



## Short communication

# N<sub>2</sub>O-assisted methanol selective oxidation to formaldehyde on cobalt oxide catalysts derived from layered double hydroxides

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## ABSTRACT

Cobalt-magnesium-aluminum oxides derived from layered double hydroxides were used as catalysts for the conversion of methanol to formaldehyde in the presence of nitrous oxide. The catalysts were characterized by XRD, FTIR, UV–vis DRS, TPR-H<sub>2</sub>, NH<sub>3</sub>- and CO<sub>2</sub>-TPD and N<sub>2</sub> adsorption. 100% methanol conversion and 91% selectivity to formaldehyde were simultaneously obtained with 100% N<sub>2</sub>O conversion at 440 °C over a Co,Mg,Al-mixed oxide catalyst. Higher hydrogen yields and lower CO and CO<sub>2</sub> yields were obtained than when air was used as oxidizing agent, under the same conditions. These findings suggest that the reaction occurs on a combination of redox and basic catalytic sites.

## 1. Introduction

Nitrous oxide (N<sub>2</sub>O) is an environmental pollutant that contributes to the greenhouse effect and destruction of ozone in the stratosphere. Due to the high thermal decomposition temperature of N<sub>2</sub>O, which occurs above 600 °C [1,2], the use of efficient catalysts is necessary to conduct this reaction, thus ensuring the minimization of atmospheric emissions from anthropogenic sources, such as nitric acid and adipic acid industrial plants. Alternatively, the use of N<sub>2</sub>O as oxidant agent for hydrocarbon conversion to useful products is an interesting strategy to mitigate these emissions and develop new technologies [3–5].

About 32% of the methanol produced worldwide is consumed in the production of formaldehyde [6], therefore the use of N<sub>2</sub>O as oxidant agent to selectively produce formaldehyde is of great technological and environmental interest.

Two main classes of catalysts are employed in the partial oxidation of methanol to formaldehyde: (i) silver catalysts, operating in the temperature range of 580–650 °C; or (ii) iron-molybdenum catalysts operating in the temperature range of 400 °C [7–10]. Based on a DFT study, M.F. Fellah [11] showed that the direct oxidation of methanol to formaldehyde using N<sub>2</sub>O would be possible on [Fe-O]<sup>+</sup> species in Fe-ZSM-5. Khan et al. [4] reported on the use of Co-ZSM-5 catalysts to partially oxidize methane to synthesis gas using N<sub>2</sub>O as oxidant. In early papers, Co-ZSM-5 and Co-oxides derived from hydrotalcites (LDH) were

reported as efficient catalysts for decomposition of N<sub>2</sub>O [12,13]. Genquin et al. [14] used Co,Mg,Al-hydrotalcites as catalyst precursors for the total oxidation of volatile organic compounds and showed that the high activity for toluene oxidation of the Co-rich catalysts was related to the presence of easily reducible Co<sub>3</sub>O<sub>4</sub> particles.

Thus, considering that cobalt catalysts are active both for N<sub>2</sub>O decomposition and for oxidation reactions, the selective conversion of methanol to formaldehyde was investigated using N<sub>2</sub>O as oxidant and Co-oxides derived from hydrotalcites as catalysts in the present study.

## 2. Experimental

## 2.1. Catalysts preparation

MgAl (1:1), CoAl (1:1), CoMgAl (1:2:1) and CoMgAl (2:1:1) LDH samples were prepared by coprecipitation, using solutions of the metal nitrates and Na<sub>2</sub>CO<sub>3</sub>/NaOH solution, at pH = 11 [14]. The gels were aged at 80 °C for 24 h, then filtered and washed with distilled water until the pH was 10. The LDH samples were calcined at 600 °C in air for 4 h before reaction, obtaining the mixed oxide, respectively named as MgAl, CoAl, CoMgAl-1 and CoMgAl-2.

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## 2.2. Catalyst characterization

The LDH and the oxides were characterized by ICP-OES, XRD, TG/DTA, SEM, N<sub>2</sub>-physisorption, TPD of NH<sub>3</sub> and CO<sub>2</sub>, TPR and UV-Vis DRS. The characterization procedures are detailed in the Supplementary Material.

## 2.3. Catalytic test

The evaluation of the catalytic performance in the conversion of methanol to formaldehyde was carried out in a fixed bed quartz tubular reactor. Prior to reaction, 200 mg of catalyst was pretreated at 350 °C under helium flow (30 mL min<sup>-1</sup>) for 1 h. A methanol saturator operating at 30 °C was used to provide a reaction mixture with total flow of 100 mL min<sup>-1</sup> of pure helium, 4% O<sub>2</sub>/He or 8.2% N<sub>2</sub>O/He, in the temperature range of 350–500 °C. Catalysts MgAl, CoAl, CoMgAl-1 and CoMgAl-2 were also evaluated in the nitrous oxide decomposition, using 100 mL min<sup>-1</sup> of 8.2% of N<sub>2</sub>O/He gas mixture, in the range of 350–500 °C. Effluent gases were analyzed by gas chromatography using an Shimadzu GC2014 equipment, using Carboxen 1010 packed column (4.5 m × 3 mm) and capillary Carbowax (25 m × 0.25 mm) operating both with a thermal conductivity (TCD) and flame ionization (FID) detectors.

