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Ceria doped with Cu for dimethyl carbonate synthesis from CO_2 and methanol

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Dimethyl carbonate (DMC) is a promising chemical due to its non-toxic and biodegradable character. It finds uses in electrolytic solution in lithium ion battery and as additive in the gasoline-based fuels. Recently, it has been shown that adding Cu to CeO_2 the yield of DMC generated from CO_2 and methanol increases. Thus, the aim of this study is to describe the role Cu in the DMC synthesis.

CeO_2 and CeO_2 with Cu catalysts (0.02Cu/Ce and 0.5Cu/Ce) were synthesized by precipitation and dry impregnation methods, respectively. The solids obtained were calcined at 500 °C. The catalysts were characterized by TPR, EPR, UV-Vis and isopropanol model reaction. Catalytic tests were carried out employing a 100 mL Parr batch reactor at 50 bar of CO_2, 170 °C, 0.1 g of catalyst during 3h. The products were analyzed by GC-MS. The catalytic tests results and isopropanol conversion are showed in Table 1.

Table 1. Cu loading (L, %wt), molar concentration of the products, propene (rP) and acetone (rA, µmol.g_{cat}^{-1}.min^{-1}) generation rates. Dimethoxy methane and methyl formate are DMM, MF, respectively.

		Molar concentration (%)				
Catalyst	L	DMC	DMM	MF	rA	-rP
CeO_2	0	9	49	35	198	9
0.02Cu/Ce	0.02	47	9	44	244	9
0.5Cu/Ce	0.5	11	11	78	344	4

The 0.02Cu/Ce exhibited the highest molar concentration of DMC and also DMC yield (not shown). Fig. 1 depicts the UV-Vis spectra of the oxidized catalysts and Fig. 2 the TPR profiles. It can be observed (Fig.1) that 0.5Cu/Ce shows vibrations related to CuO. This not occurs in the case of 0.02Cu/Ce. The TPR profile of 0.5Cu/Ce shows CuO might be reduced at low temperature and Cu^o might promote the reduction of the CeO_2 surface (see the two peaks at low temperature). Adding Cu at low concentration (0.02Cu/Ce) the first peak (broad), related to the CeO_2 surface reduction, shifts to lower temperature compared with CeO_2. Moreover, it can be observed that at the 170°C (temperature of the reaction) there is more CeO_2 reduced in the case of 0.02Cu/Ce compared with CeO_2. As is well known the reduction of CeO_2 generates O vacancies, which show the behavior of strong basic sites.

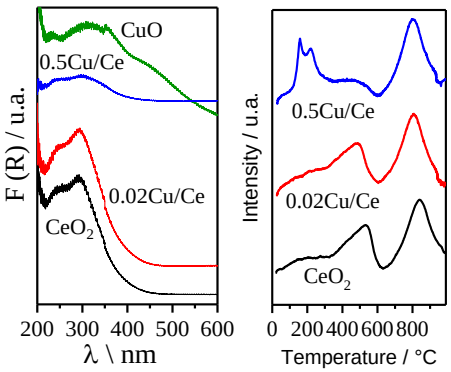

Figure 1. UV-VIS DRS spectra. **Figure 2**. TPR profiles.

The DMC synthesis occurs on acid and strong basic sites. The 0.02Cu/Ce generates more DMC than CeO_2 due to its higher basicity (see rA values and TPR profiles) compared with CeO_2. Both DMM and MF synthesis are related to the reaction of formaldehyde with methoxide species. The 0.5Cu/Ce catalyst synthetizes more MF than 0.02Cu/Ce. This happens because of the redox properties of the former (see TPR profiles) which promotes formaldehyde generation. All in all, the Cu on CeO_2 at low concentration promotes DMC synthesis due to the high basicity and reducibility of this catalyst.

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