

Development of Sulfonic Supported Acids and Their Application in Power to Gas Systems

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Abstract—Dimethyl ether (DME) is an environmentally friendly fuel that is being widely considered as an alternative fuel to replace petroleum fuels. DME can be produced by dehydration reaction of methanol by using solid catalysts in catalytic reactions. This study shows the influence of catalyst's surface acidity on the catalytic activity in the dehydration of methanol to DME. In this work, the conversion of methanol to dimethyl ether has been investigated using a continuous flow fixed-bed reactor at temperatures between 60 °C and 350 °C and 1 bar. Sulfonated catalysts with $-\text{SO}_3\text{H}$ acid function were tested and compared with conventional catalysts as $\gamma\text{-Al}_2\text{O}_3$, SiO_2 , MCM-41 and fluoropolymer were used as inorganic and organic supports for sulfonic groups. The experimental results demonstrate a good catalytic activity for the functionalized MCM-41 and the fluoropolymeric material. Effects of H_2O on the activity and deactivation of these catalysts were also studied.

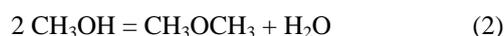
Index Terms—power to gas, methanol dehydration, dimethyl ether (DME), surface acidity, sulfonic supported acids

I. INTRODUCTION

Power to gas (P2G) is an established technology to store both renewable energy and peak-off energy production. This technology allows to store electrical energy as chemical energy. The key step in P2G process is the hydrogen production that realizes the conversion from electric energy to chemical energy. The subsequent conversion from hydrogen to carbon containing fuels corresponds to a degradation of energy due to the energetic and economic requests. The usual P2G pathway comprises water electrolysis followed by a carbon source hydrogen reduction. As carbon containing source, carbon dioxide is the most attractive raw material, so that the power to gas technology could give a contribution to the mitigation of greenhouse gas emissions. However, carbon capture technologies combined to fuels synthesis are expensive processes. In spite of that, the methanation reaction is a widely used way to treat CO_2 consuming hydrogen to form methane. The leading motivation for

such a process comes from biological production of biogas that contains large amounts of CO_2 , moreover public inducement to invest are provided in many country.

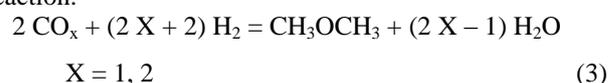
Besides methane, interesting alternative to use hydrogen and CO_2 is the synthesis of oxygenated chemicals. In particular methanol and dimethyl ether (DME) having chemical versatility, handiness and low environmental impact could be considered as alternative fuels [1]. The DME combustion evolves the less amount of air pollutants such as NO_x , SO_x and particulate matters, so that DME could be the best fuel to replace diesel [2]. Moreover DME is non-toxic, non-corrosive and easily liquefied and transportable. DME is obtained according the following two reactions:



High pressure needed for methanol synthesis (1) and copper/zinc based catalysts are used [3].

Methanol dehydration (2) is an exothermic reversible reaction that proceeds without mole number variation. For this reason, reaction pressure does not affect equilibrium conversion, while lower reaction temperatures have a thermodynamic benefit toward DME production. Methanol dehydration is an acid-catalyzed reaction and several investigations have been published with the aim to identify an active, selective and stable catalyst at relative low temperature for the above-mentioned thermodynamic advantages [4, 5]. Solid acid catalysts such as $\gamma\text{-Al}_2\text{O}_3$ and its variously modified forms, zeolites and ion exchange resins are the most common acid catalysts employed for this reaction.

Alternatively, DME can be synthesized directly from gaseous mixtures as syngas, in a single unit over a dual catalyst system comprising both methanol synthesis and dehydration functions [6] according to the following reaction:



The latter production route is thermodynamically and economically favored. Carbon oxides conversion to

methanol is highly limited by thermodynamic equilibrium and further conversion of methanol to DME during the direct DME synthesis shifts the equilibrium towards higher carbon conversion. A wide range of reactor design and catalysts has been employed [7]. Additionally, combining two reaction steps in a single unit opens up opportunities for process intensification and cost saving, while making the DME production less affected by price variations in the methanol market.

