Al/Fe-, Al/Cu- and Al/(Fe-Cu)-pillared clays: Structural features at low Atomic Active Metal Ratios (AMR)

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Structural features at low Atomic Active Metal Ratios (AMR)

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Introduction

Several studies have pointed out that smectites pillared with Keggin like Al_{13}-based polycations containing iron or copper show high performance as active solids in the catalytic wet peroxide oxidation (CWPO) of toxic organic compounds present in aqueous effluents [1,2]. Although such catalytic properties have been related with the presence of isolated species of Cu or Fe in the modified clays [3,4], enough work has not been made in order to establish the optimum preparation conditions that may promote it. Thus, in the past few years it has been studied the effect of some variables of preparation like hydrolysis ratio, temperature of calcination [3,4] and atomic active metal ratio (AMR) [5] on the preparation of Al/Fe-, Al/Cu- and Al/(Fe-Cu)-pillared clays.

In this work the effect of AMR values below 10% on the structure and physicochemical properties of the resulting modified montmorillonite were investigated for the same three mixed metallic pillaring systems.

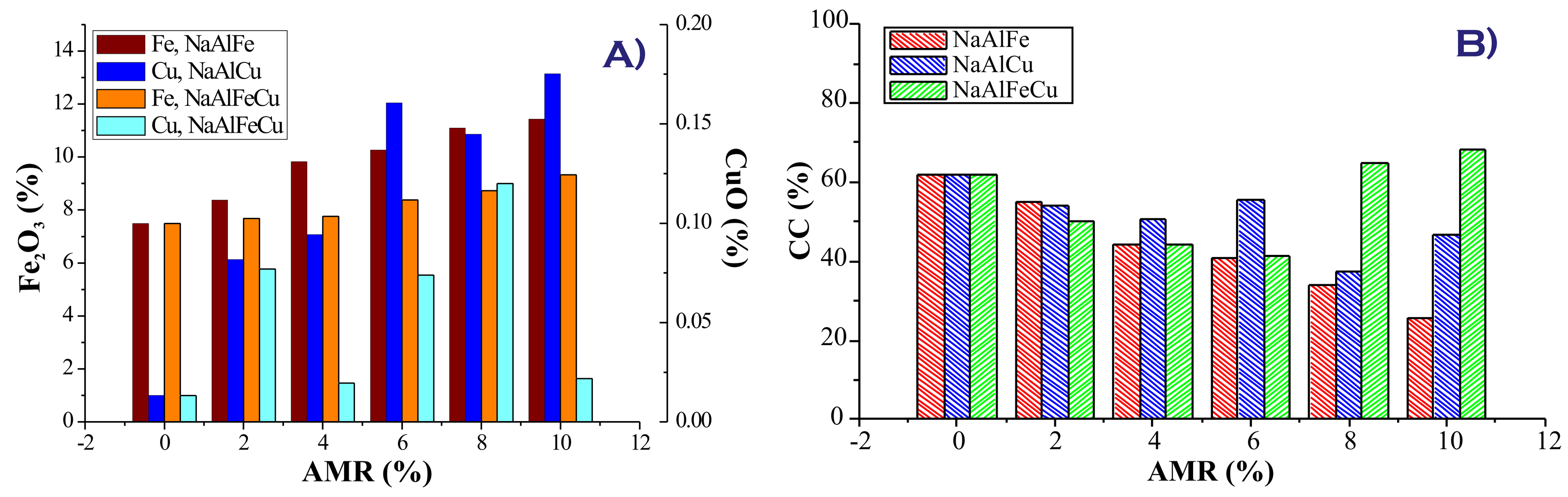
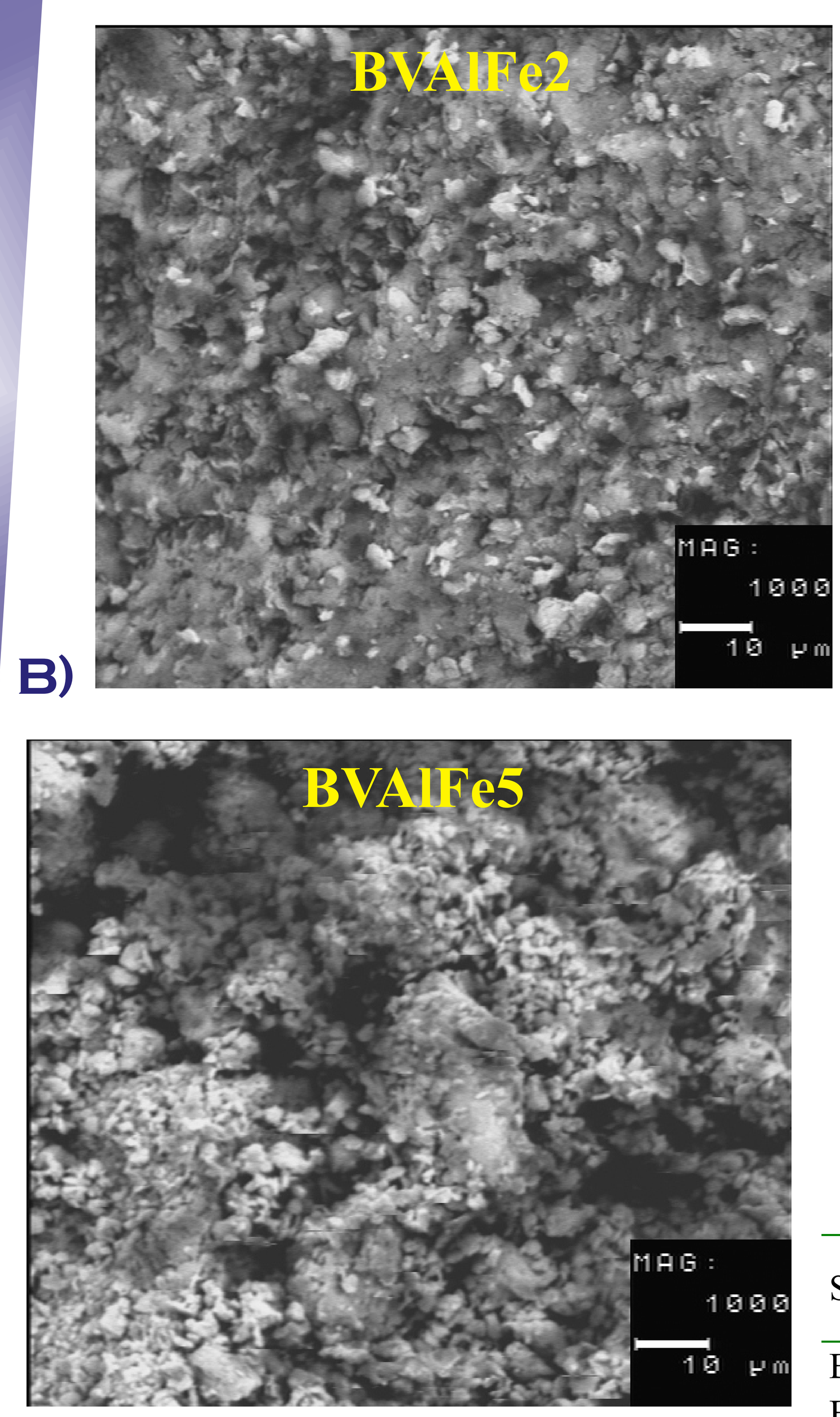


Fig. 1. A) SiO_2 - normalized active metal contents and B) CEC compensation (CC %) in NaBV-PILCs at increasing AMR values



