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Adsorption of CO_2 as a method for the characterisation of the structure of alumina-pillared clay catalysts

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Abstract The aim of this work was to study the effect of the metal loading on the structure of two series of cobalt and manganese pillared clay-supported catalysts. For this purpose, equilibrium data for CO_2 adsorption at 273 K were analysed using Freundlich, Langmuir and Toth isotherm models, in order to estimate the adsorption parameters and to relate them with the metal loading of the catalysts. The metal distributions on the porous structure of the catalysts were studied using the temperature programmed reduction results combined with information from the nitrogen physisorption data. Comparison of all results reveals that up to a certain metal loading, about 0.5 wt% of Co and 2 wt% of Mn, the metal oxide is well dispersed into the porous structure of the pillared clay. At higher metal loadings, bulk-metal oxide particles are formed on the external surface.

Keywords Alumina-pillared clays · Gas adsorption · Structure characterization · Manganese · Cobalt

1 Introduction

Pillared interlayered clays have a porous two-dimensional structure of molecular dimensions, characterized by the distance between the clay layers, the interlayer spacing, and the distance between the intercalated oxides, the interlayer spacing. These distances can be controlled by adjusting the several parameters of the synthesis process of pillared clays (Gil et al. 2008a). The potential applications of pillared clays in catalytic, separation, and sorption processes can be improved if specific cations are incorporated and dispersed into the porous structure of the pillared clays.

Various authors have reported that the micropore structure and surface nature of the pillared clays can be modified by the introduction of controlled amounts of cations without causing significant damages to the layered structure (Li et al. 1997; Zhu and Lu 1998; Zhu et al. 2000). The sorption properties of the solids could be significantly changed (Hutson et al. 1998). Therefore, the characterization of the structure of these materials is the object of a research effort in the last years (Gil et al. 2008a), with gas adsorption as the most widely considered approach.

The incorporation of alkali and alkaline-earth cations of several sizes into the structure of pillared clays has been studied by several researchers (Cheng and Yang 1995; Hutson et al. 1998; Malla and Komarneni 1990; Molinard and Vansant 1995; Zhu et al. 1999), who found that in all cases the final adsorption capacity and the surface characteristics of the materials are clearly related to the cation content. Bahranowski et al. (2000) studied the modification of the textural properties of Al-, Zr-, and Ti-pillared clays upon doping with copper, and showed that the effect of the copper addition on the texture of pillared solids depends on the nature of pillars and on the method of doping. The effect of the platinum content on the microstructure and the micropore size distribution of Pt/Al-pillared clays has been recently studied by Barrera-Vargas et al. (2005). The authors reported that the platinum species block the micropore entrances by progressive steric hindrance to nitrogen access as the platinum content increases. The platinum dispersion, calculated from hydrogen chemisorption, also indicates that platinum species may occupy the microporous network of the alumina-pillared clay after the catalyst preparation process.

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Cobalt and manganese oxide-supported catalysts have been widely studied and used in several catalytic applications. We have recently reported the incorporation of these metal oxides in pillared clays by impregnation with various precursors (Vicente et al. 2004). The resulting solids were used in the complete oxidation of various Volatile Organic Compounds (VOCs) (Gandía et al. 2002; Gil et al. 2006, 2008b).

The aim of this work, which is a part of a systematic study on the preparation of metal catalysts supported on pillared clays, is to contribute to the evaluation of the structure characteristics of two series of cobalt and manganese pillared clay-supported catalysts used for the catalytic combustion of VOCs with carbon dioxide adsorption as the selected approach.

