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Synthesis, characterization and adsorptive denitrogenation performance of bimodal mesoporous Ti-HMS/KIL-2 composite: A comparative study on synthetic methodology

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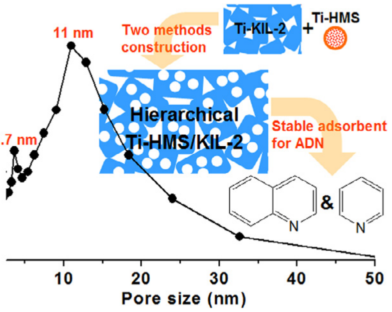
HIGHLIGHTS

- Mesoporous silicates Ti-HMS and KIL-2 as structural components for constructing hierarchical composites.
- Two-step and dual-template comparatively synthesis for Ti-HMS/KIL-2.
- Bimodal distribution of pore size and regulable larger mesopores for Ti-HMS/KIL-2.
- Improved hydrothermal stability and recyclability for adsorptive removal of NCCs.

GRAPHICAL ABSTRACT

Two methods for synthesis of bimodal mesoporous Ti-HMS/KIL-2 composites as adsorbents of nitrogen-containing compounds in fuel.



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ABSTRACT

Novel titanosilicate composites with bimodal mesopores using molecular sieves Ti-HMS and Ti-KIL-2 as structural components were successfully synthesized by two-step and dual-template methods in a comparative study. The as-synthesized Ti-HMS/KIL-2 samples were characterized by a series of techniques including X-ray diffraction, UV–vis, N_2 sorption and scanning electronic microscopy, and their performance was tested in adsorptive denitrogenation for model fuel containing pyridine or quinoline. Although Ti-HMS/KIL-2 composites were constructed following the different pathway of self-assembly, most of them obtained coexisting properties and structures of Ti-HMS and Ti-KIL-2, as well as the intact framework Ti in tetrahedral coordination. A key finding is that the mesopores size of Ti-KIL-2 component in the composite can be regulated via the introduction of Ti-HMS precursor or organic template dodecylamine. Especially, the composites of dual-template method presented hierarchical mesopores with obvious bimodal distribution. In addition to constructing the hierarchical structure, introduction of Ti-HMS into Ti-KIL-2 matrix improved the adsorptive denitrogenation performance, which was influenced by the synthetic strategy of Ti-HMS/KIL-2. The target adsorbates achieved the best match with the adjustable pores of Ti-HMS/KIL-2. Therefore, (0.6^D)Ti-HMS/KIL-2 and (0.5^T)Ti-HMS/KIL-2 as the optimized adsorbents obtained remarkable adsorption efficiency respectively for pyridine and quinoline. Essence of the adsorptive denitrogenation process was revealed via the adsorption isotherms and the adsorption

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thermodynamics. Finally, Ti-HMS/KIL-2 composites achieved the improvement in hydrothermal stability and recyclability during adsorption of pyridine and quinoline, and exhibited the potential of industrial application.

1. Introduction

Sulfur-containing compounds (SCCs), along with nitrogen-containing compounds (NCCs), are the most serious contaminants in fossil fuels that should be removed before utilization [1–7]. Currently, denitrogenation of fuels is receiving increasing attention in the worldwide research community because of the increase in stringent regulations and fuel specifications in many countries. NCCs bring the problems of process operation and process development for oil upgrading and refining, as well as harms in health and environment. In some cases, the presence of NCCs may require on-purpose pretreatment steps and even specialized process workarounds [7]. It is well know that denitrogenation is usually more difficult than desulfurization because most of the organonitrogen compounds are much less reactive than the organosulfur compounds [8,9]. Hydrodenitrogenation (HDN) has always been regarded as one of the most effective and dominant techniques for removal of NCCs from fuels [10–13]. However, HDN techniques have many limitations and problems. For instance, the process requires hydrogen, high temperature and high pressure, which increases the industrial cost. In addition, compared with hydrodesulfurization, HDN is a kinetically slow multistep process because hydrogenation of N containing heterocyclic rings is required [11,14]. Alternatively, the processes of adsorption [15–19], oxidation [20–22], acid extraction [5,11,23,24] and photocatalysis [25,26] have been proposed for deep denitrogenation. Among the reported methods, adsorptive denitrogenation (ADN) by simply using a solid material as an adsorbent arouses economic interest and has been intensively studied. Reported adsorbents include metal oxides [6,27,28], molecular sieves [4,17,29–31], metal organic frameworks [14,18,32–36] and carbon materials [19,37,38]. For a long time, many studies focused on developing novel materials with excellent adsorption efficiency and high stability for industrial application of ADN. Among those materials, mesoporous molecular sieves have always been regarded as a type of ideal adsorbent for ADN process. In the previous studies, titanosilicate such as Ti-HMS provided the acid sites by its framework tetracoordination Ti species (Ti^{4+}) for ADN. In fact, the acidity of such materials is related to the presence of isolated silanol groups (Si–OH) and acid groups (Ti–OH and Ti–O–Si–OH) [39], which enhance the acid-base interaction during adsorption. Ti-HMS could remove more than 90% of the NCCs including quinoline, indole, pyrrole and pyridine from diesel, where the adsorption process was spontaneous and exothermic. [17,29].