Development of novel catalysts for the production of DME from methanol having a higher activity, selectivity, and stability towards water is of great industrial interest. The most widely investigated and most interesting solid acid catalysts are alumina and zeolites. These materials also show some drawbacks such as rapid deactivation and hydrocarbon formation since ultimately lead to the deactivation of the catalysts. In this work, we report the use of a new class of acid catalysts that combines a high surface area inorganic support with the acidic properties of a sulfonic moieties fastened onto it.

II. EXPERIMENTAL

The non-functionalized catalysts: γ -Al₂O₃, SiO₂, MCM-41, Al-MCM 41 (Sigma Aldrich) were commercial ones and used as received. Functionalized catalysts were prepared using literature procedure [8] and details about their synthesis are reported elsewhere [9].

In the following Table I, physicochemical parameters of tested materials are summarized:

TABLE I. PHYSICOCHEMICAL PARAMETERS OF TESTED CATALYSTS

Catalyst	S _{BET} (m ² /g)	Bronsted Surface Acidity (meq H ⁺ /g)
SiO ₂	540	-
SiO ₂ -(CH ₂) ₃ -SO ₃ H	510	0.23
SiO ₂ -C ₆ H ₄ -SO ₃ H	445	0.65
MCM-41	1240	-
Al-MCM-41	940	-
MCM-41-(CH ₂) ₃ SO ₃ H	970	2.53
γ -Al ₂ O ₃	250	-

A schematic representation of the experimental apparatus for methanol dehydration is reported in the following Fig. 1.

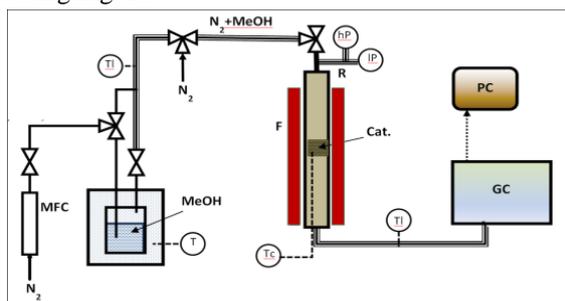


Figure 1. Schematic diagram of the experimental apparatus for catalytic production of DME from methanol: (MFC) Mass Flow Controller, (T) thermocouple, (lP) low-pressure manometer, (hP) high-pressure manometer, (R) reactor, (F) tubular furnace, (C) catalyst, (GC) gaschromatograph.

The catalyst was loaded in a tubular reactor whose temperature was varied between 60 °C and 350 °C and a flow of nitrogen saturated with methanol at 20 °C was fed to a continuous flow fixed-bed reactor (4 mm inside diameter and a total length of 500 mm) operating at 1 bar. The flow rate of nitrogen (10.7 sccm) was controlled using a MKS mass flow controller. The flow rate of gaseous methanol was 1.15 sccm. A thermocouple was positioned in the center of the catalyst bed in order to monitor the reaction temperature. To avoid possible condensation of water, methanol, DME or hydrocarbons, the inlet line and the effluent line were constantly maintained at temperatures above 100 °C. The products were analyzed online by Gas Chromatography using a Thermo TRACE 1300 equipped with a flame ionization detector (GC-FID) and a capillary column (Rt-U-BOND-30m RESTEK) to separate methanol, DME, and other possible reaction products as hydrocarbons and higher alcohols. Helium was used as a carrier gas.

The amount of DME in the outgoing mixture was measured by gas chromatography after calibration with standard DME/N₂ mixtures.

The MeOH to DME conversion yield, for each catalyst, was evaluated by direct measure of the amount of the DME product. The conversion yield (Y) was calculated as follows:

$$Y = 2 \text{ mol}_{\text{DME}} / (\text{mol}_{\text{MeOH}})^{\circ}$$

where mol_{DME} is the amount of DME product and (mol_{MeOH})[°] is the amount of initial MeOH.