2 Experimental

The purified natural clay mineral used in this work was a montmorillonite from Tsukinuno, The Clay Science Society of Japan. The clay was intercalated with $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ polycation following a standard procedure (Lahav et al. 1978). The aluminium polycation solution (Bottero et al. 1980; Bradley et al. 1990) was prepared by slow addition of a 0.5 mol/dm^3 solution of $AlCl_3{\cdot}6H_2O$ (Merck, p.a.) to a 1.5 mol/dm^3 solution of NaOH under vigorous stirring, with an OH^-/Al^{3+} mole ratio equal to 2. The hydrolysed solution was allowed to age for 48 h at 323 K under continuous stirring. An Al/clay ratio of 10 $mmol_{Al}/dm^3{\cdot}g_{clay}$ was used in the intercalation process. The clay suspensions were kept in contact with the solution for 24 h at room temperature and then centrifuged and washed. The resulting intercalated clay was dried for 16 h in air at 323 K and then calcined for 4 h at 773 K in order to obtain the alumina-pillared clay.

Metal supported catalysts were prepared by wet impregnation of the alumina-pillared clay with the required amount of the aqueous solutions of cobalt and manganese salts ($Co(NO_3)_2{\cdot}6H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$). The resulting metal/clay slurries were evaporated under reduced pressure in a rotavapor, and the obtained solids were calcined in air for 4 h at 773 K to obtain the final supported catalysts. The samples are hereafter referred to as wt%Metal/(MT-Al).

Nitrogen (Air Liquide, 99.999%) and carbon dioxide (Air Liquide, 99.998%) adsorption experiments were performed at 77 K and 273 K, respectively, using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). The samples were previously degassed for 24 h at 473 K at a pressure lower than 0.133 Pa. The weight of each sample was 0.2 g.

The metal content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX instrument.

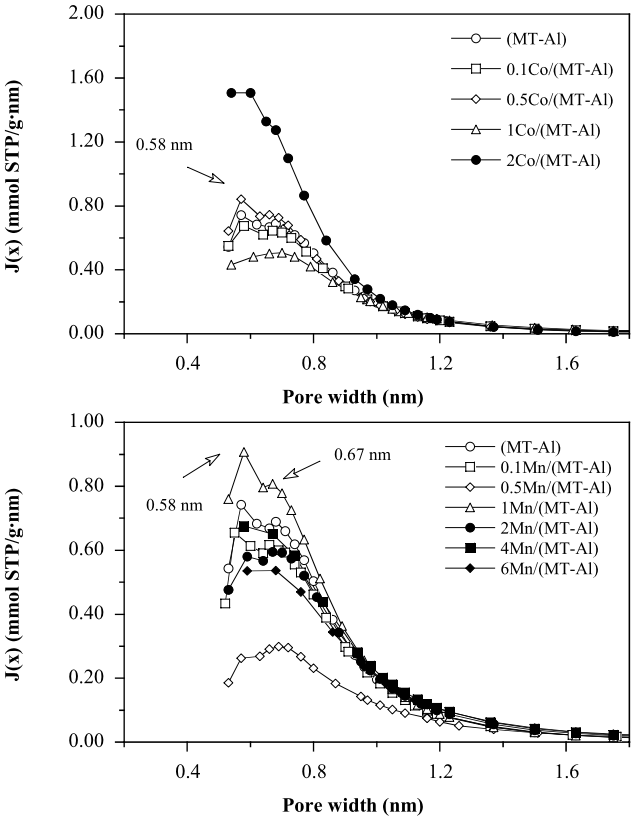

Fig. 1 MicroPore-Size Distributions (MPSD) derived from Jaroniec-Gadkaree-Choma model

Temperature-Programmed Reduction (TPR) studies were carried out on a Micromeritics TPR/TPD 2900 instrument under a total flow of 25 cm^3/min of carrier gas (5% H_2 in Ar, Praxair). Water and other compounds that might be formed during the metal reduction and precursor decomposition were retained by a cold trap, thus avoiding possible interferences with the measured signal.

3 Results and discussion

The nitrogen adsorption isotherms are of type I+II in the Brunauer, Deming, Deming and Teller (BDDT) classification (Gregg and Sing 1991). The nitrogen adsorption experiments at low relative pressures ($p/p^0 < 0.1$) show the greatest differences between the isotherms of the samples.