During the last few decades, mesoporous silicates with uniform channel and high specific surface area have been of interests as green catalyst supports or adsorbents. However, reactant and product diffusion limitations, which are inherited from the confining porous nature of some molecular sieves, substantially restrict the catalytic or adsorptive performance [40–42]. Introducing larger pores into the intrinsic structure of porous silicate is able to solve the aforementioned problem [43,44]. Compositive pores give molecular sieves a new dimension that shortens the overall required diffusion length [45,46]. Therefore, faster diffusion and more accessible active sites are made available. Moreover, by facilitating product diffusion and transport, introduced pores make the molecular sieves less susceptible to deactivation [45–47]. Many approaches have been developed to synthesis hierarchical porous silicates, including destructive approaches such as demetalation [48] and recrystallization [49]; and constructive approaches such as using kinetic regulation [40], hard templates [50,51], supramolecular templates [43,52], and surface silanization [53]. Despite these elegant achievements, more convenient and effective routes for synthesis of hierarchical porous silicates are still expected to be developed. Constructing hierarchical porous molecular sieves by recombination and multi-templating have long been two frequently-used approaches because of their simplicity and potential industrial viability [54–57]. The recombination idea mainly follows two steps including the synthesis of matrical mesoporous silicas with major structure, and the in situ assembly of zeolite nanoclusters with primary and secondary building units. As a result, the final products are often regarded as the composites with two kinds of textural structure. However, this method is only applicable to those mesoporous materials with thicker pore walls and it is inevitable that the intrinsic mesostructure of the substrate is destroyed to a certain extent [55]. The multi-templating idea, which accomplishes synchronous assembly of molecular sieves precursor around the mixed micellar templates, is more convenient and effective to fabricate hierarchical porous materials of homogeneous phase.

KIL-2 (KIL = Kemijski Inštitut Ljubljana) with the interparticle mesoporosity is classified as a new family of mesoporous silicates including HMS, MSU and NBS et al. [58,59]. The larger and adjustable pore size distribution of KIL-2 gives a new opportunity for the preparation of highly active catalysts or adsorbents [60,61]. In addition, it has been reported that KIL-2 exhibited high hydrothermal stability in applications [59]. By comparison, HMS as a type of conventional mesoporous silicate frequently faces a serious problem of its weak hydrothermal stability. So far, there is no report on the synthesis and application of a HMS/KIL-2 composite, or a silicate with coexistence of HMS and KIL-2 porous structures. Successful construction of bimodal mesoporous Ti-HMS/KIL-2 silicate makes the structure more diffusive and adsorptive for target molecules of various sizes in applications. In addition, the stability and the hydrothermal stability of the grafted HMS component are expected to be improved by the strong immobilization of KIL-2 matrix.

In the present work, novel silicate materials of Ti-HMS/KIL-2 with hierarchical mesoporous structure were successfully synthesized via two approaches including a two-step and a dual-template method. The as-synthesized molecular sieves were expected to present the bimodal mesopore size distributions of Ti-HMS and KIL-2, respectively. A two-step synthesis of Ti-HMS/KIL-2 composite followed the in situ introduction of as-synthesized Ti-HMS precursor into the crystallization process of Ti-KIL-2. The untreated organic template in Ti-HMS precursor provided adequate support for the framework to avoid its collapse during the hydrothermal synthesis of KIL-2. Finally, the porous morphology of HMS was constructed in KIL-2 crystals to improve its surface and pores structure. A dual-template method is more convenient to synthesize more homogeneous molecular sieves composite than the two-step method. In the procedure, dodecylamine and triethanolamine synchronously generated two types of liquid crystal template, around which the titanosilicate sources achieved the S^0I^0 self-assembly [59,62]. After a room temperature crystallization and hydrothermal process, the final product