TUD-1 by Maschemeyer, Hanefeld and co-workers [27–31].

TUD-1 type materials are synthesised via surfactant-free and copolymer-free routes, following important sustainable chemistry principles; e.g. use of less hazardous reagents, benefiting from decreased toxicity and costs [32]. TUD-1 family of materials possesses a sponge-like ordered mesoporous structure, with high specific surface area, pore volume and sizes. These textural properties may avoid severe diffusion limitations and/or fast catalyst deactivation due to pore-blockage by carbonaceous matter; particularly important for catalytic processes such as olefins oligomerisation which involves intermediates and/or products. TUD-1 may be furnished with acid properties by introducing, for example, aluminium species [33–35].

In the present work, Al-containing TUD-1 type mesoporous solid acids were synthesised via different approaches, and tested as catalysts for 1-butene oligomerisation, under continuous flow operation mode, in the temperature range 150–250 °C, and pressure range 20–40 bar. The catalysts were prepared via one-pot (HT; sol-gel process, using hydrothermal conditions) [30,33,34,36] or stepwise procedures (PG; post-synthesis grafting of Al-species on pre-made siliceous oxide TUD-1). To the best of our knowledge, this is the first report of TUD-1 type aluminosilicates prepared via the PG approach. The HT approach may be advantageous in terms of process intensification in relation to the PG approach; on the other hand, the latter may lead to relatively low Si/Al ratios. For comparison, a large-pore (LP) Al-containing OMPS material was synthesised via the PG approach, using a mixture of surfactants as structure directing agents (giving Al-LP(PG)). The type of reaction products formed were investigated by GC × GC–ToFMS. The influence of process parameters and material properties on the catalytic reaction, and benchmarking studies with zeolite ZSM-5 were carried out.

## 2. Experimental

### 2.1. Materials

All reagents and solvents were obtained from commercial sources and used as received. For materials syntheses: aluminium (III) isopropoxide (AIP; 98%, Aldrich), tetraethylammonium hydroxide solution (TEAOH; 35 wt% in water, Aldrich), tetraethylorthosilicate (TEOS; 98%, Sigma), triethanolamine (TEA; 97%, Fluka), ethanol (99.9%, Riedel de Haen), anhydrous isopropanol (99.5%, Sigma-Aldrich), aluminium chlorohydrate (ACH; 95.4% from Fagron). For the catalytic tests: 1-butene (99.6%, Praxair), nitrogen (Air Liquide), silicon carbide (SiC, Ø 0.31 mm, SIKA), dichloromethane (analytical reagent grade, Fisher Chemical), and *n*-pentane (95%, Fluka). Commercial microcrystalline zeolite $NH_4ZSM$-5 (CBV3024E; Zeolyst; Si/Al = 15) was used as benchmark catalyst after calcination at 550 °C in static air for 5 h (heating rate of 1 $^{\circ}C\ min^{-1}$) to give the protonic form (denoted ZSM-5).

### 2.2. Syntheses of the catalysts

Mesoporous Al-containing TUD-1 materials with different molar ratios Si/Al were prepared via (surfactant-free) sol-gel technique using hydrothermal conditions (HT), or via post-synthesis grafting of aluminium species on the pre-made silica support TUD-1 (PG). The HT synthesis was carried out following a similar procedure to that described in Ref. [37], using AIP and TEOS as Al and Si sources, respectively, and TEA as templating agent. Specifically, TEOS (83.0 mmol) was added slowly to a mixture consisting of AIP (3.33 mmol for Si/Al = 25; 1.66 mmol for Si/Al = 50) in isopropanol (6.5 mL) and ethanol (6.5 mL). After stirring for ca. 20 min, a mixture of TEA (83.9 mmol) and milliQ water (932.2 mmol) was added slowly, followed by dropwise addition of TEAOH (27.0 mmol) under vigorous stirring. The molar composition of the synthesis-gel was $SiO_2$:(0.02 or 0.04)AIP:0.33TEAOH:1.01TEA:11.23$H_2O$. The gel obtained was stirred at room temperature for 24 h and dried at 98 °C for 22 h, followed by aging in a PTFE-lined stainless steel autoclave at 180 °C for 8 h. The resultant solid was subjected to Soxhlet extraction with ethanol (ca. 3 h), dried overnight at 60 °C, and gently grinded using an Agate mortar and pestle. Finally, the solid was calcined at 600 °C in static air for 10 h (heating rate of 1 $^{\circ}C\ min^{-1}$), giving the materials denoted as Al-TUD-1(x)-HT where x is the initial molar ratio Si/Al (25 or 50) of the synthesis mixture.

The material Al-TUD-1(PG) was synthesised via post-synthesis grafting (PG) of an aluminium precursor on the pre-made mesoporous silica TUD-1 [38]. TUD-1 was prepared according to the procedure described in Ref. [39]. Specifically, TEOS (25.6 mmol) was added