The textural properties of the samples, obtained from the nitrogen adsorption data, are given in Table 1. The Langmuir surface area (S_{Lang}) was calculated from adsorption data over the relative pressure range between 0.01 and 0.05, taking the cross-sectional area of the nitrogen molecule as 0.160 nm^2 (Gregg and Sing 1991). The total pore volume (V_p) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid

Table 1 Textural properties derived from nitrogen and carbon dioxide adsorption studies at 77 K and 273 K, respectively, and metal content (%) of the metal-supported pillared catalysts

Sample	S_{Lang}[a] (m^2/g)	V_p[b] (cm^3/g)	S_{ext}[c] (m^2/g)	$V_{\mu p}$[d] (cm^3/g)	$V_{\mu p}(CO_2)$[e] (cm^3/g)	Metal content (wt%)
(MT-Al)	212 (K = 452)[f]	0.113	13	0.075	0.054	–
0.1Mn/(MT-Al)	242 (K = 454)	0.133	16	0.085	0.055	0.09
0.5Mn/(MT-Al)	186 (K = 407)	0.100	13	0.066	0.058	0.46
1Mn/(MT-Al)	185 (K = 421)	0.099	12	0.065	0.055	0.98
2Mn/(MT-Al)	190 (K = 375)	0.104	12	0.067	0.052	1.92
4Mn/(MT-Al)	91 (K = 338)	0.064	11	0.032	0.037	4.23
6Mn/(MT-Al)	84 (K = 327)	0.061	10	0.030	0.033	5.76
0.1Co/(MT-Al)	178 (K = 455)	0.102	14	0.063	0.056	0.09
0.5Co/(MT-Al)	180 (K = 480)	0.098	12	0.064	0.061	0.37
1Co/(MT-Al)	148 (K = 390)	0.085	10	0.053	0.056	0.81
2Co/(MT-Al)	152 (K = 437)	0.084	11	0.048	0.049	1.46

[a]Specific surface areas from the Langmuir equation over the pressure interval $0.01 < p/p^0 < 0.05$

[b]Specific total pore volume at a relative pressure of 0.99

[c]Specific external surface areas obtained from the t-plot method

[d]Specific micropore volumes obtained from the t-plot method

[e]Specific micropore volumes derived from the Dubinin-Radushkevich equation

[f]Langmuir K values, characteristic of the intensity of the adsorbate-adsorbent interactions

Table 2 Langmuir, Freundlinch and Toth equation parameters for the adsorption of carbon dioxide at 273 K

	(TM-Al)	0.1Co/(TM-Al)	0.5Co/(TM-Al)	1Co/(TM-Al)	2Co/(TM-Al)
Langmuir					
C_0 (mmol/g)	0.86	0.92	0.97	0.91	0.78
k_L (kPa^{-1})	0.013	0.012	0.011	0.012	0.014
χ^2	0.0016	0.0006	0.0009	0.0005	0.0008
R	0.997	0.998	0.998	0.9991	0.998
Freundlich					
k_F ((mmol·kPa^m)/g)	0.026	0.026	0.024	0.024	0.027
m_F	1.56	1.54	1.50	1.50	1.61
χ^2	0.0030	0.0013	0.0007	0.0014	0.0013
R	0.994	0.997	0.998	0.997	0.997
Toth					
C_0 (mmol/g)	1.44	1.92	5.35	1.73	1.71
k_T (kPa^{-1})	0.010	0.0080	0.0040	0.0080	0.010
m_T	0.647	0.569	0.379	0.614	0.534
χ^2	0.0013	0.0003	0.0002	0.0003	0.0003
R	0.997	0.9994	0.9997	0.9995	0.9993

nitrogen at 77 K, 0.81 g/cm^3 (Gregg and Sing 1991). The external surface area (S_{ext}) and the specific micropore volume ($V_{\mu p}$) were estimated by the t-plot method (Gregg and Sing 1991). When the results of nitrogen adsorption for the MT-Al and for the metal oxide-doped materials are compared, see Table 1, it is observed that the textural properties remain practically unchanged up to a metal content of 0.37 wt% for Co and of 1.92 wt% for Mn. The specific mesopore volume, estimated by subtraction of the micropore volume from the total pore volume, remains almost unchanged; the pore volume loss suffered by the materials is almost exclusively micropores of MT-Al. It seems that up to a certain metal

