



Cerium(IV)oxide modification by inclusion of a hetero-atom: A strategy for producing efficient and robust nano-catalysts for methanol carboxylation

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ABSTRACT

Cerium(IV) oxide has been reported to catalyse the direct carboxylation of methanol to dimethylcarbonate, DMC. Nevertheless, the life of commercially available catalysts is quite short as after the first cycle the activity decreases and after a few cycles goes to zero. Noteworthy, no reports are in the literature about the stability of catalysts and their life. We have investigated the behaviour of catalysts and their de-activation using either surface techniques, such as XPS, or structural techniques, such as XRD. The reduction of Ce(IV) to Ce(III) and surface modification seem to be responsible for de-activation of the oxide. The results of a detailed study correlating the size and structure of particles to the activity of the catalysts are reported in this paper. In particular, pure commercial CeO₂ is compared, using High Throughput Experiments (HTE), with CeO₂ synthesised in our laboratory and with the latter loaded with Al or Fe at various concentrations. The hetero-metals have a different effect on the stabilization of the Ce-catalyst and on its activity. Al-loaded CeO₂ affords the most interesting results in terms of lifetime and activity. Therefore, the correlation of the structural properties of CeO₂ loaded with Al at a concentration variable between 3 and 40% to the activity in catalysis is discussed in detail. XPS and XRD data have been used for the characterization of the catalyst before and after a catalytic run. Pure synthesised CeO₂ and CeO₂ loaded with Al are able to maintain their activity for several cycles (apparent TON of several tens) or three days of operation without any treatment after recovery, with a much better performance than the commercial catalysts that, conversely, lose their activity after a few cycles. The size of the particles determines the activity of the catalyst and we show that particles having a size 15–60 nm are the most active, while particles sized micrometers are much less active.

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1. Introduction

The direct carboxylation of methanol to dimethylcarbonate (DMC) attracts much attention worldwide because DMC finds a large utilization in several industrial applications. In fact, DMC is used in the chemical industry as monomer for polymers, [1] in transesterification reactions for the production of other carbonates such as diphenylcarbonate [2] and others, as alkylating or carboxylating agent [3,4]. It is also used in the agrochemical [5] and pharmaceutical industry [6] for the production of chemicals or in product formulation. A new potential application of DMC is an additive to gasoline that would expand its market by over one order of magnitude. Such potential use requires the implementation of new synthetic methodologies because the technologies on

stream, either that based on the use of phosgene or the newest one based on the oxidative carbonylation of methanol [7,8], suffer from several drawbacks that prevent the expansion of the production to the desired amount.

More recently, the direct carboxylation of methanol (Eq. (1)), a reaction that responds to the principles of the sustainable chemical industry, has been investigated by several research groups worldwide.

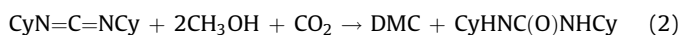


Both homogeneous and heterogeneous catalysts have been used so far. Among the former, Sn [9] and Nb [10] show interesting properties. Nevertheless, their exploitation is limited by the conversion of tin catalysts into oligomers during catalysis, that reduces their activity; while Nb(V)-alkoxo species maintain their activity until they are in an almost anhydrous reaction medium. Unfortunately, the formation of water in reaction (1) causes the de-

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activation of the catalyst or forces the adoption of energy consuming methodologies, such as the recovery of the catalyst at the end of each reaction cycle and its re-use in anhydrous methanol. The use of water-traps has also been attempted. Organic water traps such as aldols, [11] ketals, [12] ortoformates, [13] although rise the problem of separation from the reaction mixture, are more efficient than inorganic systems such as zeolites as the latter at the working temperature (470 K) may act as protonating agents of DMC, reversing the reaction. Cooling of the reaction mixture to room temperature, dewatering and reheating has been [14] adopted as a strategy for using zeolites as water traps. DCC [15] has shown a very interesting behaviour as it alone is able to promote the formation of DMC under very mild conditions (310 K and 0.2 MPa) with excellent yield (>90%) and selectivity (>98%). Unfortunately, 1 mol of DCC is converted into the relevant urea (Eq. (2)) per mol of DMC produced: this makes that unless the urea is quantitatively converted back to DCC such synthetic methodology is not economically convenient for exploitation.



Heterogeneous catalysts such as CeO_2 , [16] ZrO_2 [17] or TiO_2 [18] have also been used but they in general suffer of a serious drawback represented by their de-activation: after the first cycle their activity decreases to a marginal conversion of methanol.

In this work, we have investigated the reasons of the degradation of commercial CeO_2 and developed a new synthetic methodology for CeO_2 tested in the carboxylation of methanol. We have also synthesized and tested in catalysis CeO_2 loaded with metals such as Al and Fe. The behaviour of CeO_2 loaded with 10% Al_2O_3 is described in detail. XRD and surface techniques such as BET and XPS have been used for the characterization of the catalysts before and after use in catalysis.

2. Experimental section

All solvents, starting reagents and the commercial metal oxides listed in Table 1 were RP Aldrich products. Methanol was dried, distilled [19] and stored under dinitrogen (the residual water was 20 ppm, as determined by the Karl-Fisher method, using a Metrohm 785 DMP Titrino apparatus). Carbon dioxide was from Rivoira IP (99.999% purity).

