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The effect of FER zeolite acid sites in methanol-to-dimethyl-ether catalytic dehydration

Q2 Enrico Catizzone, Alfredo Aloise, Massimo Migliori*, Girolamo Giordano

Department of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci Cubo 42a, I-87036 Rende (CS), Italy

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ABSTRACT

In this paper, the effect of acidity of zeolites with FER framework was studied in the methanol dehydration to dimethyl ether reaction, by comparing catalysts with different Si/Al ratio (namely 8, 30 and 60). The aim of this work was to investigate how the acid sites concentration, strength, distribution and typology (Brønsted and Lewis) affect methanol conversion, DME selectivity and coke formation. It was found that the aluminium content affects slightly acid sites strength whilst a relevant effect on acid sites concentration and distribution (Brønsted /Lewis) was observed as 24% of Lewis sites were found on Al-richest samples, whilst less than 10% of Lewis acid sites were observed on FER at higher Si/Al ratio. All the investigated catalyst samples showed a selectivity toward DME always greater than 0.9 and samples with the lowest Si/Al exhibits the best performances in terms of methanol conversion, approaching the theoretical equilibrium value (around 0.85) at temperature below 200 °C. Turnover-frequency analysis suggests that this result seems to be related not only to the higher amount of acid sites but also that the presence of Lewis acid sites may play a significant role in converting methanol. On the other hand, the presence of Lewis acid sites, combined with a high acidity, promotes the formation of by-products (mainly methane) and coke deposition during the reaction. As final evidence, all the investigated catalysts exhibit very high resistance to deactivation by coke deposition, over 60 h continuous test, and a GC–MS analysis of the coke deposited on the catalyst surface reveals tetra-methyl benzene as main component.

1. Introduction

Dimethyl ether (DME) has represented a reliable alternative fuel for Diesel engines since decades and, more recently, this compound is receiving a renewed attention also as intermediate for olefins production [1–6]. Together with many other technologies this application can contribute to reduce the CO_2 footprint, mitigating the environmental impact of fossil fuels [7–9]. Apart from classic liquid phase production process via methanol dehydration [10–12], new promising direct gas-phase routes have been proposed, starting from either syngas mixture or via-carbon dioxide hydrogenation [13–15].

Whatever the route, the acid-catalysed step of methanol dehydration:

$$2CH_3OH=CH_3OCH_3+H_2O \quad \Delta H^\circ=-23.54\ \text{kJ/mol}$$

plays a key role in catalyst durability, DME productivity and production costs. Therefore, in view of economically sustainable large-scale gas-phase DME production, low temperature activity, performances and stability are essential factors to consider when developing a reliable catalyst for this step. γ-Al_2O_3 traditionally plays acid function for direct conversion of methanol to dimethyl ether, but it was also considered as first option co-catalyst for the direct route from syngas coupled with redox catalyst (e.g. $Cu/ZnO/Al_2O_3$), promoting the alcohol formation via-CO/CO_2 hydrogenation. At reaction temperature traditionally adopted for both direct and indirect routes for (up to 300 °C), γ-Al_2O_3 offers high selectivity towards DME and, due its low acidity, it also inhibits olefins formation [16–18]. Despite this unchallengeable advantage, this catalyst requires relatively high temperatures and it is rapidly deactivated by strong water adsorption as demonstrated by several studies [10,19–24]. As already mentioned some interesting studies were recently carried out on the gas phase process, replacing CO with CO_2 during direct route, adding more value to DME as “green chemical” because of the CO_2 footprint reduction [25–27]. In this process, the revers water gas shift reaction significantly increases the amount of produced water and a stable acid function is even more necessary to prevent acid sites deactivation by water adsorption. In this concern, zeolites (manly MFI) were proposed as alternative catalyst to γ-Al_2O_3, exhibiting both higher activity (even at

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Q3 * Corresponding author.
E-mail address: migliori@unical.it (M. Migliori).

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low reaction temperature) and higher resistance to water adsorption in both direct and indirect DME routes [28–31]. Specific attention was paid to the control of acid properties, in the view of maximising the DME yield [32–34]. In fact, methanol can be easily converted into different hydrocarbons (Methanol-To-Hydrocarbons - MTH), such as in the well-known UOP-Norsk Hydro process, producing olefins using SAPO-34 as catalyst [35] and DME is usually an intermediate also in the case of alternative technologies [36–40]. Different zeolites structures (MFI, BEA, CHA, TON) are well-known catalysts for MTH since textural properties of zeolites might significantly address the catalytic activity [41–43]. Therefore both acidity and structure of these microporous crystalline solids need be carefully tuned in order to mitigate or inhibit undesired hydrocarbon formation, maximising the DME yield. Recently, different zeolites have been tested to convert methanol in DME and it has been shown that, due to its high shape-selectivity, FER structure (2-dimensional, 8×10 MR) is an effective catalyst this reaction because FER exhibiting high selectivity and resistance to coke formation, compared with other zeolite structures [44,45]. Also in direct gas-phase route (mainly via-CO_2 hydrogenation), FER type zeolite was confirmed as reliable candidate for the acid functionality, whatever it is the hybrid catalyst preparation method [45,46]. Moreover, also acid sites concentration and strength are parameters to be tuned when adopting zeolites as catalysts in this reaction. Several studies report investigations over MFI zeolites with different acid sites concentration (e.g. different Si/Al ratio), showing that acidity affects strongly catalyst performances and suggesting catalysts with low acidity as suitable for high-selective DME production [47–49]. In addition, it was also demonstrated that strength, type and location of acid sites significantly affect products distribution [50].