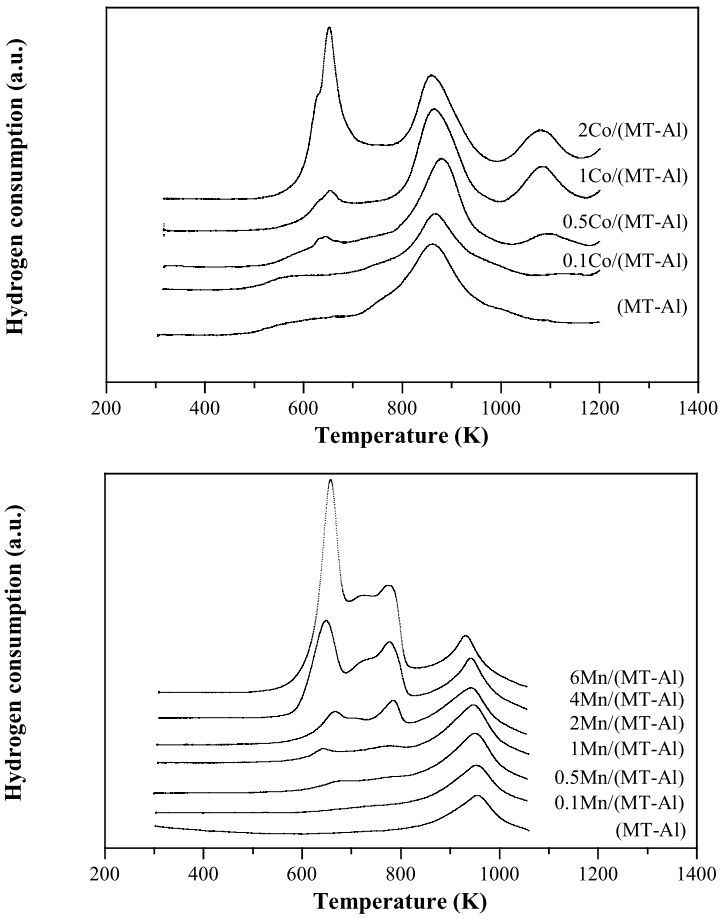

Fig. 2 TPR curves of the (**a**) cobalt oxide and (**b**) manganese oxide alumina-pillared clay-supported catalysts

Table 3 Langmuir, Freundlinch and Toth equation parameters for the adsorption of carbon dioxide at 273 K

	(TM-Al)	0.1Mn/(TM-Al)	0.5Mn/(TM-Al)	1Mn/(TM-Al)	2Mn/(TM-Al)	4Mn/(TM-Al)	6Mn/(TM-Al)
Langmuir							
C_0 (mmol/g)	0.86	0.89	0.91	0.89	0.83	0.61	0.56
k_L (kPa^{-1})	0.013	0.012	0.012	0.012	0.011	0.010	0.009
χ^2	0.0016	0.0009	0.0013	0.0009	0.0008	0.0002	0.0002
R	0.997	0.998	0.997	0.998	0.998	0.998	0.998
Freundlich							
k_F ((mmol·kPa^{m})/g)	0.026	0.024	0.026	0.024	0.021	0.013	0.011
m_F	1.56	1.53	1.54	1.53	1.50	1.45	1.43
χ^2	0.0030	0.0007	0.0005	0.0006	0.0004	0.0005	0.0005
R	0.994	0.998	0.9991	0.998	0.9991	0.997	0.997
Toth							
C_0 (mmol/g)	1.44	3.84	10.84	5.15	7.80	1.22	0.82
k_T (kPa^{-1})	0.010	0.0051	0.0031	0.0043	0.0028	0.0064	0.0073
m_T	0.647	0.409	0.288	0.365	0.320	0.612	0.741
χ^2	0.0013	0.00023	0.00018	0.00019	0.00014	0.00017	0.00016
R	0.997	0.9996	0.9997	0.9996	0.9997	0.9992	0.9990