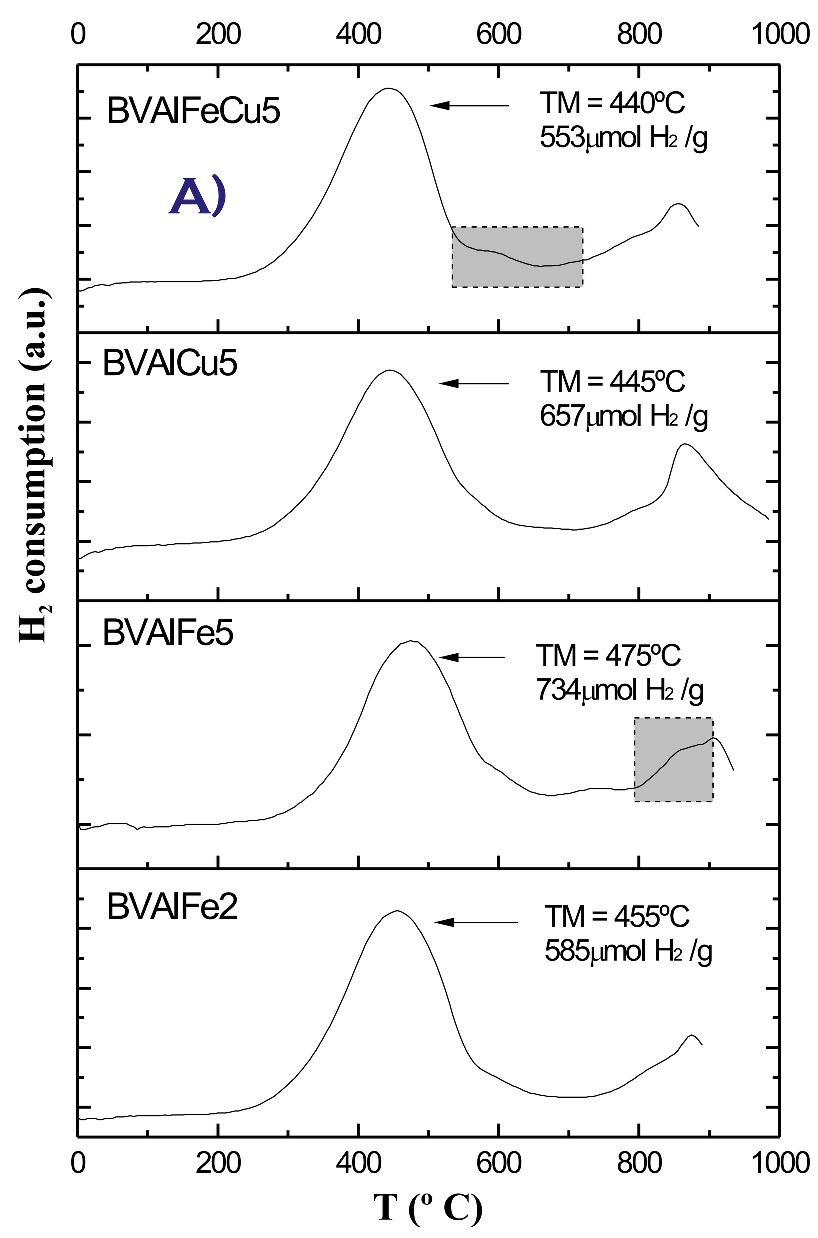


Fig 3. A) H_2-TPR diagrams of BV-PILCs. B) SEM micrographs for BVAlFe samples at increasing AMR.

Sample	d_{001} [a] (nm)	S_{BET} (m^2/g)	S_{EXT} (m^2/g)	$V_{\mu p}$ (cm^3/g)	$V_{p\ total}$ (cm^3/g)
BV	1.45	93	61	0.016	0.100
BVAl	1.92	155	77	0.038	0.120
BVAlFe1	1.99	140	75	0.036	0.113
BVAlFe2	1.97	155	90	0.037	0.129
BVAlFe5	1.90	130	75	0.040	0.121
BVAlCu1	1.98	129	65	0.035	0.107
BVAlCu3	1.96	172	87	0.048	0.133
BVAlCu5	2.08	123	62	0.034	0.098
BVAlFeCu3	1.97	147	80	0.037	0.122
BVAlFeCu5	1.94	150	82	0.038	0.129

Fig 2. Basal spacings and textural properties of BV-derived PILCs.

Experimental

A Colombian bentonite from the *Valle del Cauca* region, particle size separated (<2μm) in its Na-homoionized (NaBV) or natural Ca/Mg (BV) form was employed as starting material. The clay was modified with intercalating solutions ranging AMR values between 2 and 10% of the active metals: percent AMR = (((M/(Al+M))·100), with M = Fe, Cu, or Fe + Cu. In Al/(Fe-Cu)- system a 1:1 ratio for Fe:Cu was adopted. Intercalating solutions were prepared from the metal chlorides (Sigma-Aldrich), and added to 2.0 wt.% Clay suspensions to load 20 meq. (positive charge)/g clay [5].

