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Role of dehydration catalyst acid properties on one-step DME synthesis over physical mixtures

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Abstract

The direct synthesis of dimethyl ether (DME) was studied in a continuous high-pressure unit composed basically of a Berty reactor and online gas chromatograph. A commercial methanol synthesis catalyst and some solid-acid catalysts (alumina, HZSM-5, tungsten–zirconia and sulfated-zirconia) were used as physical mixtures. The dehydration catalysts were characterised by pyridine adsorption followed by IR spectroscopy and tested in the methanol dehydration reaction itself. All samples were active regardless of the differences in their acidity and a relationship between catalytic activity for methanol-to-DME and acidity could be envisaged; the activity of a solid acid on this reaction was found to be determined mainly by the number of its more acidic sites. On the one-step DME synthesis from syngas the addition of an acid catalyst to the catalytic system strongly shifted the methanol synthesis reaction, increasing significantly the pass conversion of CO. As a general rule, it could be concluded that the determining rate of DME direct synthesis is determined by the acid properties of the dehydrating catalyst, i.e., its acid strength and number of acid sites.

Keywords: Dimethyl ether; Methanol; Natural gas; Synthesis gas; Solid-acid catalysts

1. Introduction

Dimethyl ether (DME) is considered the fuel for 21st Century. It can be applied in diesel trucks, for power generation, in fuel cells and also replacing LPG as cooking gas. This last application is an important alternative for developing countries, like China, India and Brazil that need portable fuel (bottled) for people who live far from the facilities of the big cities [1,2]. It is also worth stressing that DME is a clean fuel, as it is non-toxic and burns without particulate emission.

DME can be synthesized from natural gas, coal and also from agriculture residues. Two processes have been claimed so far; the first uses traditional methanol synthesis followed by a dehydration step. The second needs a catalyst or a mixture of catalysts capable of producing methanol and ether from synthesis gas in the same reactor. The latter approach is thermodynamically more favorable, being also an opportunity for the development of new processes [3,4].

Some research groups [5–7] tried to prepare bifunctional catalyst by getting together both dehydration and hydrogenation sites in the same catalyst. Considering that the best methanol catalyst is obtained through a hydrotalcite precursor, the association of this kind of structure with dehydration catalysts based on porous acid materials is not straightforward. Different preparation procedures have thus been evaluated in the literature. The best results were obtained with coprecipitation-deposition synthesis [7]. Basically, this procedure consists of adding a suspension of alumina or zeolites to another one containing the hydrotalcite precursor previously prepared by coprecipitation. Indeed, this catalyst could be considered as a mixture of $Cu/ZnO/Al_2O_3$ and alumina or zeolites small particles.

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Some patents reports high DME yields using physical mixtures of the classical methanol catalyst and alumina or zeolites [8]. They mostly deal with activity and selectivity aspects given no reference about the catalysts features that should be considered essential to the synthesis. Likewise, there is only a few information in the scientific literature concerning the behavior of such systems as they have so far been focused on different approaches to obtain a bifunctional system. However, it should be mentioned that the role of both hydrogenation and dehydration sites on determining the overall reaction rate has been rarely considered to design a suitable catalyst. Therefore, the aim of this work is to compare the activity and selectivity of different physical mixtures, prepared with commercially available catalysts, in an attempt to identify the role of the catalyst acid properties for the direct synthesis of DME.

2. Experimental

Several physical mixtures composed of a methanol synthesis catalyst (ACZ) and some solid-acid catalysts were investigated. Only commercially available materials were taken and ACZ/acid catalyst ratio of one was kept constant in all experiments. Two different aluminas, a porous (Al_2O_3-C) and a non-porous (Al_2O_3-D), were used. The Al_2O_3-D was supplied by Degussa; Al_2O_3-C and a HZSM-5 sample (SAR = 40) were provided by Petrobras. Two zirconia-based powders were also studied, basically a sulfated-zirconia (S–ZrO_2) and a tungsten–zirconia (W/ZrO_2), both supplied by MEL Chemicals. The specific surface areas of all solid-acid samples used are listed in Table 1.

