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Dehydration of methanol to dimethyl ether over modified vermiculites

La déshydratation du méthanol en diméthyléther avec des vermiculites modifiées

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ABSTRACT

Vermiculite materials pillared with alumina and modified with titanium were tested as catalysts for methanol dehydration to dimethyl ether. The different samples were characterized by powder XRD, TG, nitrogen adsorption, and pyridine adsorption followed by FTIR. Catalytic activity was evaluated in the temperature range 250–450 °C using different hourly space velocities, in the absence and in the presence of water in the feed. Modified vermiculites were shown to be active and selective in methanol dehydration. Al pillaring was found to result in more active catalysts than in the case of the modification with TiO_2. The influence of methanol hourly space velocity did not have a significant effect on methanol conversion, but it changed drastically selectivity to dimethyl ether at the beginning of the reaction. The addition of water had a negative effect on the catalysts' activity and led to a faster catalyst deactivation.

RÉSUMÉ

Les vermiculites à piliers d'alumine et modifiées avec du titane ont été testées comme catalyseurs pour la déshydratation du méthanol en diméthyléther. Les différents échantillons ont été caractérisés par diffraction des rayons X (DRX), TG, FTIR de la pyridine adsorbée et par adsorption d'azote à basse température. Les vermiculites modifiées se sont avérées être actives et sélectives dans la déshydratation du méthanol à 450 °C. De plus, l'influence de la vitesse spatiale horaire et de l'addition d'eau sur l'activité et la distribution des produits a également été étudiée. Cette dernière n'a pas eu d'effet significatif sur la conversion du méthanol, mais elle change considérablement la sélectivité en diméthyléther au début de la réaction. L'addition d'eau, quant à elle, a eu un effet négatif sur l'activité des catalyseurs.

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1. Introduction

During the last decades, more and more attention has been paid to the problems concerning energy, such as depletion of fossil fuels, pollution of the environment, and energy security. The generally accepted conclusion is that new alternative energy sources are needed. One of the chemicals that could be considered as the fuel of 21st century is dimethyl ether (DME). DME has several advantages as a fuel or an energy carrier [1]. It can be used as a diesel substitute in engines currently produced [2,3]. DME combustion results in exhaust gas containing lower amounts of NO_x, SO_x and soot than conventional fuels. DME can be also used as a LPG-substitute fuel for heating and cooking. Thus, as an alternative fuel, the application of DME can address several problems connected with energy: security, conservation and accessibility, as well as environmental concerns [1].

DME can be produced by dehydration of methanol using solid acid catalysts following the exothermic reaction (Eq. 1) [4,5]:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad \Delta H_R{}^0 = -23,41\ \text{kJ/mol} \tag{1}$$

This reaction is generally accepted as the initial stage of the methanol-to-olefins and methanol-to-gasoline processes. The acidity of the catalysts influences the distribution of the obtained products. Over the catalysts with strong acidic sites beside the formation of DME, the simultaneous formation of hydrocarbons as byproducts and subsequent coke formation was observed [5]. Accordingly, catalysts with moderate or weak acid sites are desirable for methanol dehydration at relatively low temperature [6]. Several materials have been tested as catalysts for this reaction [5]. Among the studied catalysts are:

- zeolite-like materials (H-ZSM-5, H-[F]-ZSM-5, H-Y, $AlPO_4$ [7], SAPO-5 [8]);
- and oxides (mesoporous silica [9], TiO_2–ZrO_2 [10], γ-alumina, aluminosilicates, silica-titania and alumina-titania [6,11–13]).

The selected catalysts for methanol dehydration to DME and also their catalytic performance are presented in Table 1. The synthesis of DME from methanol over γ-alumina and silica-titania catalysts at 300 °C was studied by Yaripour *et al.* [11]. In general, silica-titania turned out to be not suitable for DME formation. On the other hand, both γ-alumina samples (commercial and prepared) showed similar catalytic performance and were selective and active for methanol dehydration. Yaripour *et al.* [6] also compared the catalytic performance of γ-Al_2O_3 to that of the aluminosilicates with different contents of silica at 300 °C. The catalytic performance of aluminosilicates depended on the silica content. All of the studied catalysts turned out to be active. Laugel *et al.* [8] studied synthesized zeolites (H-ZSM-5, H-[F]ZSM-5) with different textural properties and compared them to commercial catalysts (H-Y, SAPO-5 and γ-alumina). Zeolites having different structures exhibited different catalytic performances at 275 °C. The H-ZSM-5 catalyst showed high methanol conversion equal to 73%, while the conversion for samples H-Y and SAPO-5 was only 39 and 8%, respectively.

Lertjiamratn *et al.* [7] investigated $AlPO_4$ as methanol dehydration catalyst at 300 °C. The main goal of their studies was to find the influence of a 10% water pretreatment on the catalytic performance. The investigations showed that the pretreatment with water at 200–300 °C improved the catalytic performance of $AlPO_4$. This might be due to an increase in the acid strength and acidity of the catalyst.

Khaleel [13] examined the performance of a titanium-doped alumina catalyst prepared by sol-gel method in the 180–300 °C temperature range. The study showed that the addition of 3–5 wt.% of titania to alumina had a positive effect on both the activity of the catalyst and its selectivity to DME. The author explained the enhanced catalytic performance by an increase in the acidity of the titania–alumina samples due to the introduction of titanium atoms into the alumina lattice. The positive effect of titania addition into heteropolyacids in DME production via methanol dehydration was also observed by Ladera *et al.* [14].

In this work, the catalytic performances of different modified vermiculites were studied. Vermiculite belongs to clay minerals. It is a hydrated phyllosilicate with a 2:1 layer type structure [15]. This material found various applications in a number of fields. The most interesting ones for the chemical industry concern the use of vermiculite as an adsorbent, a catalyst or a catalyst support. Especially modified vermiculite is a promising material when it comes to catalysis. Chemical and thermal modifications, such as acid treatment or clays pillaring, improve the catalytic properties of the final materials. Acid-treated vermiculite demonstrated to be an efficient acid catalyst in reactions, such as dehydration of 1-butanol and dealkylation of cumene [16,17]. On the other hand, Al-pillared vermiculite showed catalytic activity in reactions, such as hydroisomerisation of *n*-octane, selective reduction of NO by ammonia or hydroconversion of decane [16,18].

There are only a few reports that described mineral clays as catalysts for methanol dehydration. Sun Kou *et al.* [19] studied the catalytic activity of Zr-pillared betonites with or without the addition of an active component (Cu). The best methanol conversion obtained was ca. 80% with DME and hydrocarbons from C_1 to C_5 as the main products. Hoshimoto *et al.* [20] studied an Al-pillared montmorillonite that gave 20, 33 and 35% methanol conversion at 260, 300 and 340 °C, respectively, with 100% selectivity to DME. Montmorillonites were also investigated by Mishra and Parida [21]. An acid-activated vermiculite was studied by Ravichandran *et al.* [17]. They obtained olefins as the main product, but unfortunately the formation of DME was not discussed.

The main goal of this work was to study vermiculite-based catalysts in the reaction of methanol dehydration to DME. The application of such a material can be beneficial since vermiculite is a relatively cheap mineral. Additionally, its catalytic properties can be tailored by chemical and thermal modifications. Since there is no report on using