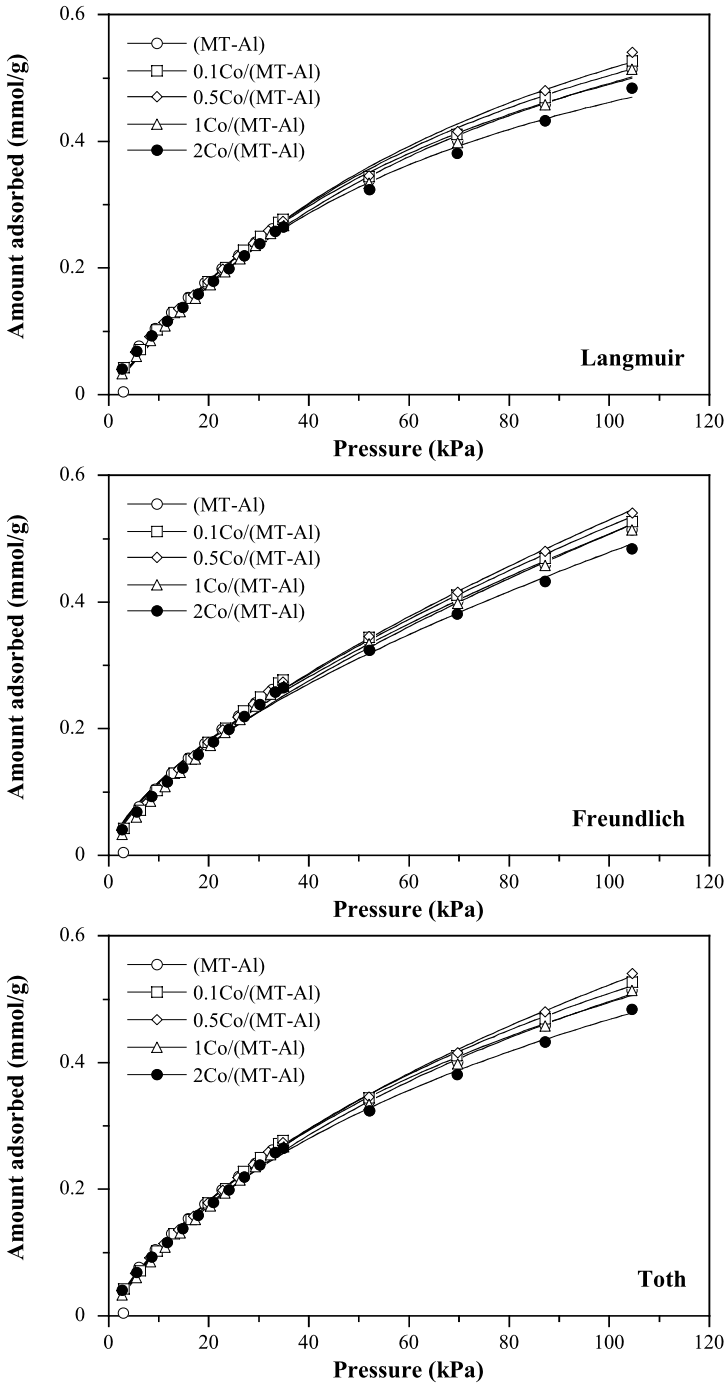

Fig. 3 Experimental (*symbols*) and model (*lines*) isotherms for the adsorption of carbon dioxide at 273 K

loading the oxide occupies the inner pores of MT-Al, while at higher loadings the metal species may be located on the external surface, blocking the entrance of the pores.