Nuclear magnetic resonance (NMR) experiments were carried out with a 400 MHz Varian INOVA apparatus (9.39 T) using the MAS technique with a basic frequency of 104.215 MHz for the aluminium nucleus. The samples were packed in a 5 mm diameter zirconia rotor and spinned at 5 kHz during the analysis. The 90° pulse duration was 4.5 μs with a subsequent relaxation time of 4 s. The number of transients changed with the aluminium content in order to obtain good spectra in terms of signal-to-noise ratio. All the chemical shifts were calculated taking as reference an aqueous solution of aluminium as $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

FTIR spectra were recorded with a Shimadzu Prestige 21 instrument.

X-ray Photoelectron Spectroscopy (XPS) spectra were obtained using a ThermoVG Thetaprobe spectrometer, equipped with a microspot monochromatised Al-K α source and the gun of low-energy electrons for compensation of electrostatic charging of samples. The Al-K α line (1486.6 eV) was used throughout this work and the base pressure of the instrument was 10^{-9} mbar. Survey scans (binding energy range 0–1200 eV, FAT mode, pass energy = 200 eV) and detailed spectra (FAT mode, pass energy = 50 eV) were recorded for each sample. Data analysis of the latter was performed using the Avantage software package, which consists of a non-linear least-squares fitting program. The values of binding energies BE (eV) were taken relatively to the binding energy of Cls-

Table 1

Comparison of the activity of single metal- or bimetallic-oxides

Entry	Catalyst	Conversion (%)	mmol of DMC/ mmol of catalyst
1	$\text{Al}(\text{OH})_3$	0.051	0.045
2	$\text{Al}(\text{OH})_3^{\text{a}}$	0.002	0.001
3	CeSO_4	0.048	0.095
4	Ce_2O_3	0	0
5	Al_2O_3 SiO_2	0	0
6	Al_2O_3 SiO_2^{a}	0.001	0.002
7	La_2O_3	0	0
8	$\text{La}_2\text{O}_3^{\text{a}}$	0.001	0.001
9	KTiNbO_5	0.001	0.001
10	CeO_2 sint 2 h calc. ^b	0.352	0.30
11	Al/Ce (3%) 2 h calc.	0.400	0.37
12	Al/Ce (3%) 3 h calc. ^c	0.425	0.40
13	Al/Ce (10%) 2 h calc.	0.243	0.20
14	Al/Ce (10%) 3 h calc.	0.423	0.34
15	Al/Ce (20%) 2 h calc.	0.207	0.15
16	Al/Ce (20%) 3 h calc.	0.325	0.25
17	Fe/Ce (1%)	0.101	0.09
18	Fe/Ce (3%)	0.314	0.27
19	Fe/Ce (7%)	0.448	0.38

The yield of DMC was estimated after 3 h of reaction between 4 mL of methanol, CO_2 (5.0 MPa) and 100 mg of catalyst, at 408 K. The "conversion" means the percent of alcohol converted into DMC (the latter was evaluated gas-chromatographically using toluene as internal standard). In the last column, the molar ratio of DMC to the total number of moles of the metal is reported.

^a Commercial compounds calcinated for 2 h at 923 K on air.

^b Oxide obtained via calcination for 2 h at 923 K on air of the synthesized mixed hydroxide.

^c Oxide obtained via calcination for 3 h at 923 K on air of the synthesized mixed hydroxide.

electrons of hydrocarbons on the sample surface (produced by adventitious carbon), which is accepted to be equal to 285.0 eV. Quantification was performed using peak areas; comparison between data from different elements was possible after correction (division) by empirically derived atomic sensitivity factors.

X-rays diffraction spectra-XRD spectra were taken using a Bruker D8-DISCOVER diffractometer, in reflection geometry using a flat sample, with a X-Ray tube using the Cu-K α line (λ -K α 1 = 1.54056 Å and λ -K α 2 = 1.54439 Å). The tests were done in a short period of time so that the same experimental conditions were preserved. The experimental parameters were: step-scan 0.03°, 2 θ range from 25 to 135°, 20 s acquisition time.

XRD-spectra were compared with different diffraction patterns of cerium oxide present in PDF (powder diffraction file) data bank using DIFFRACplus EVA [20] for qualitative analysis to check out the chemical phase present in the powder. XRD-spectra data were processed using EXPO2006 [21] for structural analysis and FullProf/Topas [22,23] for structural refinement according to the Rietveld method [24]. The peak profiles were fitted with Pearson VII function to calculate the crystallite size and the full width at half maximum (FWHM).

GC-MS analyses were carried out with a gas chromatograph Shimadzu 17 A (capillary column: 30 m; MDN-5S; \varnothing 0.25 mm, 0.25 μm film) coupled to a Shimadzu QP5050 A mass spectrometer. Quantitative determinations on the reaction solutions were performed using Hewlett Packard 6850 GC-FID (capillary column: 30 m; Carbowax; \varnothing 0.25 mm, 0.25 μm film).

BET areas were determined with a Micromeritics Chemisorb 2750 equipment.

2.1. Synthesis of CeO_2

Two methodologies were used for the synthesis of the oxide, starting from either $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (method A) or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (method B).

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