Fe and Al hydrotalcite-based catalysts for the abatement of trichloroethylene

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Background

Chlorinated volatile organic compounds (CVOCs) as trichloroethylene (TCE) are widely used in industry and are considered a major source of environmental pollution and health problems. Their emissions result in problems related to the ozone layer destruction, groundwater pollution and photochemical smog. Catalytic oxidation is presented as an effective option for the control of different CVOCs emissions. Usually, metal oxides and noble metals have been proposed as active catalysts for TCE oxidation, but they are easily poisoned by chlorine [1] or they generate polluting by-products at high temperatures [2]. Recently, catalysts based in zeolites have been also proposed as active catalysts for this reaction [3] obtaining interesting results although more active, selective and stable catalysts need to be found.

Objective

- To study the catalytic behaviour for the TCE oxidation of new catalysts based on (Mg, Ni, Cu or Co)/(Fe or Al) mixed oxides derived from hydrotalcite-like compounds.

Experimental

Catalysts preparation

Simultaneous co-precipitation technique at constant pH
→ Heat treatment at 550°C for 6 h

Reaction conditions

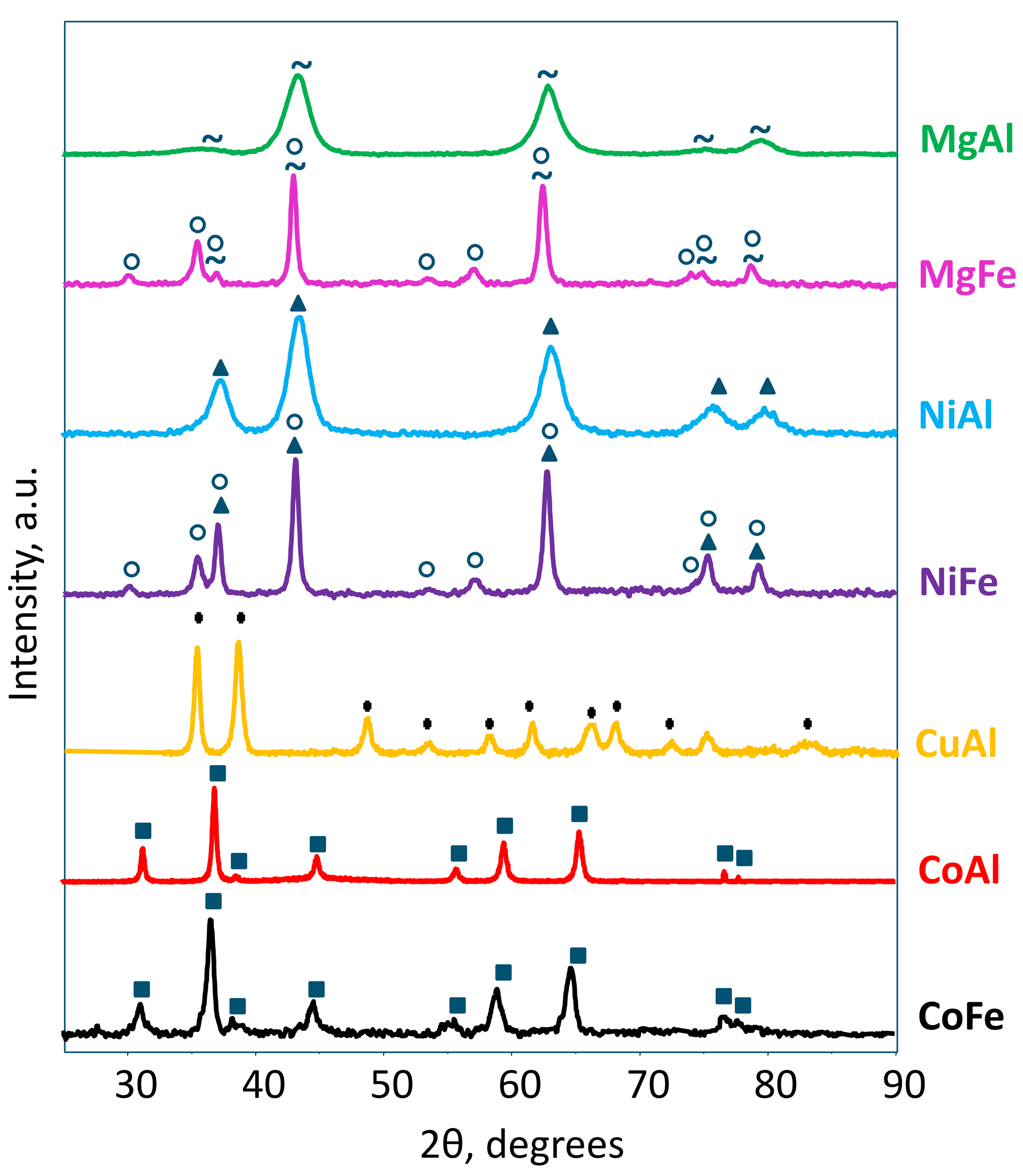
- quartz fixed bed reactor
- catalyst bed = 0.68 g
- gas flow rate = 400 ml min^{-1}
- GHSV = 15000 h^{-1}
- [TCE] = 1000 ppm in air

Characterization

Table 1. Physic-chemical properties of the mixed oxides.

