EFFECT OF CHROMATE ANION ON THE PHOTOCATALYTIC ACTIVITY OF Mg-Al LAYERED DOUBLE HYDROXIDE

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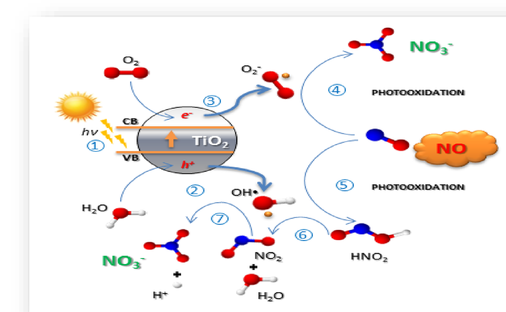
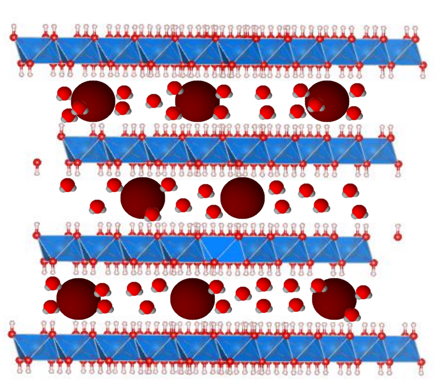
INTRODUCTION

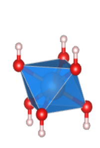
Nowadays, the world large urban areas present problems related to air pollution. The last report of the European Environment Agency [1] estimates around 400.000 premature deaths per year in the European Union due to the quality of the air. The presence of particulate material (PM), ozone, sulphur and nitrogen oxides origins harmful to the human health and the environment. Nitrogen oxides (NO_x, the sum of nitrogen monoxide, NO, and nitrogen dioxide, NO_2) are consider as one of the priority air pollutant due to its several adverse and harmful effects. They are responsible for such environmental problems as photochemical smog, tropospheric ozone or acid rain and, related to the human health, they can cause emphysemas, bronchitis, etc. [2].This gases are produced in the city by the burning of fossil fuels. Photocatalytic oxidation of NO_x gases with different materials (TiO_2, ZnO, etc.) has proven to be an effective method to reduce the concentration of these compounds. However, in recent year layered double hydroxides have been shown as a promising photocatalysts [3].



STRUCTURE OF LDH

GENERAL FORMULA: $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{n-})_{x/n} \cdot m\, H_2O$





$[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$

- M^{II} = Mg^{2+}, Zn^{2+}, Ni^{2+},...
- M^{III} = Al^{3+}, Cr^{3+}, Fe^{3+}, ...

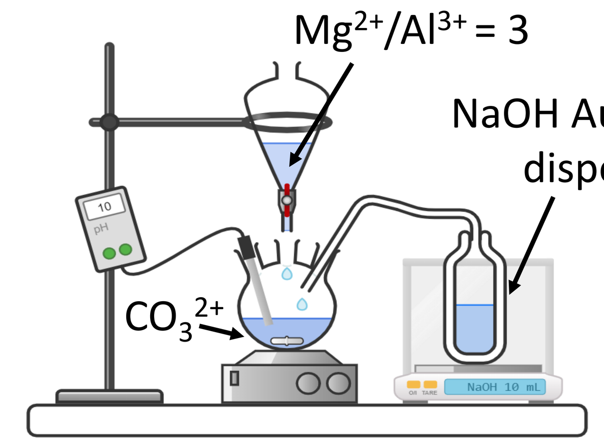
A^{n-}

- Inorganic anions: Cl^-, CO_3^{2-}, NO_3^-,...
- Organic acid: adipic, oxalic, succinic, ...

H_2O

SYNTHESIS

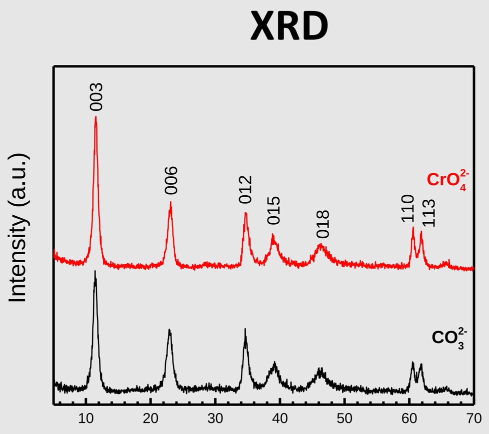
COPRECIPITATION METHOD → Washed 3 times → Dried 80℃ → Mg_3Al-CO_3 sample → 500℃ / 6h → $Mg_3AlO_{4.5}$ → $Mg_3AlO_{4.5}$ + Concentrated chromium solution → Mg_3Al-CrO_4 sample