Conversion, selectivity and yields were calculated by the following equations:

$$\text{Conversion (\%)} = \frac{n_{\text{reactant,in}} - n_{\text{reactant,out}}}{n_{\text{reactant,in}}} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{n_{\text{product,formed}}}{n_{\text{reactant,consumed}}} \times 100 \quad (2)$$

$$\text{Yield (\%)} = \frac{n_{\text{product,formed}}}{n_{\text{reactant,in}}} \times 100 \quad (3)$$

In which:

$n_{\text{reactant,in}}$  is the inlet amount of substance of a given reactant;

$n_{\text{reactant,out}}$  is the outlet amount of substance of a given reactant;

$n_{\text{product,formed}}$  is the amount of substance of a given product;

$n_{\text{reactant,consumed}}$  is the amount of substance of a given reactant consumed in the chemical reaction.

## 3. Results and discussion

### 3.1. Preparation and characterization

The precursors were characterized by XRD (Fig. S1), to confirm the production of the LDH structures [15,16], and by TG/DTG (Fig. S2), to determine the calcination temperature to produce the corresponding oxides (600 °C). The main physicochemical properties of the oxide catalysts thus prepared are summarized in Table 1. Complete catalysts characterization is presented as Supplementary Materials as Figs. S3, S4 and S5.

The mixed oxide catalysts have shown type IV isotherms, typical of

mesoporous materials, according to the IUPAC classification (Fig. S4.b). The BET surface area of the oxides varied from 194 to 82 m<sup>2</sup> g<sup>-1</sup> and decreased with the substitution of Mg ions for Co ions into the hydroxalcalite precursor structure (Table 1). Average pore diameter increases with cobalt content. The ratio acid to basic sites indicates the basic character of the oxide catalysts prepared by calcination of the hydroxalcalite precursors. The hydrogen uptakes shown in Table 1 confirmed that the redox properties of the oxides are played by the Co<sup>3+</sup>/Co<sup>2+</sup> species, so that they increased with the increase of Co<sub>3</sub>O<sub>4</sub> content, a more easily accessible and reducible phase [14].

### 3.2. Catalytic test

Fig. 1 shows the conversion of methanol (a) and nitrous oxide (b) over the oxide catalysts, in the range of 350–500 °C and 50 mL min<sup>-1</sup> flow of MeOH:N<sub>2</sub>O (molar ratio = 3:1). Higher methanol conversions were obtained over the catalysts containing cobalt and magnesium, but the highest formaldehyde yield (Fig. 1.c) was obtained at 440 °C over catalyst CoMgAl-2, which contained a higher amount of cobalt. Simultaneously, higher N<sub>2</sub>O conversions were also observed over catalyst CoMgAl-2 (Fig. 1.b), attaining 100% N<sub>2</sub>O conversion at 410 °C while N<sub>2</sub>O conversions lower than 10% were observed for catalyst MgAl over the temperature range. These results are consistent with the presence of both redox sites related to Co species and basic sites related to Mg and Al species produced by calcination of the hydroxalcalite precursors, as shown in Table 1 and Supplementary Material.

The selectivity of the reaction assisted by nitrous oxide was calculated based on the methanol conversion over catalysts CoMgAl-2 (Fig. 2). Both methanol and nitrous oxide conversions were nearly constant and complete, at 440 °C, during 12 h. The selectivity to formaldehyde, around 95%, was stable and hydrogen was major by-product, suggesting a dehydrogenation path through the catalytic basic sites. CO, CO<sub>2</sub>, methane and water were also formed in small amounts, < 5%.

In order to investigate the influence of nitrous oxide on the conversion of methanol, the reaction was carried out over the CoMgAl-2 catalyst varying the molar ratio CH<sub>3</sub>OH/N<sub>2</sub>O and the results are presented in Fig. 3. Both methanol and nitrous oxide conversions were nearly complete at 440 °C but the selectivity toward formaldehyde was much higher using molar ratio CH<sub>3</sub>OH:N<sub>2</sub>O = 3:1. It has been previously reported that the oxidative dehydrogenation of methanol over silver-based catalysts is particularly preferably using CH<sub>3</sub>OH:N<sub>2</sub>O molar ratio between 7:1 and 4.5:1, in the ranges of 600–720 °C and 0.8–2 atm and that the oxidation of H<sub>2</sub> formed during the dehydrogenation is suppressed, resulting in higher hydrogen contents in the reaction products [9].

To further investigate the influence of nitrous oxide, the methanol conversion over the CoMgAl-2 catalyst was carried out at 440 °C in 4.1 mol% O<sub>2</sub>/He and in pure helium reaction atmosphere and the results are presented in Fig. 4.

Lower conversions and higher deactivation were observed in He atmosphere, while no deactivation was observed in N<sub>2</sub>O atmosphere,

**Table 1**  
Elemental, textural, acid-base and redox properties of the catalysts.

Sample	Co (wt %) <sup>a</sup>	Mg (wt %) <sup>a</sup>	Al (wt %) <sup>a</sup>	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	V <sub>pore</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	d <sub>pore</sub> (nm) <sup>b</sup>	Basic sites (mmol g <sup>-1</sup> ) <sup>c</sup>	Acid sites (mmol g <sup>-1</sup> ) <sup>c</sup>	H <sub>2</sub> consumption (mmol g <sup>-1</sup> ) <sup>d</sup>
MgAl	–	33.8	23.0	194	0.69	14.1	1.16	0.11	–
CoAl	40.0	–	23.0	96	0.45	19.8	0.65	0.06	9.04
CoMgAl-1	27.4	21.6	13.5	139	0.57	16.5	1.16	0.09	6.20
CoMgAl-2	43.7	9.9	11.7	82	0.71	34.2	0.52	0.06	9.74

<sup>a</sup> Determined by ICP OES.

<sup>b</sup> Determined by BET and BJH methods.

<sup>c</sup> Determined by TPD-CO<sub>2</sub> and TPD-NH<sub>3</sub>, respectively.

<sup>d</sup> Determined by TPR-H<sub>2</sub>.

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