Catalyst	BET ($m^2 g^{-1}$)	Composition, %wt						Molar ratio
		%Mg	%Ni	%Co	%Cu	%Al	%Fe	
MgFe	189	25.7	-	-	-	-	17.2	Mg/Fe = 3:1
NiFe	143	-	40.1	-	-	-	19.2	Ni/Fe = 2:1
CoFe	81	-	-	45.9	-	-	14.7	Co/Fe = 3:1
MgAl	169	24.8	-	-	-	6.9	-	Mg/Al = 4:1
NiAl	122	-	45.9	-	-	7.1	-	Ni/Al = 3:1
CoAl	106	-	-	46.5	-	9.9	-	Co/Al = 2:1
CuAl	92	-	-	-	47.1	4.9	-	Cu/Al = 4:1

Figure 1. XRD patterns of the catalysts after calcination.

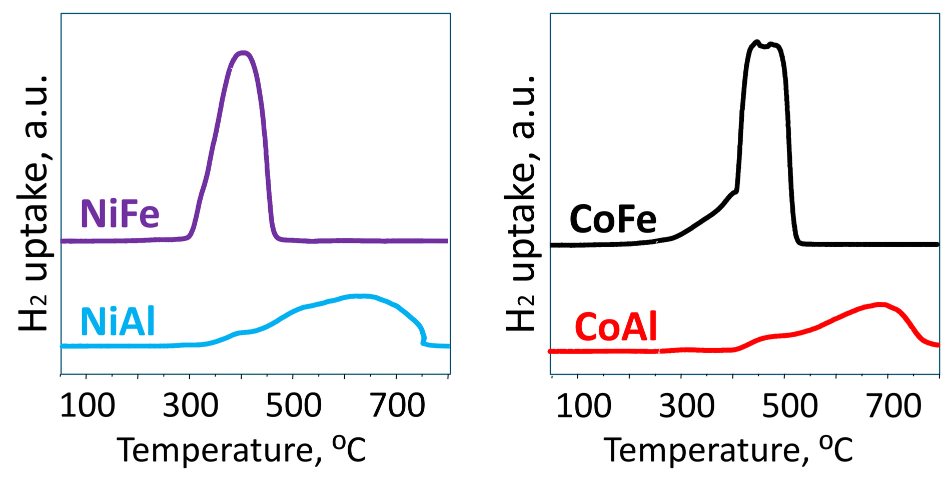


After calcination HT are transformed into mixed oxides.

~ MgO ▲ NiO
○ Fe_3O_4 ■ Co_3O_4
• CuO

MgFe and NiFe samples show together with the peaks of MgO or NiO, new peaks associated to a magnetite-like structure (Fe_3O_4), indicating that in this case we have a mixture of phases.

Figure 2. H_2-TPR results.



Al-containing catalysts are reduced at higher temperature because of the interaction between Al and Ni or Co.

Table 2. NH_3-TPD results.

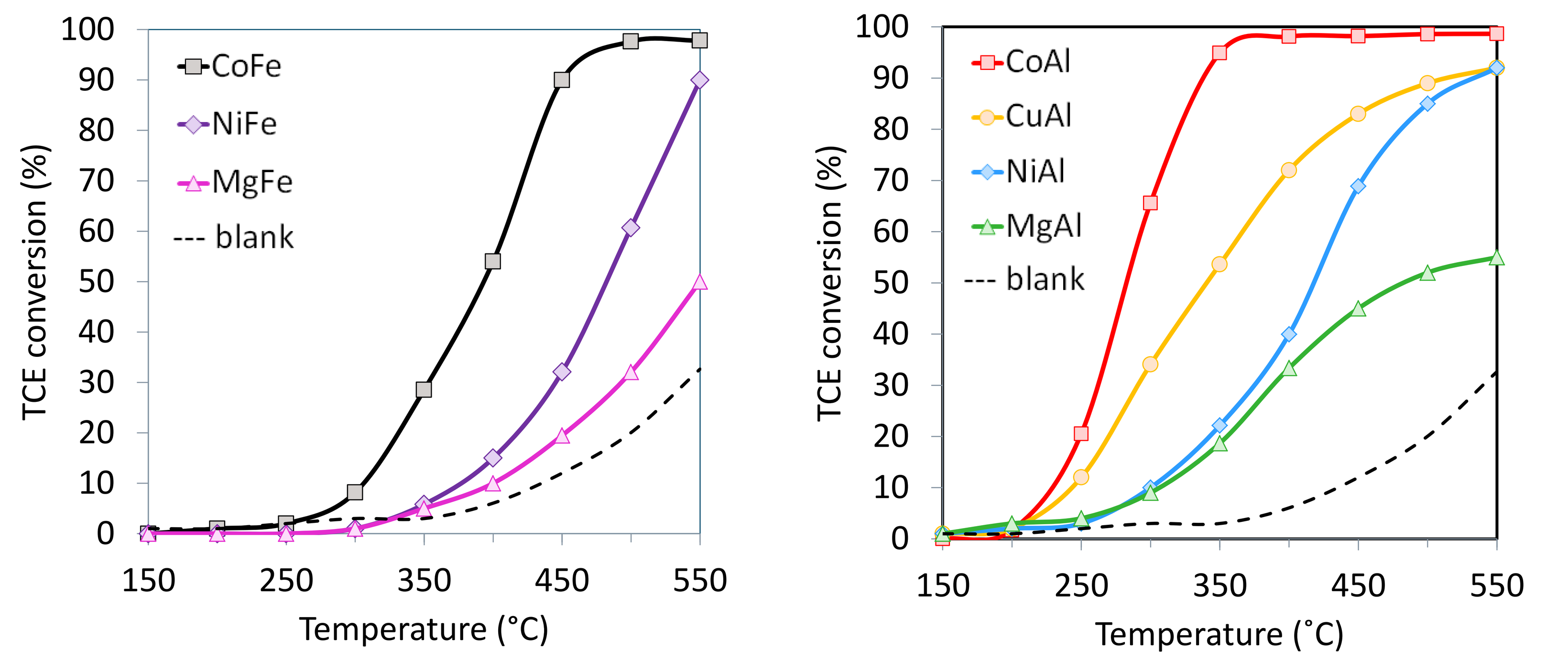
Catalyst	NH_3 adsorbed (μmol_{NH_3} /g)
NiFe	138
NiAl	349
CoFe	174
CoAl	539