The elemental composition of the materials was determined by ICPS. CEC was followed by micro-Kjeldahl analysis. X-ray diffraction patterns were recorded on oriented films in a Siemens D-500 instrument at 40 kV, 30mA, scanning speed of 2 º/min, with Cu Kα filtered radiation (λ=1.5418 Å). Textural properties were determined from nitrogen (Air Liquide, 99.999%) adsorption data, obtained at -196 ºC with a Micromeritics Gemini 2375 apparatus. Specific surface areas were calculated from the BET method; external surface areas and micropore volumes by means of the *t*-method. Temperature-programmed reduction (H_2-TPR) analyses were carried out in a Micromeritics TPR/TPD 2900 instrument, from RT to 900 ºC at 10 ºC/min, under a total flow of 20 cm^3/min of carrier gas (5% H_2 in air, Air Liquide). Hydrogen consumption measured by a TCD detector where CuO (Merck, 99.99%) was used as external standard. SEM microscopy was taken in a Digital Scanning Microscope DSM940 Zeiss operated at 15 kV. The samples were coated with a thin gold layer.

Results

It can be seen that Fe and Cu uptake by NaBV rise almost linearly with AMR in the bimetallic systems (Fig. 1A). Besides, the insertion efficiency of Cu was in average 15 times lower than Fe for a given AMR value, which can be attributed to its lower ability to isomorphically substitute Al^{3+} in the Keggin Polycation. CEC compensation shows decreasing trend only for Al/Fe- system, while random for the other systems at increasing AMR values (Fig. 1B). The X-ray basal spacings show opposite trends for Fe and Cu with AMR for BV modified materials (Fig. 2). It might be explained by the opposite values of ionic radii of Fe^{3+} (0.67Å) and Cu^{2+} (0.73Å) against that of Al^{3+} (0.68Å), all in octahedral coordination. It is also remarkable the growing of two shoulders at increasing Fe loadings (ca. 600 and 850 ºC), which appear framed in gray dashed squares at the TPR diagrams (Fig. 3A), which according with literature could be rationally assigned by the first time to *i)* the so-called Fe "decorating" Al_2O_3 pillars and *ii)* Fe into the framework of true mixed Al/Fe pillars. Moreover, SEM micrographs show a higher incidence of tiny particles, probably oxide aggregates, deposited on the clay surface when AMR only changed from 2.0 to 5.0 % (Fig. 3B). It probably explains the drastic worsening of the textural properties, mainly the micropore volume, observed at increasing loading of the second metal in the Al-based metallic systems studied.

Conclusions

☑ Iron results around 15 times more efficiently stabilized than Cu in binary metallic, Al-based Keggin pillared clays.
☑ Opposite trend observed in the XRD-basal spacings with increasing AMR suggests that isomorphic substitution of Al by Fe or Cu is also so far possible.
☑ H_2-TPR analyses seem to evidence the presence of Fe "decorating" Al_2O_3 and Fe making part of true mixed Al/Fe- pillars, at low AMR values.

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References

[1] M.N. Timofeeva, S.Ts. Khankhasaeva, Y.A. Chesalov, S.V. Tsybulya, V.N. Panchenko, E.Ts. Dashinamzhilova. Appl. Catal. B, 88 (2009) 127-134.
[2] A. Rodríguez, G. Ovejero, J.L. Sotelo, M. Mestanza and J. García. Ind. Eng. Chem. Res., 49 (2010) 498-505.
[3] E. Guélou, J. Barrault, J. Fournier, J-M. Tatibouët, Appl. Catal. B, 44 (2003) 1-8.
[4] J. Barrault, J-M. Tatibouët, N. Papayannakos. CR de l'Academie des Sci – Ser IIC–Chem, 3(2000)777-783.
[5] L.A. Galeano, A. Gil, M.A. Vicente. App. Catal. B, (2010) submitted.