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Full Length Article

Co-based MOR/ZSM-5 composite zeolites over a solvent-free synthesis strategy for improving gasoline selectivity

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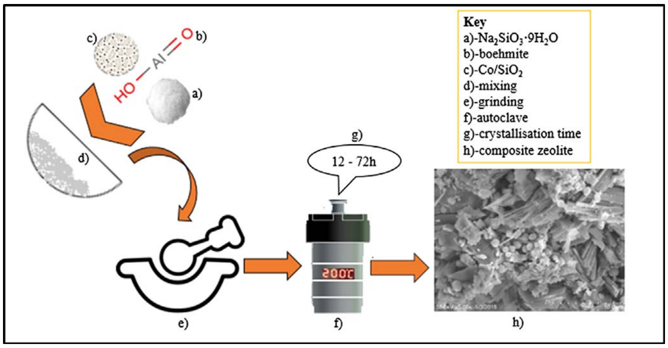
GRAPHICAL ABSTRACT



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ABSTRACT

Composite zeolites containing ZSM-5 are known to be very active for catalytic conversion of syngas into gasoline range hydrocarbons under Fischer-Tropsch synthesis. In this work, a novel MOR/ZSM-5 composite zeolite with immersed Co particles was successfully fabricated under a facile solvent-free synthesis method. The final catalysts were characterised by XRD, SEM and TEM procedures to evaluate the structural properties and morphologies of Co@MOR/ZSM-5. Variation in the crystallization time played a vital role during zeolite synthesis. Perfect crystal structure for solvent-free Co@MOR/ZSM-5 was found at 72 h of crystallization time and proved to exhibit the greatest gasoline selectivity of 72.3%. This composite zeolite synthesized by solvent-free method with outstanding performance, has all potential to act as highly effective heterogeneous catalyst in the near future.

1. Introduction

There is a great need of synthesizing clean liquid fuel, comprising diesel and gasoline, from renewable biomass to resolve the world-wide petroleum depletion and bearing in mind a green process. Fischer-Tropsch synthesis (FTS) is a favourable route, using (CO + H_2) as feed gas, originating from nature gas, coal, biomass and garbage to develop ecologically nonthreatening sulphur- and nitrogen-free liquid fuels [1]. Linear alkanes/alkenes are the principal products developed by conventional FTS over Fe-, Co- and Ru-based catalysts [2,3]. Based on these three metals, Co is an auspicious catalyst because of its enhanced activity, greater selectivity to straight-chain hydrocarbons and minimised

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water-gas shift (WGS) reaction activity and also low cost in comparison to Ru [4]. This product molecular weight dispersal obeys the Anderson-Schulz-Flory (ASF) rule [5–7]. Exploitation of the product selectivity in favour of a specific hydrocarbon portion such as gasoline or diesel is always a challenge. Attached catalysts merging the conventional FTS catalysts in union with acidic zeolites were reported to outstand the restrictions in product selectivity and quality [8]. This occurred on the zeolite's secondary reactions of the linear hydrocarbons leading to development of aromatic compounds and branched alkanes but facing challenges of catalyst deactivation and retarded CO transformation [9].

During the past two decades, efforts again have been deployed to modify the Fischer-Tropsch product, comprising of straight chain aliphatics, through assembling FTS catalysts with zeolites A, X, Y, or ZSM-5, so as to develop lower hydrocarbons [10,11]. The use of zeolite crystals with sophisticated micropores, greater acidity, and redox sites have been extensively used as heterogeneous catalysts in the fuel and fine chemical industries [12]. Hierarchically organised zeolites assimilate at slightest two levels of porosity and give out the benefits related to each level of porosity, beginning from selectivity to mass conveyance [13,14]. Hydrocracking and isomerisation is highly stimulated by zeolites due to their shape-selective and acidity features. Consequently, zeolites such as ZSM-5, parades selectivity in favour of light and branched hydrocarbons [15]. Middle-chain products also tend to be developed by mordenite and β-zeolite via FTS reaction [16].

Precisely, Nakanishi et al. matched the catalytic activities of Co/zeolite exhausting on zeolites under a variety of different preparation methods [17]. They testified that Co/β-zeolite catalyst demonstrated low CO transformation following an enhanced C_5-C_9 hydrocarbon (gasoline fuel portion) selectivity. Co/SiO_2 was mixed with numerous zeolites such as mordenite, ZSM-5, USY and β-zeolite by Martínez et al. observed that β-zeolite portrayed increased gasoline selectivity [18]. Kong et al. reported the exceeding growth of continuous ZSM-5 shells over mordenite crystals achieved in a two-step route to develop a hierarchical core/shell structures [19]. Initially, MOR crystals were hydrothermally pre-treated in organic amine solution followed by overgrowth of ZSM-5 films over the altered mordenite crystals [19]. This MOR zeolite highlights orthorhombic crystal morphology occupying straight 12-membered ring channels (0.65 nm × 0.70 nm) and further occupy crossed 8-membered ring channels (0.28 nm × 0.57 nm). Regardless of these wide-ranging studies, the consequence of different preparation methods on the effectiveness of the catalysts through FTS has not sufficiently been matched so far. Tan et al. also developed a composite zeolite (Fe-Zn-Zr@HZSM-5/Hbeta) by a simple cladding method. In their work, preparation of Fe-Zn-Zr core was firstly achieved by a co-precipitation method, followed by cladding method for the development of core-shell catalyst with Fe-Zn-Zr as core and zeolite (one or two forms of HZSM-5, HY and Hbeta) as shell. This made an evidently enhanced confinement outcome on furthering iso-alkanes direct synthesis from CO_2 [20].