The interaction between Al and Ni or Co (bonds Al^{3+}-O-(Co^{3+} or Ni^{2+}) enhances the Lewis acidity of Al^{3+} [4,5].

Acidity
→ catalysts with Al > catalysts with Fe
→ catalysts with Co > catalysts with Ni

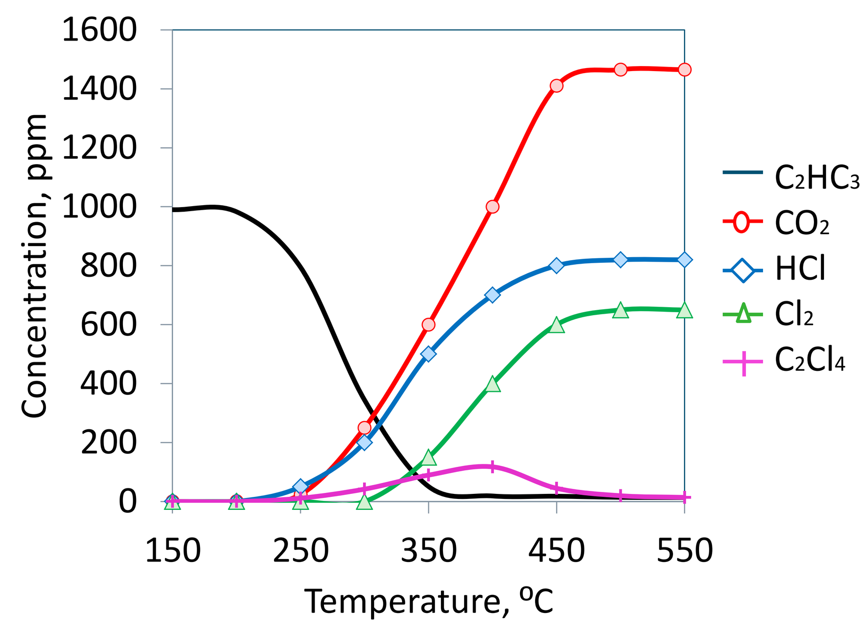
Catalytic results

Figure 3. TCE oxidation light-off curves.



Activity
→ catalysts with Al > catalysts with Fe
→ catalysts with Co > Cu > Ni > Mg

Figure 4. Product distribution over CoAl catalyst.



Main reaction products:
→ CO_2, HCl and Cl_2.
No CO formation is observed.

Reaction scheme

$C_2HCl_3 + 2O_2 \rightarrow 2CO_2 + HCl + Cl_2$
$C_2HCl_3 + Cl_2 \rightarrow C_2Cl_4 + HCl$
$C_2Cl_4 + 2O_2 \rightarrow 2CO_2 + 2Cl_2$

Conclusions

- All catalysts tested present a relatively high activity for the removal of TCE in the temperature range studied (350-550ºC).
- It has been observed that catalysts containing Co are more active than those with Ni. Mg in the support results in a lower activity.
- Moreover, the replacement of Fe by Al results in an increase in the catalytic activity. CoAl sample showed the highest catalytic activity ($T_{50\%}$=280°C and $T_{90\%}$=340°C).
- The catalytic activity of these materials depends on both their redox and their acid properties. In fact, the good results obtained with the CoAl catalyst can be related to the acidity of the material, which enhances the TCE adsorption, and to the presence of reactive O^{2x-} species which oxidize the adsorbed TCE.
- This catalyst has shown a good selectivity towards CO_2, HCl and Cl_2.

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