RESULTS

CHARACTERIZATION

XRD



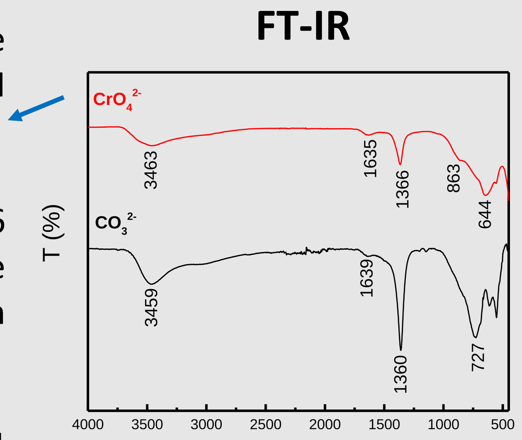
XRD patterns show a pure phase of LDH. The value of d_{003} = 7.7 Å in both cases(CO_3^{2-}).

FT-IR spectra are characteristic of the LDH compounds.

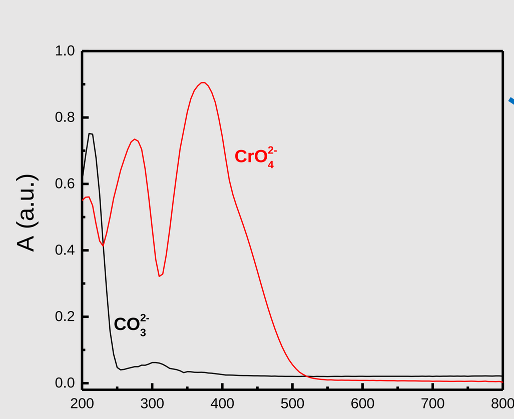
The bands at (1360-1366 cm^{-1}) correspond to the interlayer carbonate in both cases.

The weak band at 863 cm^{-1} is assigned as the v_1 stretching mode of CrO_4^{2-}.

FT-IR



DIFFUSE REFLECTANCE SPECTROSCOPY



LDH-CO_3 sample can only absorb light from the UV region while LDH-CrO_4 absorbs in the UV-Vis region.

XRF and TGA

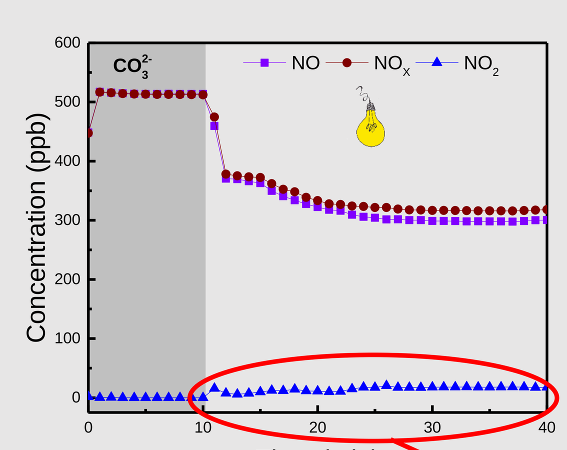
Sample	% w/w			M^{2+}/M^{3+} Molar ratio	Proposed formula	S_{BET} ($m^2\,g^{-1}$)
	Mg	Al	Cr			
CO_3^{2-}	23.5	8.68	<LOD	3	$[Mg_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125} \cdot 0.62\, H_2O$	30
CrO_4^{2-}	22.3	8.54	1.85	2.9	$[Mg_{0.745}Al_{0.255}(OH)_2](CrO_4)_{0.036}(CO_3)_{0.092} \cdot 0.69\, H_2O$	74

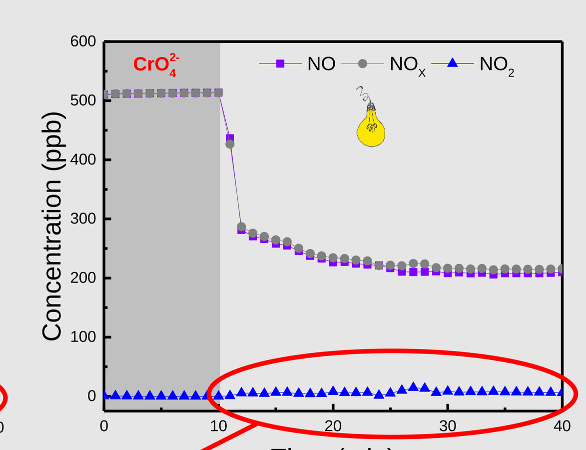
Samples containing chromate exhibit a higher BET surface area.