Referring to FER zeolite, despite encouraging catalytic performances, the literature does not fully cover the effect of acid sites concentration, type and strength on catalytic performances of this structure on DME synthesis. In this concern, this work presents results of catalytic performances of FER structure at different aluminium content obtained by varying the Si/Al ratio during the hydrothermal synthesis. Zeolites with different amount, distribution and typology (Brønsted/Lewis) of acid sites were characterised via NH_3-TPD and FT-IR measurements. Furthermore, the effect of acid properties on catalytic performances was investigated during methanol dehydration reaction step in a temperature range 160–280 °C. A quanti/qualitative analysis of coke deposited on catalyst surface was also carried out by thermo-gravimetric measurements and GC–MS technique, in order to study also the effect of acidity on carbon deposit composition and formation mechanism.

2. Experimental

2.1. Catalyst synthesis

Zeolite catalysts with FER structure and different Si/Al ratio in the gel (8, 30 and 60) were synthesised in hydrothermal condition by starting from an alkaline synthesis gel. Sample with Si/Al = 8 (FER8) was synthesised by adopting the procedure suggested by Chen et al. [51]. Sample with Si/Al = 30 (FER30) was synthesised by following the procedure suggested by Kamimura et al. [52], using pyridine as structure directing agent. Synthesis of sample with Si/Al= 60 (FER60) was performed by slightly modifying the gel composition and procedure reported for the synthesis of FER zeolite with a Si/Al = 75 [52]. In order to guarantee a Si/Al = 60 ratio in the starting gel, the composition was established as it follows:

$$0.0575\ Na_2O - 2\ \text{pyridine} - 0.0083\ Al_2O_3 - 1\ SiO_2 - 25\ H_2O$$

The crystallization was carried out in a PTFE-lined stainless steel autoclaves at 165 °C for 96 h in tumbling conditions (20 rpm).

The following chemicals were used for the synthesis of investigated materials: for synthesis of FER8, colloidal silica Ludox AS-40 (SiO_2, 40% suspension in H_2O, Aldrich) and pyrrolidine (99%, Aldrich) were used as silica source and template, respectively, whilst for synthesis of samples FER30 and FER60, silica fumed (surface area $200 \pm 25\ m^2/g$, Aldrich) and pyridine (VWR, AnalaR NORMAPUR) were adopted. In all the proposed syntheses, sodium aluminate (Al_2O_3: 50–56%, Na_2O: 40–45%, Aldrich) and sodium hydroxide (ACS reagent, $\geq$ 99% pellets, Aldrich) were used as aluminium and alkali sources, respectively. After crystallization, the solid phase was recovered by filtration, washed with distilled water and dried at 105 °C for 8 h. After removing of organic template from the structure by calcination in airflow ($20\ mL\ min^{-1}$) at 550 °C, the acid active forms were obtained by ion-exchange with ammonium chloride solution followed by a secondary calcination [48].

2.2. Catalyst characterization

X-ray powder diffraction spectroscopy (APD 2000 Pro) and scanning electron microscopy (FEI model Inspect) were respectively used to evaluate crystallinity and morphology of obtained phases, whilst the Si/Al ratio in the solid was measured by atomic absorption (GBC 932 AA). The BET area and the *t*-plot micropores volume were calculated from porosimetry data (ASAP 2020 Micromeritics) under nitrogen adsorption at −196 °C, after a pre-treatment in vacuum at 200 °C for 12 h.

Acid sites concentration was measured by NH_3 -TPD analysis (TPDRO1100, ThermoFisher) [45]. The analysis of the acid sites strength was carried out by evaluating the ammonia desorption-heat ($Q_{des,NH3}$) evaluated by carrying out test of ammonia desorption at different temperature ramp (r) taking into account the shift of the temperature peaks (T_M) during desorption. By plotting $\ln(T_M{}^2/r)$ versus $1/T_M$ a linear correlation is usually obtained and the calculated slope can be related to the ammonia desorption energy [53]. The higher is the value of $Q_{des,NH3}$ for any peak, the stronger are the acid sites. In this work, thermal ramps of $10\ °C\ min^{-1}$, $20\ °C\ min^{-1}$ and $30\ °C\ min^{-1}$ have been adopted to perform the desorption-heat analysis.

Brønsted and Lewis acid sites concentration was estimated via FT-IR analysis, by using D_3-acetonitrile as probe molecule. Infrared spectra were recorded with a Bruker Equinox 55 spectrometer. The adsorption of D_3-acetonitrile was performed at room temperature with a pressure of 10 Torr, thereafter samples were degased under high vacuum condition (cell pressure: 10^{-6} Torr) at 300 °C for 4 h, in order to purge adsorbed water. Physisorbed acetonitrile was removed by further degassing until the vacuum condition was recovered. The amount of D_3-acetontrile adsorbed on Brønsted and Lewis was determined by using a molar absorption coefficient from the literature [54]. The number of Brønsted sites was calculated from the integrated area of the bands observed at $2297\ cm^{-1}$ by adopting an extinction coefficient of 2.05 cm/μmol, whilst the number of Lewis acid sites was calculated by integrated area of the bands between 2310 and $2325\ cm^{-1}$ by adopting an extinction factor of 3.6 cm/μmol. Peaks analysis and deconvolution for either NH_3-TPD or FT-IR profiles were performed by using a commercial software (PeakFit 4.12, Seasolve – USA).

2.3. Catalytic tests

Catalytic tests were performed using an experimental apparatus described elsewhere [45,55]. A mixture of methanol (0.06 mol/mol) and nitrogen as a carrier ($60\ Nml\ min^{-1}$) was fed in a quartz reactor where 70 mg of catalyst was loaded in pellets form

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