Pyridine thermodesorption experiments followed by IR spectroscopy were conducted to probe the acid–base properties of the dehydration catalysts using a Nicolet Magna spectrophotometer. The spectra were recorded from thin (20 mg) self-supporting wafers. The samples were pre-treated at 500 °C for 1 h under vacuum, submitted to a stream of air for 30 min and finally exposed to high vacuum for 30 min (10^{-7} Torr). Pyridine was adsorbed at room temperature, at 10 Torr for 1 h. Spectra were collected after desorption at 25, 150, 250 and 350 °C for 1 h under high vacuum.

The bare acid-solid samples were firstly tested in the methanol dehydration reaction, which were performed in a conventional system with flow micro-reactor, monitored by on-line gas chromatography, with flame ionization detector (FID). The solid-acid catalysts were pre-treated at 500 °C during 1 h under air at 30 mL min^{-1}. After, they were purged with nitrogen and cooled up to 200 °C, temperature at which methanol was admitted to the reactor. The reaction proceeded under a methanol partial pressure of 14.4 kPa, which was introduced to the system through a saturator, using N_2 flux (30 mL min^{-1}). The catalysts samples mass varied in order to guarantee differential condition, allowing to calculate the methanol dehydration reaction rate [9].

Table 1
Specific surface area and catalytic activity in methanol dehydration of the solid-acid catalysts

Samples	S_{BET} ($m^2 g^{-1}$)	r_{MetOH} (μmol $s^{-1} g^{-1}$)	r_{MetOH} (μmol $s^{-1} m^{-2}$)
Al_2O_3-D	110	6.82	0.062
Al_2O_3-C	210	10.50	0.050
S–ZrO_2	143	19.31	0.135
W/ZrO_2	94	7.33	0.078
ZSM-5	341	89.34	0.262

The DME direct synthesis was carried over the physical mixtures composed of the methanol synthesis catalyst and the dehydration solid in a continuous unit composed basically of a Berty reactor (Autoclave Engineers, 50 mL of total volume) and a gas chromatograph connected in line (Varian CP-3800), equipped with both a thermal conductivity detector (TCD) and a FID.

The Berty reactor is an internal recycle gradientless reactor, equipped with a fixed basket to hold the catalyst and with a fan over the basket. The reactor was equipped with temperature control and pressure indication.

The feed gas flow was controlled by a mass flow meter (Brooks). The output stream and the reactor pressure were controlled by a micrometric valve. The effluent was then analyzed by gas chromatography. In order to prevent methanol and water condensation, the line between the reactor and the chromatograph injection valve, including the micrometric valve, was electric heated and kept at around 100 °C during the tests.

The catalysts physical mixture was reduced under H_2/He flow (5% H_2, 30 mL min^{-1}), for 1 h at 250 °C. After reduction, the gas was changed for synthesis gas (H_2/CO = 1) and the reaction conditions (24 mL min^{-1}, 250 °C, 5 MPa) were adjusted. For the conditions used in this work, the steady state was achieved after 4 or 5 h of reaction.

Additional tests were carried out with different ACZ and HZSM-5 physical mixtures; basically distinct ACZ/HZSM-5 ratios, ranging from one to four, were evaluated.

The catalysts activities were evaluated based on the overall reaction rate and the products selectivities were calculated at the same CO conversion level, around 10%.

3. Results and discussion

3.1. Acid properties of the dehydration catalysts

The FTIR spectra of pyridine adsorbed on the solid-acid catalysts is depicted in Fig. 1. The absorption bands at 1450 cm^{-1} (ν19b), 1490 cm^{-1} (ν19a), 1575 cm^{-1} (ν8b), 1595 cm^{-1}, 1613 cm^{-1} (ν8a) and a shoulder at 1620 cm^{-1} presented in Fig. 1(A) are typically observed over alumina samples and are indicative of their Lewis acid sites [9,10]. On the other hand, the spectra shown in Fig. 1(B) are more complex exhibiting bands assigned to pyridine coordinated