III. RESULTS AND DISCUSSION

SiO₂ and MCM-41 can exhibit high surface area as shown in the Table I, but due to their low acidic properties the catalytic use of these materials result inhibit [10]. To increase the catalytic performances of MCM-41, metallic atoms, usually Al atoms, are introduced in the structure with the aim of enhancing its acidic character. Aluminum doped MCM-41 (Al-MCM-41) represents indeed a good solid catalyst in acid catalyzed reactions because its Lewis type acidity. As an alternative way to increase both the acidity and catalytic properties of such a material, a sulfonic group can be tethered onto its surface generating a sulfonated solid acid catalyst because their Bronsted type acidity.

Thermal analysis of prepared catalysts, with propyl- and phenyl- linker, shown a good stability up to 350 °C with a little weight loss (about 2 %) for both SiO₂ and MCM-41 sulfonated catalysts [9].

Methanol dehydration capability for SiO₂ and MCM-41 sulfonated catalysts was measured in the temperature range 60 °C – 350 °C at atmospheric pressure. In Fig. 2 the catalytic activity of SiO₂, MCM-41 and SiO₂-propyl-SO₃H, SiO₂-phenyl-SO₃H, Al-MCM-41 and MCM-41-propyl-SO₃H are reported. In the same figure, the catalytic activity of γ -Al₂O₃ is also reported as reference material:

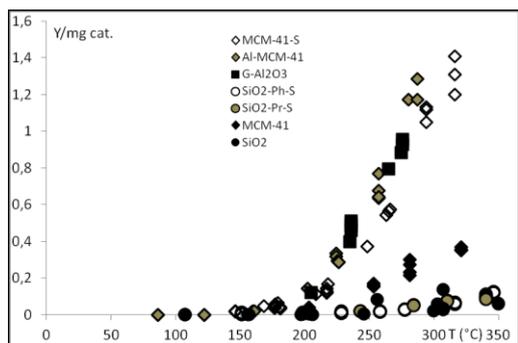


Figure 2. Conversion yield, normalized to catalyst weight, as a function of temperature for SiO_2 , SiO_2 - $(\text{CH}_2)_3$ - SO_3H , SiO_2 - $\text{C}_6\text{H}_4\text{SO}_3\text{H}$, MCM-41, Al-MCM-41, MCM-41- $(\text{CH}_2)_3$ - SO_3H and γ - Al_2O_3 .

As expected, silica both in amorphous and mesostructured form (MCM-41), shows low efficiency in methanol dehydration. Silica sulfonated behaves in similar manner with a little enhancement in catalytic activity for SiO_2 -phenyl- SO_3H at temperature above 300 °C. As can be seen in the Fig. 2, the aluminum doping of MCM-41 and the sulfonic functionalization of MCM-41 induce a formidable improvement in the catalytic performances. No significant differences are observed between Al-MCM-41 and MCM-41-propyl- SO_3H materials and both are comparable with γ - Al_2O_3 . The main differences between the two groups of materials can be found in the surface area values and in the surface acidity. As reported in the Table I, SiO_2 based catalysts suffer for a lower surface area respect to the MCM-41 based catalysts. Also the surface acidity of the SiO_2 catalysts is lower than that of MCM-41 catalysts variously activated. Therefore the introduction of sulfonic groups results in a simple and power way to increase the catalytic activity in poor inorganic materials able to undergo the sulfonic functionalization.

Sulfonic group supported on polymeric materials has been extensively used in methanol dehydration since 60's of the last century in form of sulfonated resins [11]. More recently sulfonated fluoropolymers was used for the same reaction. Fluoropolymers can claim high surface acidity even though the specific surface area is normally low. One of the most used fluoropolymer is the Nafion [12]. In the following Fig. 3 the conversion yield of DME in the function of temperature is reported for Nafion. This catalyst shows measurable activity at temperature as low as 90 °C and reach a conversion yield of 60 % at temperature of 130 °C.

