



# Synthesis of formaldehyde from dimethyl ether on alumina-supported molybdenum oxide catalyst



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## ABSTRACT

The selective oxidation of DME to formaldehyde over alumina-supported  $\text{MoO}_x$  catalyst (prepared by dry impregnation) is studied in this work. The activity and stability of the catalyst were evaluated in a fixed-bed continuous reactor at different temperatures and reactant concentrations.

The influence of the main operating conditions, (DME,  $\text{O}_2$ ,  $\text{CO}_2$  and CO feed concentrations; reaction temperature) on reaction rate and product selectivity was experimentally determined. Thus, DME conversion decreases on increasing DME feed concentration and increases on increasing  $\text{O}_2$  feed concentration. Formaldehyde selectivity remained almost unaffected. A reaction mechanism, based on a Mars-van-Krevelen redox cycle representing DME oxidation to formaldehyde was used as a basis to develop a kinetic model for the reaction. The resulting simplified model suggests power law dependences for the reaction rate of 0.2 for the  $\text{O}_2$  and 0.5 for the DME.

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## 1. Introduction

The possibility of obtaining dimethyl ether (DME) from biomass with high yields has substantially increased the interest of this product as biofuel and a renewable chemical intermediate [1–4]. The process is based on the gasification of biomass into syngas, followed by syngas cleaning and its catalytic conversion into DME. In the traditional manufacture process of DME, the catalytic conversion of the syngas consists of two steps: the conversion to methanol and then the dehydration of methanol to DME [5].

Recent advances have shown that the direct synthesis of DME from syngas, where both reactions take place in the same reactor using bifunctional catalysts, is an attractive alternative. As an advantage, the thermodynamic limitations associated with the classical process are relaxed, leading to higher conversion and selectivity at lower pressure [1,6]. Thus, at the reaction conditions at which methanol synthesis process reaches only a 40% of CO conversion, DME synthesis from syngas can achieve more than 95% of CO conversion, with a high DME selectivity (67%) [7]. Therefore, DME production costs are largely lower, making this molecule into a competitive platform molecule.

Although DME can be used as alternative fuel, with limited soot formation when used in internal combustion engines [1,2], the syn-

thesis of chemicals from DME is a very promising pathway in the chemical industry.

At this point, formaldehyde is a major product obtained by partial oxidation of methanol [8,9] (more than half amount of global methanol is used to produce formaldehyde [10]). The possibility of producing formaldehyde from DME would be a promising alternative route. In addition, several new generation fuels and fuel additives, such as 1,1-dimethoxymethane and polyoxymethylene dimethylethers (POMMs), are synthesized from DME-formaldehyde mixtures [11].

A new alternative formaldehyde production method has emerged, after the new developments in the production of DME. Formaldehyde can be obtained by partial oxidation of DME over metal oxide catalysts. Several different catalysts have been proposed and tested for this reaction, but low reaction rates and selectivities have been reported. Mitsushima et al. proposed tungsten oxide (with or without additives) as catalyst, with a formaldehyde yield of 65–80%, although high temperatures, 673–773 K, are required [12]. Manganese nodules [13] are another material proposed in the literature for this reaction, but low formaldehyde yields were reported (<4%). The oxidation of DME over metallic silver catalysts yields a mixture of HCHO, alkanes, carbon oxides and water [14,15]. In addition, several authors suggest the use of mixtures of bismuth and molybdenum oxides with iron or copper oxides, or including with phosphorus and silicon [16,17]. These catalysts achieve values between 24 and 46% of conversion, with a formaldehyde selectivity of 14–45%, operating at

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high temperatures (673–773 K). Some of these catalysts have significant yields but temperatures that are high are required and the oxidation of formaldehyde to carbon oxides was frequently reported, so it is necessary to propose alternative catalysts.

Recent studies of this reaction have proposed catalysts based on Mo and V oxides [18,19]. It has been reported that MoO<sub>x</sub> and VO<sub>x</sub> supported on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and SnO<sub>2</sub> present a good balance between reactivity and accessibility of oxide surfaces. The use of these materials has many advantages over other reported catalysts, mainly higher reaction rate and formaldehyde selectivity, together with a lower reaction temperature. In this sense, according to the reported results, MoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> is the most selective catalyst [18].

These studies suggest that the reaction proceeds via redox cycles where DME dissociation was followed by an oxidation using lattice oxygen. This is based on the fact that methanol oxidation to formaldehyde occurs via Mars-van-Krevelen redox cycles with surface methoxy intermediates and these intermediates can also be generated via C–O bond cleavage of the DME molecule [20–22].

Detailed kinetic studies have been developed for this reaction using zirconia-supported MoO<sub>x</sub> catalysts [23]. For the alumina-supported MoO<sub>x</sub> catalyst, several published studies report the reaction orders for DME and O<sub>2</sub> partial pressures [24,25].

Although alumina supported molybdenum oxide catalysts presented the best behavior, there are several aspects that have not been considered, such as the influence of carbon oxides on catalyst performance (typical components on DME feedstock derived from syngas), or the development of a more detailed kinetic model for this reaction with a MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

The scope of this work is to fill these gaps providing the fundamental information necessary for design industrial processes for transforming DME into formaldehyde. To accomplish this goal, an alumina-supported MoO<sub>x</sub> catalyst was prepared, characterized and tested in a fixed-bed continuous reactor. First, the stability of the catalyst upon time was studied. Then, a kinetic study was conducted varying the most important operating conditions (concentration of DME, O<sub>2</sub>, CO and CO<sub>2</sub>, and temperature). The experimental data was used for proposing a simplified kinetic model inspired on the mechanism proposed for the reaction.