The MicroPore-Size Distributions (MPSDs), derived from the model proposed by Jaroniec-Gadkaree-Choma (Jaroniec et al. 1996; Gil et al. 2008a), were used in this work to examine the micropore characteristics of the materials studied, see Fig. 1. It can be seen from the figure that there is a first maximum in the distributions at 0.58 nm with a second maximum at a pore diameter of 0.67 nm.

The evolution of the TPR curves supports the conclusions on the textural properties drawn from the nitrogen adsorption, see Fig. 2. The TPR patterns show reduction profiles of bulk-like cobalt and manganese oxide particles, indicating that above a given metal oxide content the microporous network is blocked and the values of the textural properties of the doped alumina-pillared clay decrease. The TPR

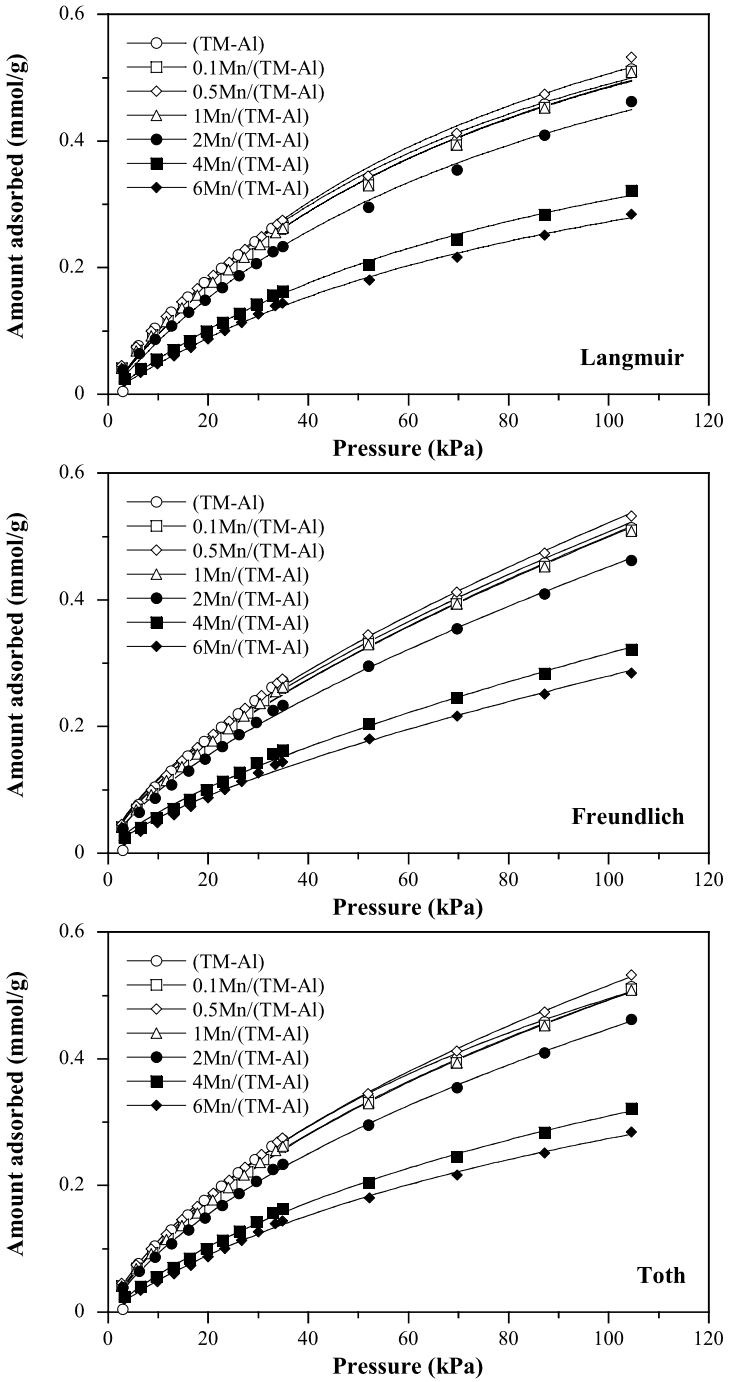

Fig. 4 Experimental (*symbols*) and model (*lines*) isotherms for the adsorption of carbon dioxide at 273 K

curves of Co/(MT-Al) samples having a metal loading of about 0.5 wt% or higher, have a first peak at 640 K corresponding to the reduction of bulk-like cobalt oxide particles (Sin and Chen 2004; Li et al. 2004). The reduction peak above 1090 K indicates the presence of Co species that interact strongly with the support, such as spinel type Co_2SiO_4 compounds (Ernst et al. 1999). The TPR curves of Mn/(MT-Al) samples having a metal content of about 2 wt% or more, are also similar to those of bulk-like manganese oxide particles. Two reduction peaks are observed, which are consistent with the successive reduction of both MnO_2 and Mn_2O_3 to Mn_3O_4, followed by a final reduction to MnO (Stobbe et al. 1999). In all samples, the contribution of the reduction of the structural Fe^{3+} cations of the pillared clay support at 860 and 950 K is rather significant. The difference in the two temperatures is due to different heating rates during the TPR experiments: 10 and 20 K/min were used for cobalt and manganese samples, respectively.