PHOTOCATALYTIC TEST

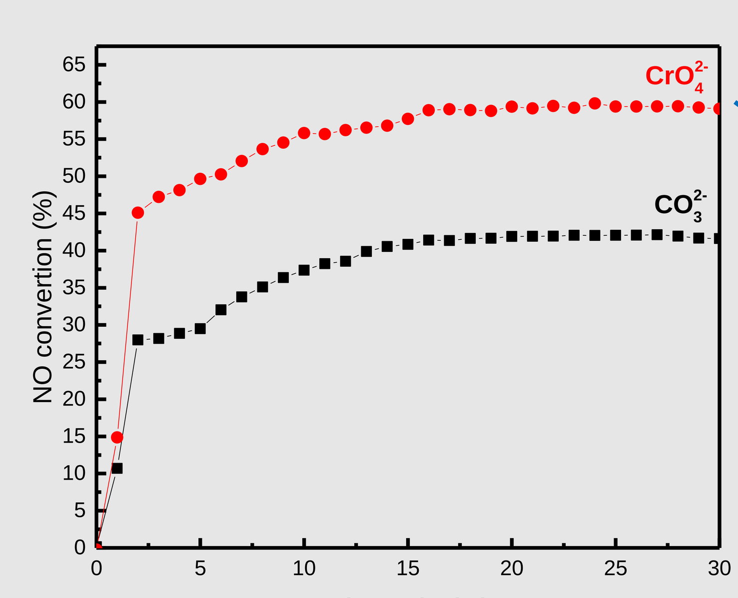
The NO abatement is expected to follow the next summarized photo-oxidation mechanism [4]:

$$NO \xrightarrow{\bullet OH} NO_2^- \xrightarrow{\bullet OH} NO_2 \xrightarrow{\bullet OH} NO_3^-$$





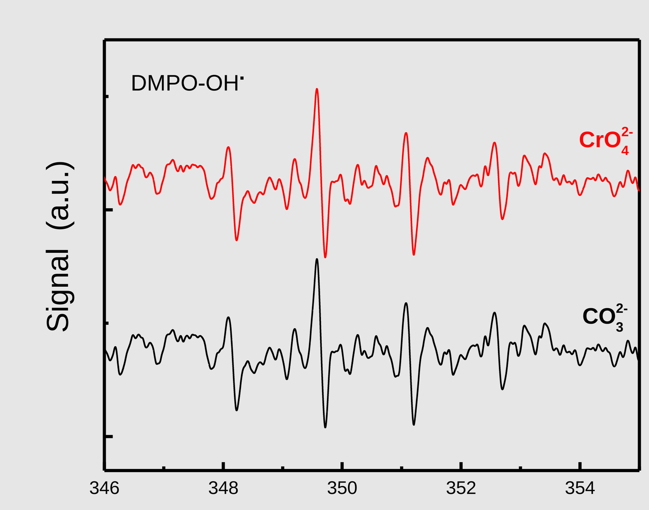
Both samples are selective to the complete oxidation of NO to NO_3^-, because there is not release of NO_2.



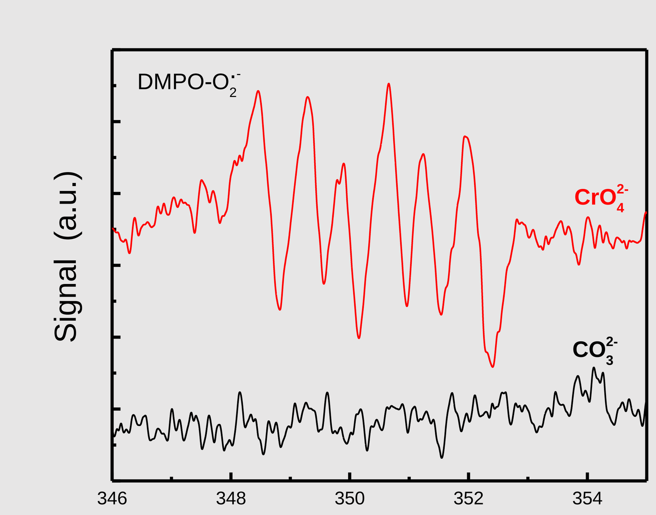
LDH-CrO_4 sample show a greater NO conversion.

REACTIVE OXIGEN SPECIES DETERMINATION

DMPO SPIN-TRAPPING EPR



LDH-CO_3 and LDH-CrO_4 samples produce similar amount of •OH radical. However, LDH-CrO_4 show an intense signal of $\bullet O_2^-$ radical.



CONCLUSIONS

A. The presence of chromate on MgAl-CO_3 LDH enables the UV-Vis light absorption. The chromate sample exhibits a higher specific surface area.
B. Physical and morphological characteristics of the chromate sample facilitate a high NO conversion of 60 %.
C. The relevant production of $\cdot O_2^-$ radicals could be ascribed to the new electronic pathways for the chromate the sample.

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