## 2. Materials and methods

### 2.1. Chemicals and reactants

The reactant mixture consisted of dimethyl ether, O<sub>2</sub>, CO, CO<sub>2</sub> and N<sub>2</sub> as balance gas. These reaction gases and chromatographic gases (He, H<sub>2</sub>, Air) were supplied by Air Liquide with purities higher than 99%, and used without further purification.

### 2.2. Preparation of the MoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst

The catalyst was supported on γ-Al<sub>2</sub>O<sub>3</sub> particles (BASF, surface area of 242 m<sup>2</sup> g<sup>-1</sup>), previously ground to 100–250 μm. The active phase was added by incipient wetness, using an aqueous solution of ammonium heptamolybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, 99% Fluka). The impregnated solid was dried at 373 K overnight and treated in an air flow at 775 K (10 K min<sup>-1</sup> until 775 K, holding for 3 h) [10,18].

### 2.3. Catalyst characterization

The textural characteristics of the fresh and used catalysts were determined by nitrogen physisorption at 77 K in a Micromeritics ASAP 2020 analyzer by the Brunauer–Emmett–Teller (BET) method for the specific surface area, and the Barrett–Joyner–Halenda (BJH) approach to determine the pore volume and diameter.

The total amount of Mo on alumina was measured by Inductively Coupled Plasma Mass Spectrometer, ICP-MS, with collision cell (HP 7700, Agilent Technologies), after the total digestion of the sample in *aqua regia*.

The morphology of the catalytic material was investigated by Scanning Electron Microscope (SEM). The analysis was conducted using a JEOL-6610LV SEM-EDX. The samples were deposited on a standard aluminum holder and gold-coated. The metal surface concentration was also determined by EDX analysis.

X-Ray Diffraction (XRD) tests were carried out in a Seifert XRD 3000 diffractometer, which is equipped with a temperature controlled chamber.

Used catalysts were analyzed by Temperature-Programmed Oxidation (TPO) using a Micromeritics TPD/TPR 2900 coupled to a Pfeiffer Vacuum Omnistar Quadrupole Mass Spectrometer (MS). The samples were exposed to an oxidant gas (2% vol. O<sub>2</sub>) while the temperature was increased (2.5 K min<sup>-1</sup>) from 293 K to 1273 K. The evolution of CO and CO<sub>2</sub> concentrations was monitored continuously by MS. Temperature-programmed reduction (TPR) was also performed in the same device to determine the oxidation states of the catalyst, before and after the reaction. In the case, the samples were exposed to a reducing gas (10% vol. H<sub>2</sub> in Ar). The Origin Pro 8 analysis program was used for the signal processing.

The surface composition and binding energy of Mo, Al and C in the oxides were measured by X-ray Photoelectron Spectroscopy (XPS), using a SPECS system equipped with a Hemispherical Phoibos detector operating in a constant pass energy (Mg Kα radiation,  $h\nu = 1253.6$  eV). During the deconvolution of the spectra, the full widths at half maximum of Mo3d<sub>3/2</sub> and Mo3d<sub>5/2</sub> were taken the same value, and the peak area ratio between both peaks was equal to 2:3. The full widths at half maximum of the C1s spectra for the different species were assumed to be equal, and this procedure was also applied for the O1s spectra.

### 2.4. Experimental device

Experiments were carried out in a continuous fixed-bed isothermal reactor. The reactor consisted of a stainless steel tube (9 mm diameter and 600 mm length) with the catalyst sample (2 g, 100–250 μm) placed inside. The catalyst was diluted with glass particles (6 g, 355–710 μm) in order to minimize temperature gradients within the catalyst bed. Temperature was measured by several thermocouples along the tube wall and one thermocouple placed inside the reactor tube. The latter was used to control the reactor temperature using a PID controller. The reactants were mixed at the desired proportions using different mass flow controllers (Bronkhorst High-Tech instruments).

The reactor effluent was maintained at 423 K using a heating tape to prevent formaldehyde condensation or oligomerization. On-line analysis of the reactor feed and effluent streams was carried out using a Gas Chromatograph (GC Agilent HP 6890N). It is equipped with a HP Plot Q capillary column for CO<sub>2</sub>, DME, methanol, water and formaldehyde analysis, and a HP MoleSieve 5A capillary column for CO, O<sub>2</sub> and N<sub>2</sub> determination. The HP MoleSieve 5A column is connected to a valve which allows its connection or isolation from the system, according to the required analysis. Both columns are connected to two detectors: thermal conductivity (TCD) and flame ionization detectors (FID). The temperature program of the analysis is the following: 70 °C for 4.5 min, then a ramp of 10 °C/min up to 160 °C and a second ramp of 20 °C/min up to 200 °C and hold 5 min; finally, cold down to 70 °C at 30 °C/min and hold 11 min.

### 2.5. Reaction experiments

The catalyst stability was studied by operating the reactor at constant pass conditions for long reaction times (typically more

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