Composite zeolites have been extensively studied because of for their excellent catalytic performances. Recently, Li et al. reported an HZSM-5/MnAPO-11 composite zeolite prepared via hydrothermal synthesis, where Mn was merged into the framework of AlPO-11, followed by direct crystallization of MnAPO-11 gel with the addition of HZSM-5 [21]. In comparison to HZSM-5 and mechanical mixture of HZSM-5 and MnAPO-11, the composite HZSM-5/MnAPO-11 exhibited greatest gasoline yield and isoparaffin selectivity due to moderate acid sites and extra mesopores. Fan et al. fabricated HZSM-5/SAPO-11 composite for the hydro-enhancement of FCC gasoline, and proved that the composite has increased mesoporosity permitting for mass diffusion and also reasonable acidity resulting to an increased synergistic consequence between Brønsted and Lewis acid sites [22]. Also core-shell composites of USY@Mesosilica with the mesoporous shell and a small dealuminated USY zeolite were developed by splitting two procedure of assembly and crystallization in the separate conditions [23]. This composite zeolite exhibited admirable catalytic performances with greater activity and enhanced selectivity in comparison to catalyst prepared from pure USY zeolite.

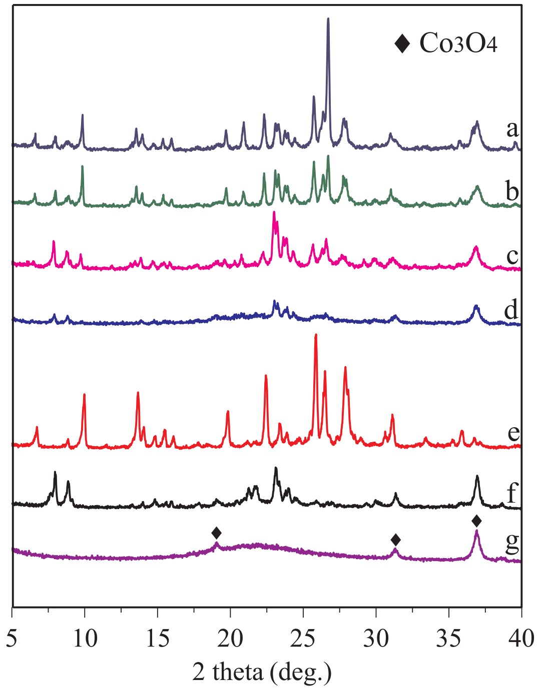

Fig. 1. XRD patterns of (a) Co@MOR/ZSM-5(72 h), (b) Co@MOR/ZSM-5(48 h), (c) Co@MOR/ZSM-5(24 h), (d) Co@MOR/ZSM-5(12 h), (e) Co/NaMOR, (f) Co/NaZSM-5, (g) Co/SiO_2.

Mostly, the synthesis of zeolite is accomplished under hydrothermal, solvothermal, and ionothermal environments, where abundant solvents such as water are essential [24]. Synthesizing zeolites by using water results in dilution of the nutrients of silicate, aluminophosphate and aluminosilicate liquefied in the waste water. This significantly leads to minimised zeolite yield per given reactor volume [25]. Moreover, the application of solvents leads to reduced synthesis efficiency resulting to autoclave space being exploited by the solvent, and develops the enhanced pressure following high pressure solvothermal controls [26]. The ionothermal method can effectively eliminate the high pressure challenge, when creating aluminophosphate-centred zeolites, due to lowered ionic liquids' vapour pressure, but it is expensive [27]. Xiao et al. lately described a solvent-free synthesis route of aluminosilicate zeolites offering a gigantic advantage of reducing waste development and heightening zeolite yield [28]. Therefore, the solvent-free strategy for prepared novel composite zeolites, will provide possible and special properties.

In this article, we fabricated Co-based in MOR/ZSM-5 composite zeolites under different crystallization time using a solvent-free synthesis route. The different crystal morphologies of combined MOR and ZSM-5 substrates were obtained at different crystallization time and their effect on syngas conversion for improving gasoline selectivity. Also we appreciated that the solvent-free synthesis not only minimised the disadvantages of conversional hydrothermal method, but contributed to crystal firmness and increased zeolite yield.

2. Experimental section

2.1. Materials

Boehmite (Al_2O_3 −70 wt%, Zibo Senchi Chemical Co., Ltd.), $Na_2SiO_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, EDA and NaOH (Sinopharm Chemical Reagent Co., Ltd.), silicic acid ($SiO_2{\cdot}xH_2O$, Sinopharm Chemical Reagent Co., Ltd.) SiO_2 (pore size of 10 nm, Fuji Silysia Chemical Ltd.).