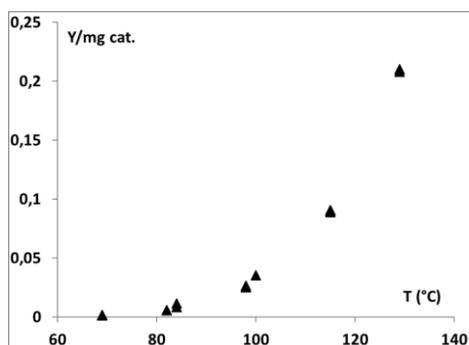


Figure 3. Conversion yield, normalized to catalyst weight, as a function of temperature for Nafion.

No deactivation in catalytic activity of Nafion catalyst was noted in 50 hours of operation at the temperature of 135 °C as shown in the Fig. 4, where the conversion yield normalized to its initial value is reported in the function of the time.

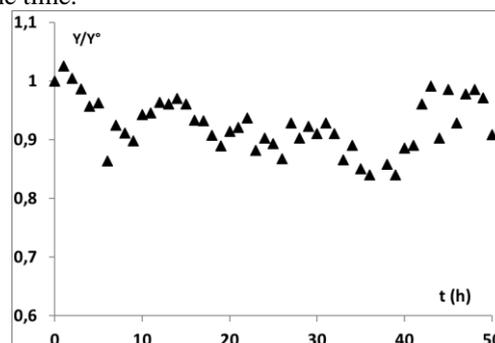


Figure 4. Relative conversion yield in the function of time for Nafion at 135 °C.

Good stability against age was registered also for the sulfonated inorganic catalysts (SiO_2 -propyl- SO_3H), no deactivation was observed for 480 minutes of operation at 280 °C for that catalyst.

Concerning the stability when water containing feed gas is used, preliminary results on a perfluoropolymer show a strong resistance to the water for 50 hours of operation at 137 °C when feed mixture was constituted by methanol and water (10 %). It is known that water acts as inhibitor due to the competitive adsorption on catalytic sites and γ -alumina suffers a deactivation on relatively short time [13]. On γ -alumina, we have measured a conversion yield decrease of about 20 % from its initial value in 30 hours of operation at the temperature of 232 °C.

IV. SUMMARY

A novel class of SO_3H -functionalized materials has been proposed as efficient catalysts to perform the methanol dehydration process. The acidity of both silica and MCM-41 surfaces has been increased through the tethering of sulfonic moieties such as propylsulfonic or phenylsulfonic ones. These materials were found to be active, selective and stable catalysts for methanol to DME transformation. The best performance was exhibited by MCM-41- $(\text{CH}_2)_3$ - SO_3H , whose superior activity can be related to its higher surface area and acidity. The inhibitory effect of water during MeOH to DME reaction over these sulfonated materials and perfluoropolymer has been investigated. Preliminary results reveal the superiority of perfluoropolymer in terms of water resistance respect to commercial γ -alumina that was strongly inhibited.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Rosanna Viscardi and Vincenzo Barbarossa conducted the experimental research, collected and analyzed the

data. Raimondo Maggi and Francesco Pancrazzi synthesized all materials tested in this work. All authors has approved the final version.

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Rosanna Viscardi was born in Nocera Inferiore (SA), Italy, in 1982. She obtained a BSc in Organic Chemistry in 2004 and a MSc in Physical and Analytical Chemistry in 2006 from the University of Salerno. In 2009 she completed her PhD thesis in electrochemistry at University of Salerno with a work developed in collaboration with ACTA S.p.A. From 2007 to 2012 she worked as Researcher at ACTA. Major research interests involved the synthesis and characterization of electrocatalysts for alkaline fuel cells and electrolyzers. Since 2012 she is a Researcher of ENEA at Casaccia Research Center. Her area of research interest is the development and understanding of new processes and technologies for the capture and conversion of carbon dioxide into fuels and chemicals.



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