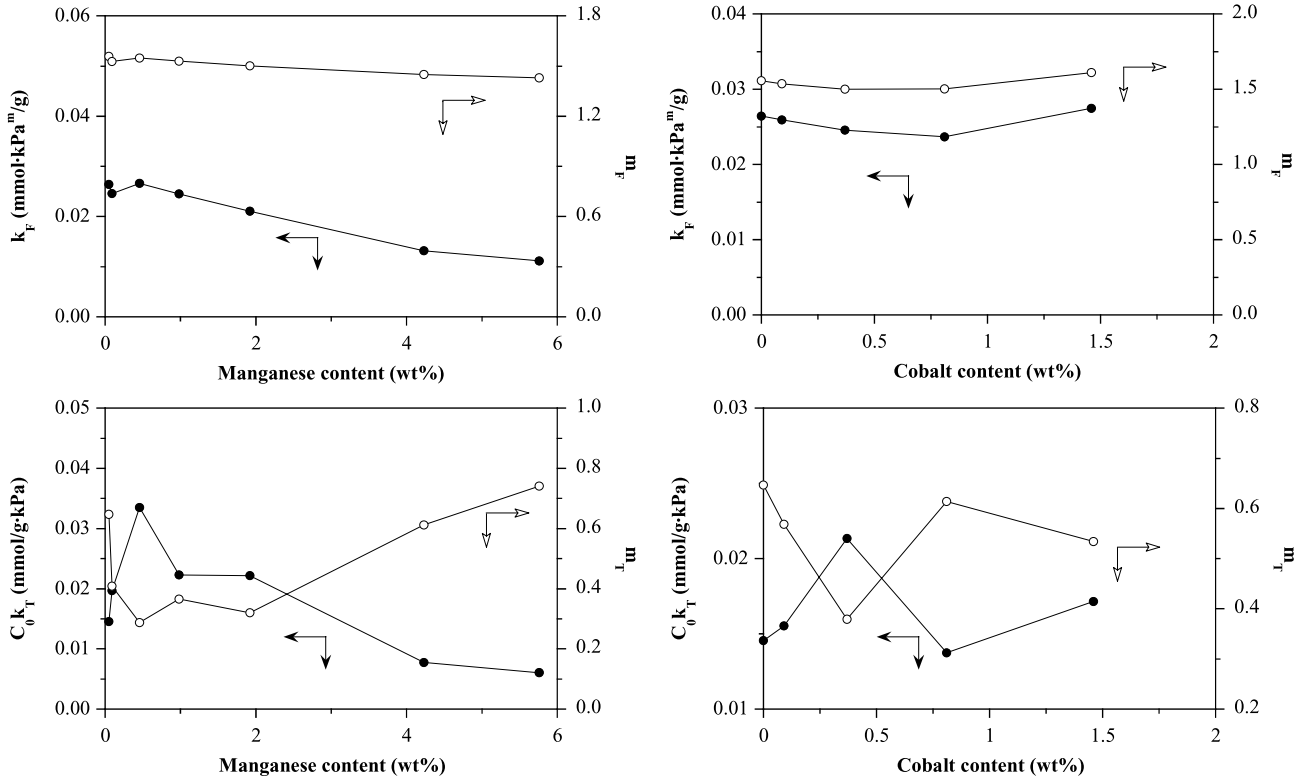

Fig. 5 Effect of the metal oxide content on the fitted parameters k_F and m_F obtained from the Freundlich equation and on $C_0 \cdot k_T$ and m_T obtained from the Toth equation

The adsorption of CO_2 at 273 K is shown in Figs. 3 and 4. The micropore volumes ($V_{\mu p}(CO_2)$) included in Table 1 have been calculated using the Dubinin-Radushkevich equation (Dubinin 1989) applied over the relative pressure range of 0.01 to 0.05. In all cases, the micropore volume calculated from nitrogen adsorption is higher than the one obtained from carbon dioxide adsorption. Rodríguez-Reinoso and Linares-Solano (1989) related this behaviour with a wide and very heterogeneous micropore-size distribution.

Several isotherm equations have been proposed to describe the experimental data from the adsorption of gases on porous materials. Freundlich, Langmuir and Toth equations (Do 1998) have been applied to the experimental CO_2 adsorption results obtained in the present work.

$$\text{Langmuir equation:} \quad C = \frac{C_0 k_L p}{1 + k_L p} \tag{1}$$

$$\text{Freundlich equation:} \quad C = k_F p^{1/m_F} \tag{2}$$

$$\text{Toth equation:} \quad C = \frac{C_0 k_T p}{[1 + (k_T p)^{m_T}]^{1/m_T}} \tag{3}$$

where C is the amount adsorbed, C_0 is the monolayer capacity, k is the equilibrium constant and m_F and m_T characterize the heterogeneity of the system (Do 1998). The parameters are estimated by non-linear regression and the values obtained are summarized in Tables 2 and 3.

The monolayer capacity, C_0, which can be calculated from the Langmuir and Toth equations, presents a maximum at a metal content of 0.5% in both series of samples. In Fig. 5, the values of $k_F - m_F$ and $C_0 \cdot k_T - m_T$, have been plotted versus the cobalt and manganese content of the solids. It can be seen from the figure that k_F and m_F remain practically constant as the metal content increases. The product of the Toth parameters ($C_0 \cdot k_T$) could be related to the interaction of carbon dioxide with the surface; first it increases with increasing metal content, passes through a maximum at about 0.5 wt% of metal and then it decreases as the gas-solid interactions become weaker at higher metal loadings.

4 Summary and conclusions

The textural properties of the studied metal pillared clay catalysts, calculated from nitrogen adsorption at 77 K, indicate that the surface area and micropore volume of the materials decrease as the metal content increases.

The adsorption parameters, estimated by fitting the carbon dioxide adsorption results at 273 K to Freundlich, Langmuir and Toth equations, indicate that the presence of metal oxides modifies the texture and the surface properties of the

catalysts. No direct effect of the amount of metal on the textural properties has been observed.

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